Metalloligands based on Robson-type Amino-Thiophenolato Macrocycles for Assembly of Heterotrimetallic Complexes

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Author Contributions The manuscript was written through contributions of all authors. SS synthesized and characterized the compounds (IR & UV-vis spectroscopy, mass spectrometry, cyclic voltammetry, and X-ray crystallography), performed magnetic measurements, and determined the magnetic parameters. SN performed all DFT calculations, determined the NH stretching vibrations, and calculated the stability constants and charge shifts of the complexes. MB repeated the synthesis of compound **3** for EPR analysis. AP performed EPR spectroscopic on **3**. BA and BK interpreted the data and wrote the manuscript. BK designed the concept of the manuscript. All authors have given approval to the final version of the manuscript.

Contents

1) Synthesis of Compounds

Materials and methods: The ligand $H_2L(HBr)_6$ and the nickel complex **2** were prepared as described in the literature.[S1] All reagents and solvents were commercial grade and used without further purification. The syntheses of the metal complexes were carried out under a protective atmosphere of argon unless stated otherwise. Melting points were determined with an Electrothermal IA9000 series instrument using open glass capillaries and are uncorrected. Elemental analyses were carried out on a VARIO EL elemental analyzer (Elementar Analysensysteme GmbH, Hanau). Mass spectra were recorded using the positive ion electrospray ionization modus (ESI) on a Bruker APEX II FT-ICR instrument. Infrared spectra (4000–400 cm^{-1}) were recorded at 1 cm^{-1} resolution on a Bruker TENSOR 27 (equipped with a MIRacle ZnSe ATR accessory from PIKE Technologies) FT-IR spectrometer. Solution electronic absorption spectra were collected on a Jasco V-670 UV–vis–NIR device using 1 cm quartz cells (Hellma). The magnetic susceptibility measurements were performed with the use of a MPMS 7XL SQUID magnetometer (Quantum Design) working between 1.8 and 330 K for applied dc fields ranging from -7 to 7 T. Measurements were performed on polycrystalline samples over the temperature range 2–330 K at applied magnetic field of 1.0 T. The observed susceptibility data were corrected for the underlying diamagnetism using Pascals constants.

Safety note: CAUTION! *Although no problems were encountered during this work perchlorate salts are potentially explosive. The perchlorate salts should be prepared only in small quantities and handled with appropriate care.*

Attempted synthesis of $[LCo^{II}Co^{III}(\mu\text{-}F)](ClO_4)_2$. A solution of $Co(OAc)_2{\cdot}4H_2O$ (43.1 mg, 0.173 mmol, 2.00 eq.) in MeOH (5 mL) was added to a colorless solution of $H_2L{\cdot}6HBr$ (100 mg, 86.5 µmol, 1.00 eq.) in MeOH (30 mL) followed by the base NEt_3 (70.0 mg, 0.692 mmol, 8.00 eq.). To the resulting brown solution was added an excess of $N(n\text{-}Bu)_4F{\cdot}3H_2O$ (54.6 mg, 0.173 mmol, 2.00 eq.) and the reaction mixture was stirred at room temperature overnight. The flask was then exposed to air, and stirring was continued for further 12 h. A solution of $LiClO_4{\cdot}3H_2O$ (690 mg, 4.30 mmol) in EtOH (5 mL) was added and the mixture was stirred for 2 h. The mixture was evaporated to half of its original volume, to give a residue, which was filtered, washed with cold ethanol and recrystallized by slow evaporation from a mixed acetonitrile/ethanol solvent system. Yield: 235 mg (62 %) of brown crystals. M.p. > 258 °C (decomposes without melting). ESI mass spectrometry (Figure S1) reveals the presence of the hydroxo-bridged complex $LCo^{II}Co^{III}(\mu\text{-}OH)](ClO_4)_2$ (**1**), not the anticipated $[LCo^{II}Co^{III}(\mu\text{-}F)](ClO_4)_2$ complex , i.e. ESI(+)-MS: *m/z* (CH_3CN) = 902.3 [**1**-ClO_4]$^+$, 401.7 [**1**-$2ClO_4$]$^{2+}$

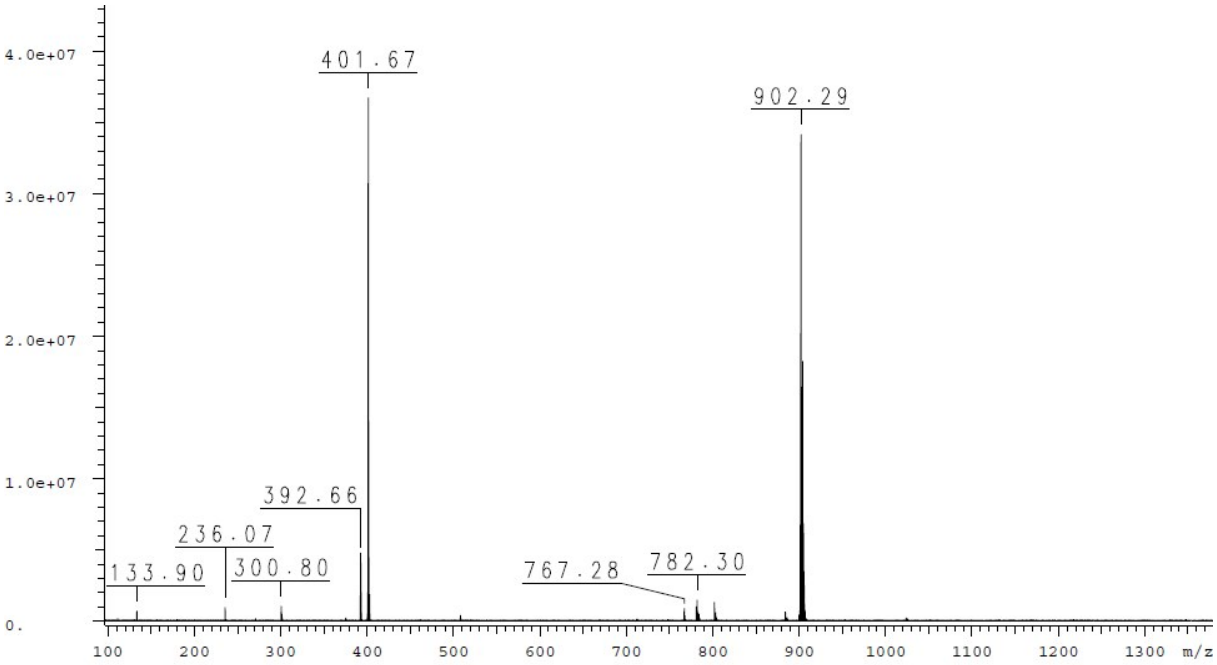

Figure S1. ESI-MS spectrum of the above reaction product in MeCN (c ~ 10^{-3} M). The peak at *m*/*z* = 902.28 is due to the $\{[LCo^{II}Co^{III}(\mu\text{-OH})]ClO_4\}^+$ cation.

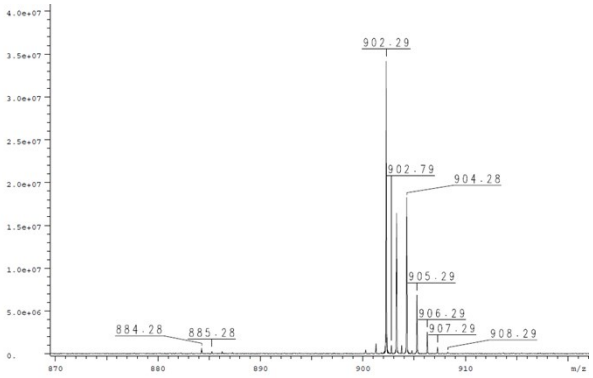

Figure S2. Enlarged section of the ESI-MS spectrum shown in Figure S1. The peak at *m*/*z* = 902.28 is due to the $\{[LCo^{II}Co^{III}(\mu\text{-OH})]ClO_4\}^+$ cation not a fluorido-bridged species $\{[LCo^{II}Co^{III}(\mu\text{-F})]ClO_4\}^+$, which would show up (with 100% intensity) at *m*/*z* = 904.29.

Synthesis and characterization data for $[LCo^{II}Co^{III}(\mu\text{-F})(CuBr_2)]ClO_4$ (3). A solution of $Co(OAc)_2{\cdot}4H_2O$ (43.1 mg, 0.173 mmol, 2.00 eq.) in MeOH (5 mL) was added to a colorless solution of $H_2L{\cdot}6HBr$ (100 mg, 86.5 µmol, 1.00 eq.) in MeOH (30 mL) followed by the base NEt_3 (70.0 mg, 0.692 mmol, 8.00 eq.). To the resulting brown solution was added an excess of $N(n\text{-}Bu)_4F{\cdot}3H_2O$ (54.6 mg, 0.173 mmol, 2.00 eq.) and the reaction mixture was stirred at room temperature overnight. Then $Cu(ClO_4)_2{\cdot}6H_2O$ (32.0 mg, 86.5 µmol, 1.00 eq.) in MeOH was added to the reaction mixture. The resulting dark-brown solution was stirred for 15 min, after which EtOH (20 mL) was added. The mixture was concentrated under reduced pressure, to give a brown precipitate, which was filtered off, and washed with cold EtOH. The crude product was purified twice by recrystallization from a mixed MeCN/EtOH (1:1 by volume) solution and dried in vacuum. Yield: 58 mg (58 %, 50.6 µmol), brown, microcrystalline powder. M.p. > 250 °C (decomposes without melting.). *m*/*z* (ESI+, MeCN): $C_{38}H_{64}Br_2Co_2CuFN_6S_2ClO_4$

(1125.04) [M-ClO_4^-]$^+$ calcd: 1028.09; found 1028.10. IR: (KBr, cm^{-1}): $\tilde{\nu}$ = 3271w, 3205m, 3121w (all νNH), 1089s ν(ClO_4^-), 624s δ(ClO_4^-). Magnetic moment: μ_{eff} = 4.99 μ_B (at 330 K). UV-vis (CH_3CN): λ [nm] (ε [$M^{-1}\,cm^{-1}$]): 201 (106333), 275 (15491), 306 (14501), 557 (1397). Elemental analysis calcd (%) for $C_{38}H_{64}Br_2ClCo_2CuFN_6O_4S_2{\cdot}H_2O$ (1128.76 + 18.02): C 39.80, H 5.80, N 7.33; found: C 39.75, H 5.53, N 7.41. Single crystals of [$LCo^{II}Co^{III}$(μ-F)($CuBr_2$)]$ClO_4{\cdot}2CH_3CN$ suitable for X-ray crystallography were obtained by slow evaporation of a mixed acetonitrile/ethanol (1/1 v/v) solution.

Synthesis and characterization data for [LNi^{II}_2(μ-F)($Cu^{I}Cl_2$)] (4). *Method A)* A solution of copper(I) chloride (21.8 mg, 0.22 mmol, 2.00 eq.) in MeCN (5 mL) was added to a solution of the nickel complex **2** (99.5 mg, 0.11 mmol, 1.00 eq.) in MeCN (30 mL), to give a dark green suspension which was stirred for further 12 at r.t. after which EtOH (20 mL) was added to the reaction mixture. The resulting solution was concentrated under reduced pressure to give a turquoise precipitate, which was isolated by filtration and washed with cold EtOH. The crude product was purified by recrystallization from a mixed MeCN/EtOH solution, and dried in vacuum. Yield: 66 mg (64 %, 70 μmol), turquoise, microcrystalline powder. *Method B.* A solution of copper(I) chloride (10.9 mg, 0.110 mmol, 0.11 eq) and *n*Bu_4NCl (27.8 mg, 0.110 mmol, 0.11 eq) in MeCN (10 mL) was added to a solution of **2** (99.5 mg, 0.110 mmol, 1.00 eq.) in MeCN (30 mL). After stirring for 12 at r.t., EtOH (25 mL) was added. The resulting solution was concentrated under reduced pressure to give a turquoise precipitate, which was isolated by filtration and washed with cold EtOH. The crude product was purified twice by recrystallization from a mixed MeCN/EtOH solution, and dried in vacuum to give 58 mg (52 %, 62 μmol) of a turquoise, microcrystalline powder. M.p. >332°C (decomposes without melting). *m/z* (ESI+, MeCN): $C_{38}H_{64}CuFCl_2N_6Ni_2S_2$ (936.200), [M+H]$^+$ calcd: 937.20; found 937.21; [M-Cl]$^+$ calcd: 901.23, found 901.2, [M-$CuCl_2$]$^+$ calcd: 803.33, found 803.3. IR (KBr, cm^{-1}): $\tilde{\nu}$ = 3447 (w), 3285 (w, νNH), 3256 (w, νNH), 2965 (m), 2951 (m), 2925 (m), 2862 (m), 2815 (w), 1742 (w), 1651 (m), 1462 (m), 1447 (m), 1416 (w), 1392 (w), 1362 (m), 1300 (w), 1282 (w), 1228 (w), 1204 (w), 1189 (w), 1158 (m), 1087 (m), 1065 (m), 1054 (m), 1016 (w), 981 (m), 943 (w), 925 (w), 904 (w), 872 (m), 851 (w), 816 (m), 755 (w), 674 (w), 624 (m), 550 (w), 497 (w). Magnetic moment: μ_{eff} = 4.35 μ_B (at 330 K), $\mu_{eff,max}$ = 4.63 μ_B (at 14 K). UV-vis (CH_3CN/CH_3CH_2OH 1:1 v/v): λ [nm] (ε [$M^{-1}cm^{-1}$]): 204 (95327), 280 (12173), 324 (6925), 611 (1194), 1014 (511). Elemental analysis calcd (%) for $C_{38}H_{64}CuFCl_2N_6Ni_2S_2{\cdot}2H_2O$ (939.92 + 36.03): C 46.77, H 7.02, N 8.61; found: C 46.53, H 6.79, N 8.43.

Synthesis and characterization data for [LNi_2(μ-F)($CuBr_2$)] (5). *Method A)* A solution of copper(I) bromide (31.6 mg, 0.22 mmol, 2.00 eq.) in MeCN (5 mL) was added to a solution of **2** (99.5 mg, 0.11 mmol, 1.00 eq.) in MeCN (30 mL), to give a green suspension which was stirred for further 12 at r.t. after which EtOH (20 mL) was added to the reaction mixture. The resulting solution was concentrated under reduced pressure to give a turquoise precipitate, which was isolated by filtration and washed with cold EtOH. The crude product was purified by recrystallization from a mixed MeCN/EtOH solution, and dried in vacuum. Yield: 106 mg (93 %, 0.103 mmol), turquoise, microcrystalline powder. *Method B.* A solution of copper(I) bromide (15.8 mg, 0.11 eq) and *n*Bu_4NBr (35.5 mg, 0.11 eq) in MeCN (10 mL) was added to a solution of **2** (99.5 mg, 0.11 mmol, 1.0 eq) in MeCN (30 mL). After stirring for 12 at r.t., EtOH (25 mL) was added. The resulting solution was concentrated under reduced pressure to give a turquoise precipitate, which was isolated by filtration and washed with cold EtOH. The crude product was purified twice by recrystallization from a mixed MeCN/EtOH solution, and dried in vacuum to give 73 mg (65 %, 0.071 mmol) of a turquoise, microcrystalline powder. M.p. >329°C (decomposes without melting). *m/z* (ESI+, MeCN): $C_{38}H_{64}Br_2CuFN_6Ni_2S_2$ (1024.10),

$[M]^+$ calcd: 1024.1; found 1024.1; $[M\text{-}Br^-]^+$ calcd: 947.18, found 947.2, $[M\text{-}CuBr_2]^+$ calcd 803.3; found 903.3. IR (KBr, cm^{-1}): $\tilde{\nu}$ = 3445 (m), 3282 (m, νNH), 3250 (m, νNH), 2962 (s), 2932 (m), 2905 (m), 2868 (s), 2818 (m), 1628 (w), 1597 (m), 1477 (m), 1463 (s), 1446 (s), 1417 (w), 1377 (w), 1363 (m), 1301 (w), 1229 (m), 1187 (m), 1159 (m), 1118 (m), 1086 (m), 1059 (m), 1015 (w), 1002 (w), 982 (m), 943 (w), 927 (w), 899 (w), 875 (m), 851 (w), 819 (w), 754 (w), 624 (m), 556 (w), 499 (w), 469 (w), 440 (w). Magnetic moment: μ_{eff} = 4.16 μ_B (at 330 K), $\mu_{eff,max}$ = 4.54 μ_B (at 14 K). UV-vis (CH_3CN/CH_3CH_2OH): λ [nm] (ε [$M^{-1}\,cm^{-1}$]): 205 (178995), 279 (13323), 317 (9836), 614 (744), 1019 (398). Elemental analysis calcd (%) for $C_{38}H_{64}Br_2CuFN_6Ni_2S_2{\cdot}6H_2O$ (1028.82 + 108.09): C 40.14, H 6.74, N 7.39; found: C 40.24, H 6.34, N 7.39.

Compound 8. Synthesis and characterization data for [$LNi_2(\mu$-F)(CuI_2)] (6). *Method A)* A solution of copper(I) iodide (41.9 mg, 0.22 mmol, 2.0 eq.) in MeCN (5 mL) was added to a solution of **2** (99.5 mg, 0.11 mmol, 1.0 eq.) in MeCN (30 mL), to give a green suspension which was stirred for further 12 at r.t. after which EtOH (20 mL) was added to the reaction mixture. The resulting solution was concentrated under reduced pressure to give a turquoise precipitate, which was isolated by filtration and washed with cold EtOH. The crude product was purified by recrystallization from a mixed MeCN/EtOH solution, and dried in vacuum. Yield: 62 mg (50 %, 55.2 μmol), turquoise, microcrystalline powder. *Method B*. A solution of copper(I) iodide (20.9 mg, 0.11 eq) and $n$$Bu_4NI$ (40.6 mg, 0.11 eq) in MeCN (10 mL) was added to a solution of **2** (99.5 mg, 0.11 mmol, 1.0 eq) in MeCN (30 mL). After stirring for 12 at r.t., EtOH (25 mL) was added. The resulting solution was concentrated under reduced pressure to give a turquoise precipitate, which was isolated by filtration and washed with cold EtOH. The crude product was purified twice by recrystallization from a mixed MeCN/EtOH solution, and dried in vacuum to give 58 mg (47 %, 0.052 mmol) of a turquoise, microcrystalline powder. M.p. >280°C (decomposes without melting). *m/z* (ESI+, MeCN): $C_{38}H_{64}CuFI_2N_6Ni_2S_2$ (1120.071), $[M+H_2O+H]^+$ calcd: 1139.089; found 1139.8; $[M+H]^+$ calcd: 1121.08, found 1121.08, $[M\text{-}I]^+$ calcd 995.167; found 995.2. IR (KBr, cm^{-1}): $\tilde{\nu}$ = 3443 (m), 3283 (m, νNH), 3238 (m, νNH), 2963 (s), 2930 (m), 2865 (s), 2817 (m), 1626 (w), 1477 (m), 1462 (s), 1446 (s), 1416 (w), 1393 (w), 1376 (w), 1362 (m), 1300 (m), 1281 (m), 1273 (m), 1228 (m), 1187 (w), 1158 (m), 1119 (m), 1085 (s), 1053 (m), 1014 (w), 1002 (w), 981 (m), 942 (w), 925 (w), 899 (w), 872 (m), 817 (w), 755 (w), 675 (w), 623 (m). Magnetic moment: μ_{eff} = 4.51 μ_B (at 330 K), $\mu_{eff,max}$ = 4.92 μ_B (at 14 K). UV-vis (CH_3CN/CH_3CH_2OH): λ [nm] (ε [$M^{-1}\,cm^{-1}$]): 203 (115108), 280 (19233), 317 (14709), 618 (248), 1021 (152). Elemental analysis calcd (%) for $C_{38}H_{64}CuFI_2N_6Ni_2S_2{\cdot}2H_2O$ (1122.83 + 36.03): C 39.39, H 5.91, N 7.25; found: C 39.62, H 5.55, N 7.21. Crystals of $[LNi_2(\mu\text{-}F)(CuI_2)]{\cdot}2CH_3CN$ (**6**·2MeCN) were obtained by slow evaporation of a mixed acetonitrile/ethanol (1/1 v/v) solution of the complex.

2) Characterization of new compounds by mass spectrometry

a) ESI mass spectrometry for $[LCo_2(\mu\text{-}F)(CuBr_2)]ClO_4$ (3). The ESI mass spectrum of a dilute MeCN solution of **3** (Figure S3) reveals a molecular ion peak at m/z = 1028.1 attributable to the $[LCo^{II}Co^{III}(\mu\text{-}F)(CuBr_2)]^+$ cation (see Figure S4 for an enlarged section of the spectrum). The more intense peaks at m/z = 886.2 and 904.3 can be assigned to a $[LCo^{II}Co^{II}](ClO_4)^+$ and a $[LCo^{II}Co^{III}(\mu\text{-}F)](ClO_4)^+$ cation, respectively.

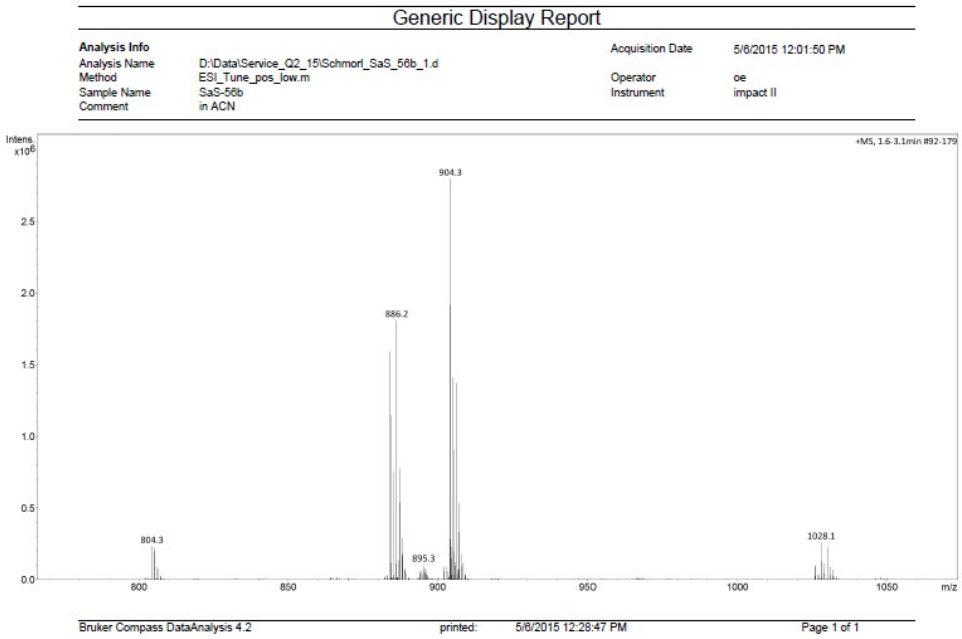

Figure S3. ESI-MS spectrum for $[LCo_2(\mu\text{-}F)(CuBr_2)]ClO_4$ (**3**) in MeCN (c ~ 10^{-3} M).

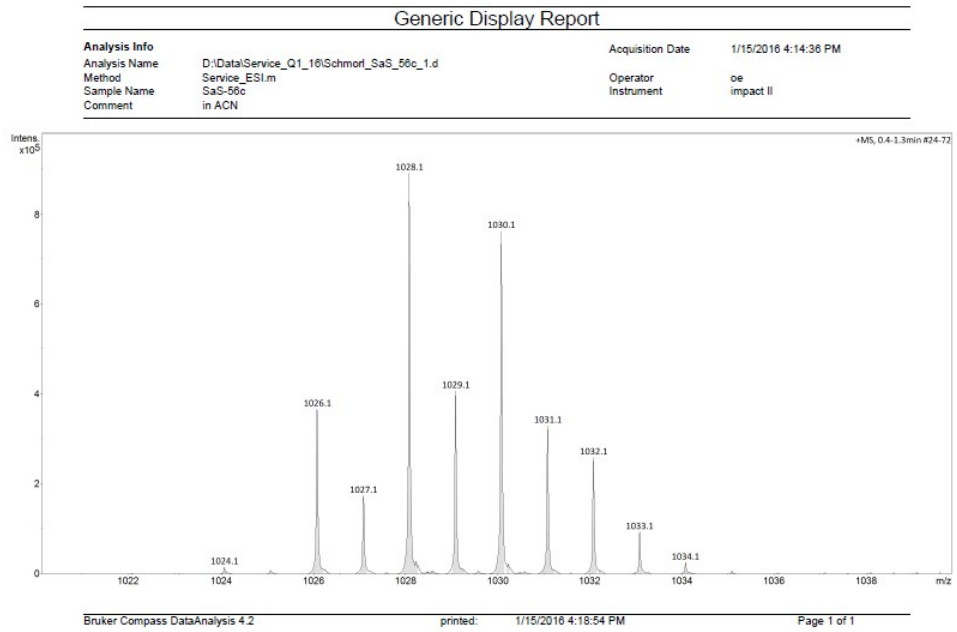

Figure S4. Section of the ESI-MS spectrum for $[LCo_2(\mu\text{-}F)(CuBr_2)]ClO_4$ (**3**) (c ~ 10^{-3} M).

b) ESI mass spectrometry for [$LNi_2(\mu$-F)($CuCl_2$)] (4). The ESI mass spectrum of a dilute MeCN solution of **4** (Figure S5) reveals a molecular ion peak at m/z = 936.2 attributable to a $[LNi^{II}Ni^{III}(\mu\text{-}F)(Cu^{I}Cl_2)]^+$ cation (see Figure S6 or S7 for enlarged sections of the ESI mass spectrum). The more intense peaks at m/z = 803.3 and 901.2 can be assigned to $[LNi^{II}Ni^{II}(\mu\text{-}F)]^+$ and $[LNi^{II}Ni^{II}(\mu\text{-}F)(Cu^{I}Cl)]^+$ cations, respectively.

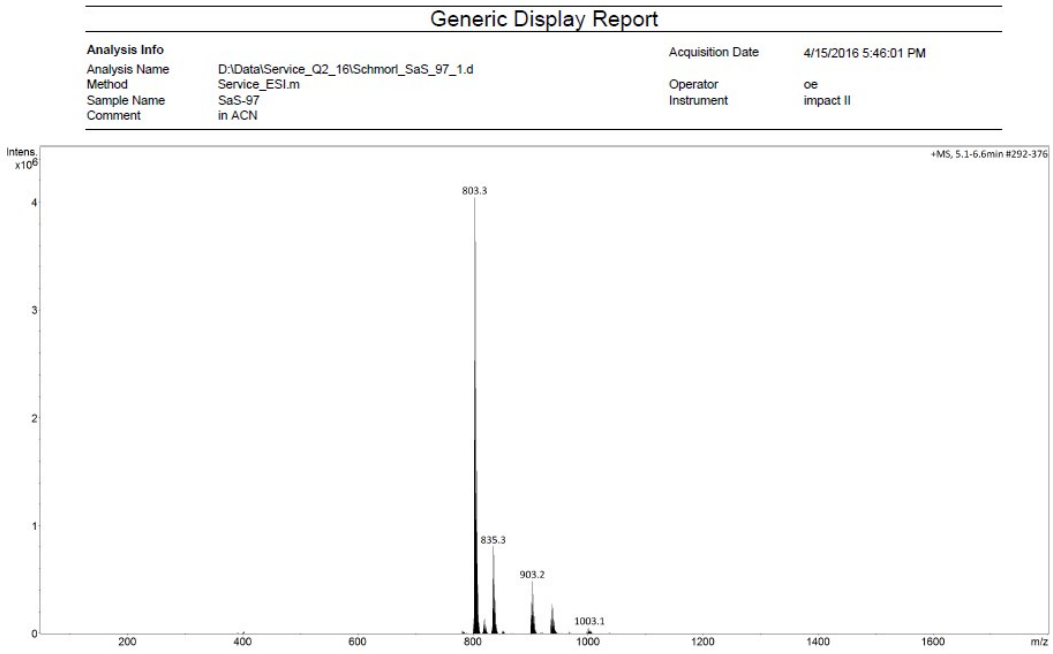

Figure S5. ESI-MS spectrum for $[LNi_2(\mu\text{-}F)(CuCl_2)]$ (**4**) in MeCN (c ~ 10^{-3} M).

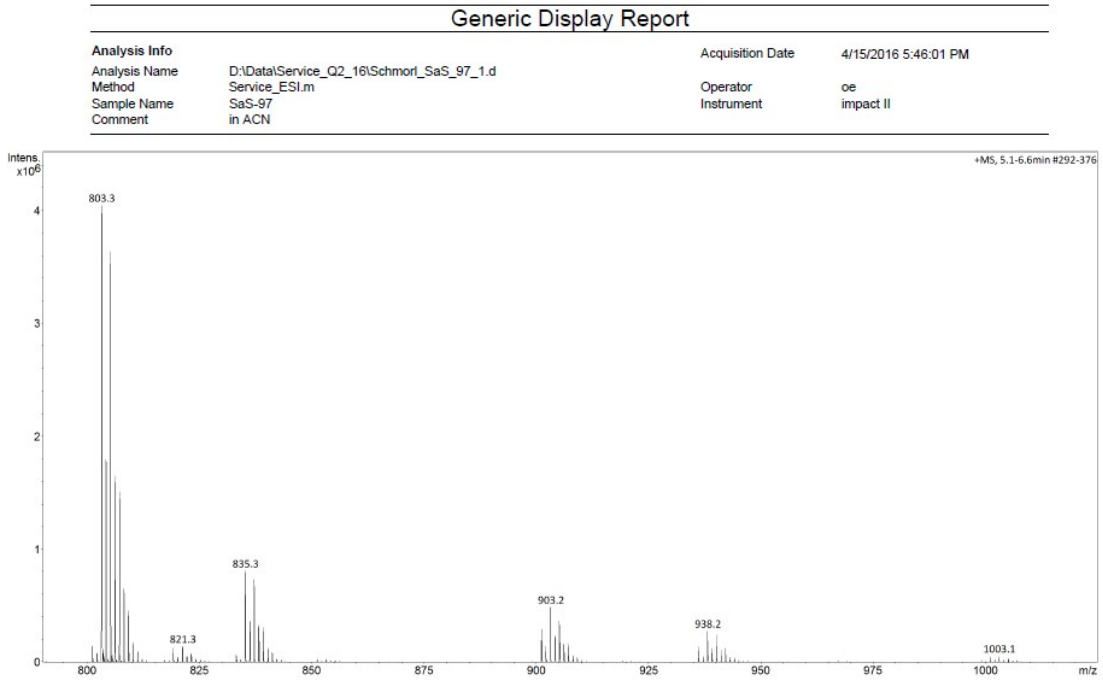

Figure S6. Section of the ESI-MS spectrum for $[LNi_2(\mu\text{-}F)(CuCl_2)]$ (**4**) (c ~ 10^{-3} M).

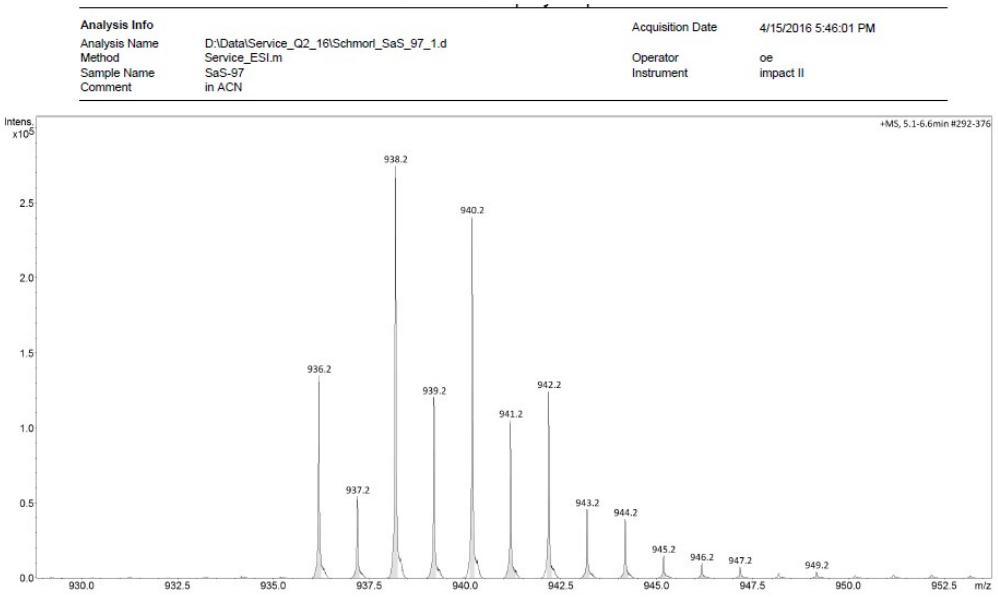

Figure S7. Section of the ESI-MS spectrum for $[LNi_2(\mu\text{-F})(CuCl_2)]$ (**4**) (c ~ 10^{-3} M).

c) ESI mass spectrometry for $[LNi_2(\mu\text{-F})(CuBr_2)]$ (5).The ESI mass spectrum of a dilute MeCN solution of **5** (Figure S8) reveals a molecular ion peak at *m*/*z* = 1028.2 attributable to a $[LNi^{II}Ni^{III}(\mu\text{-F})(Cu^{I}Br_2)]^+$ cation (see Figure S9-S11 for an enlarged section of the spectrum, $E^{\circ 1/2}(Ni^{II}Ni^{III}/Ni^{II}Ni^{II}$ = +0.26 V vs SCE)). The more intense peaks at *m*/*z* = 803.3 and 947.2 can be assigned to a $[LNi^{II}Ni^{II}(\mu\text{-F})]^+$ cation and a $[LNi^{II}Ni^{II}(\mu\text{-F})(Cu^{I}Br)]^+$ cation, respectively.

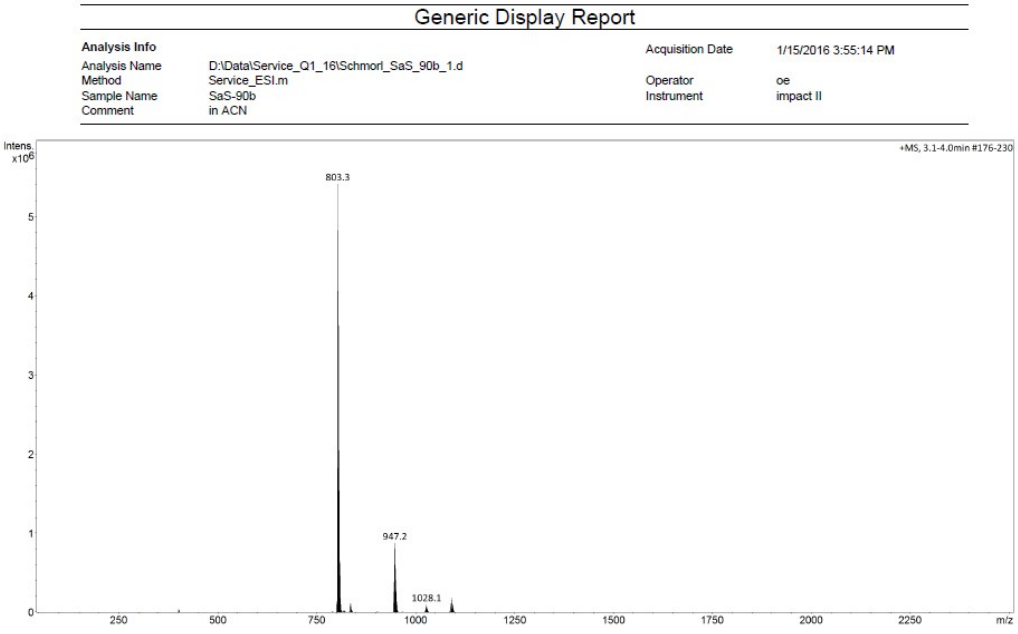

Figure S8. ESI-MS spectrum for $[LNi_2(\mu\text{-F})(CuBr_2)]$ (**5**) in MeCN (c ~ 10^{-3} M).

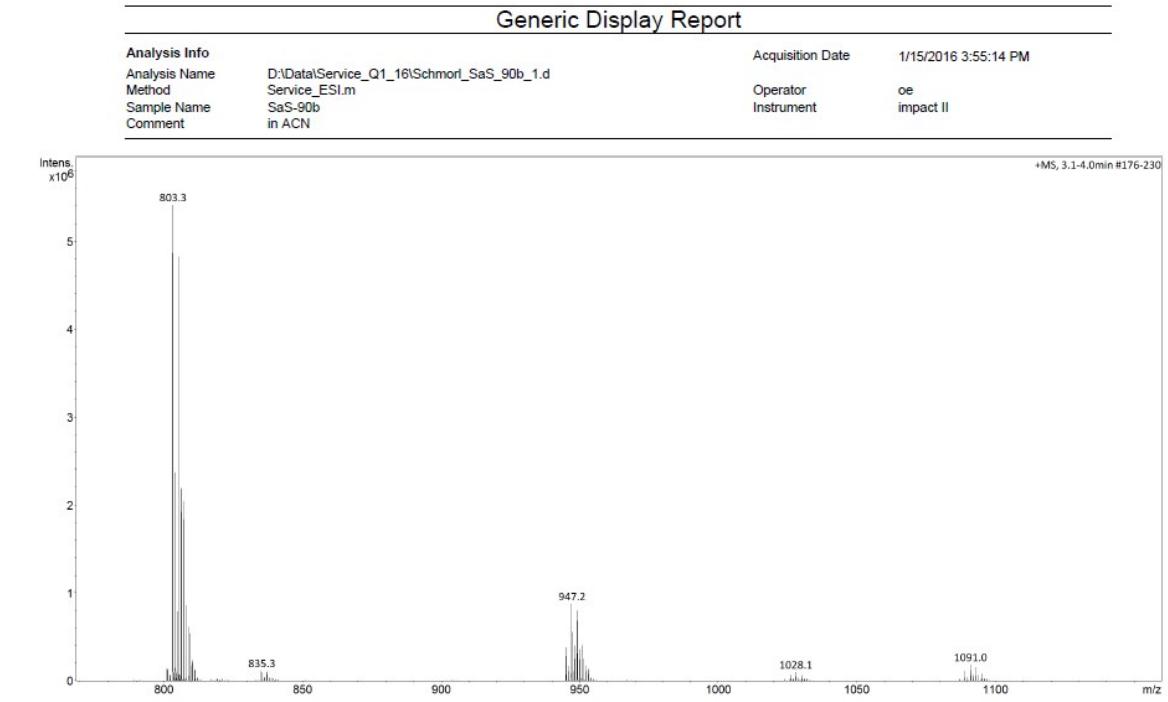

Figure S9. Section of the ESI-MS spectrum for $[LNi_2(\mu\text{-}F)(CuBr_2)]$ (**5**) (c ~ 10^{-3} M).

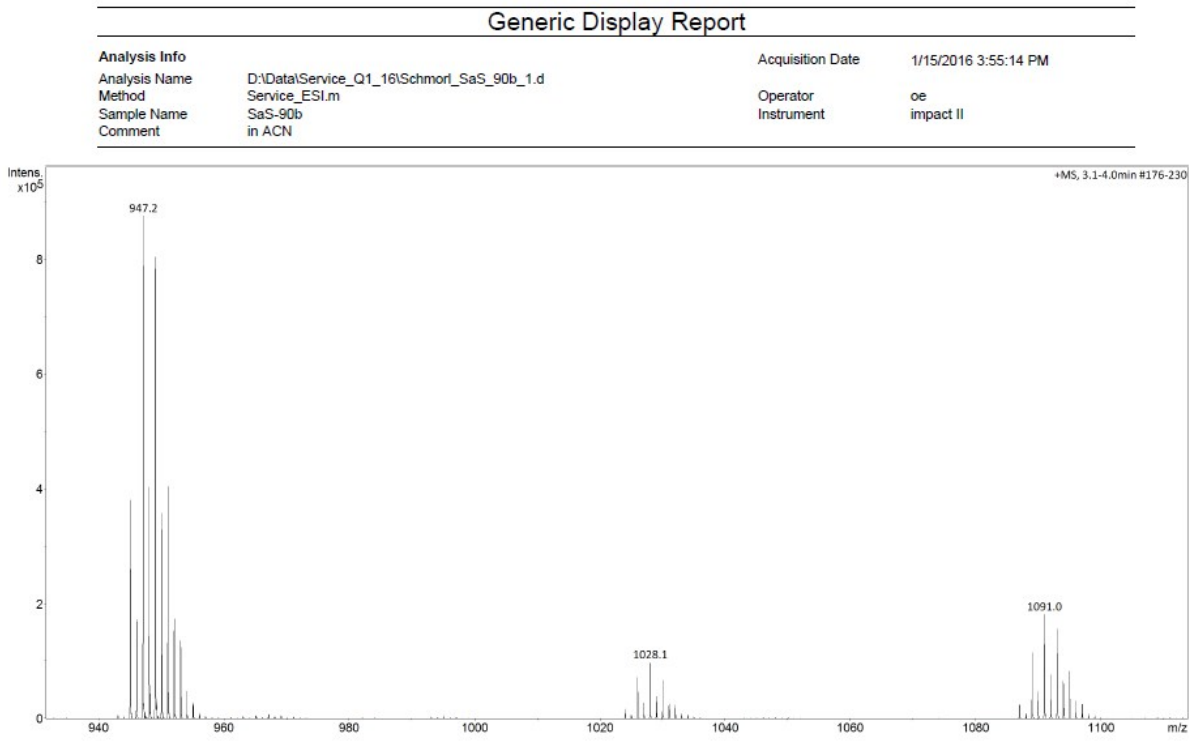

Figure S10. Section of the ESI-MS spectrum for $[LNi_2(\mu\text{-}F)(CuBr_2)]$ (**5**) (c ~ 10^{-3} M).

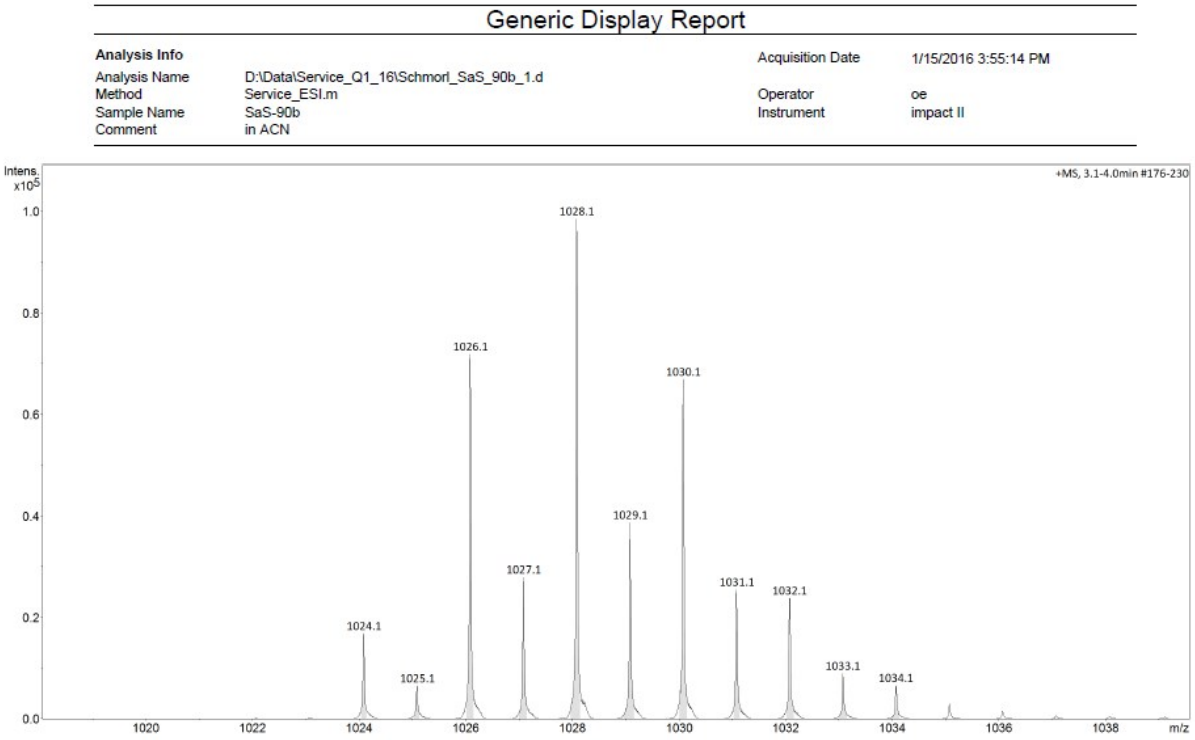

Figure S11. Section of the ESI-MS spectrum for $[LNi_2(\mu\text{-}F)(CuBr_2)]$ (**5**) (c ~ 10^{-3} M).

d) ESI mass spectrometry for $[LNi_2(\mu\text{-}F)(CuI_2)]$ (6). The $^+$ESI mass spectrum of a dilute MeCN solution of **6** (Figure S12) reveals a weak peak at *m*/*z* = 1122.08 attributable to a $[LNi^{II}Ni^{III}(\mu\text{-}F)(CuI_2)]^+$ cation (see Figure S13, S14 for an enlarged section of the spectrum). The more intense peaks at *m*/*z* = 803.3 and 995.2 can be assigned to a $[LNi^{II}Ni^{II}(\mu\text{-}F)]^+$ cation and a $[LNi^{II}Ni^{II}(\mu\text{-}F)(Cu^{I}I)]^+$ cation, respectively

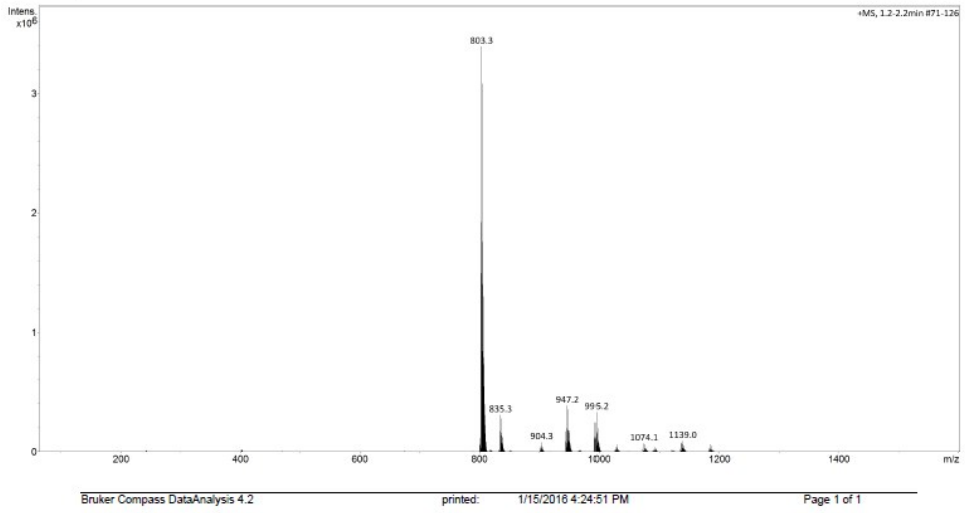

Figure S12. ESI-MS spectrum of a 10^{-3} M solution of $[LNi_2(\mu\text{-}F)(CuI_2)]$ (**6**) in MeCN.

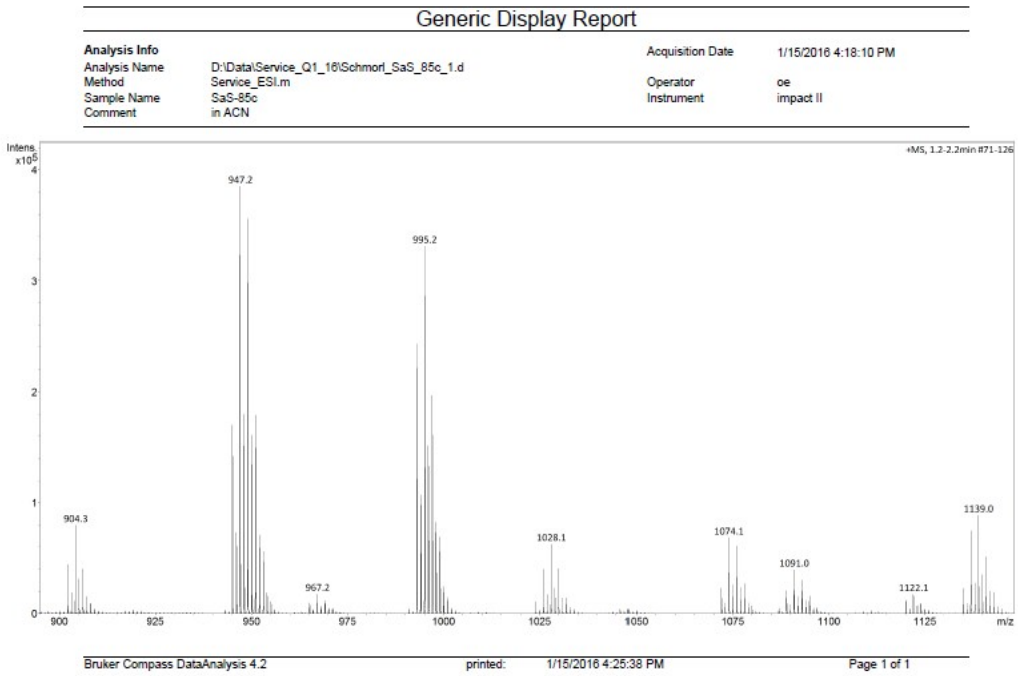

Figure S13. Section of the ESI-MS spectrum of $[LNi_2(\mu\text{-}F)(CuI_2)]$ (**6**) in MeCN.

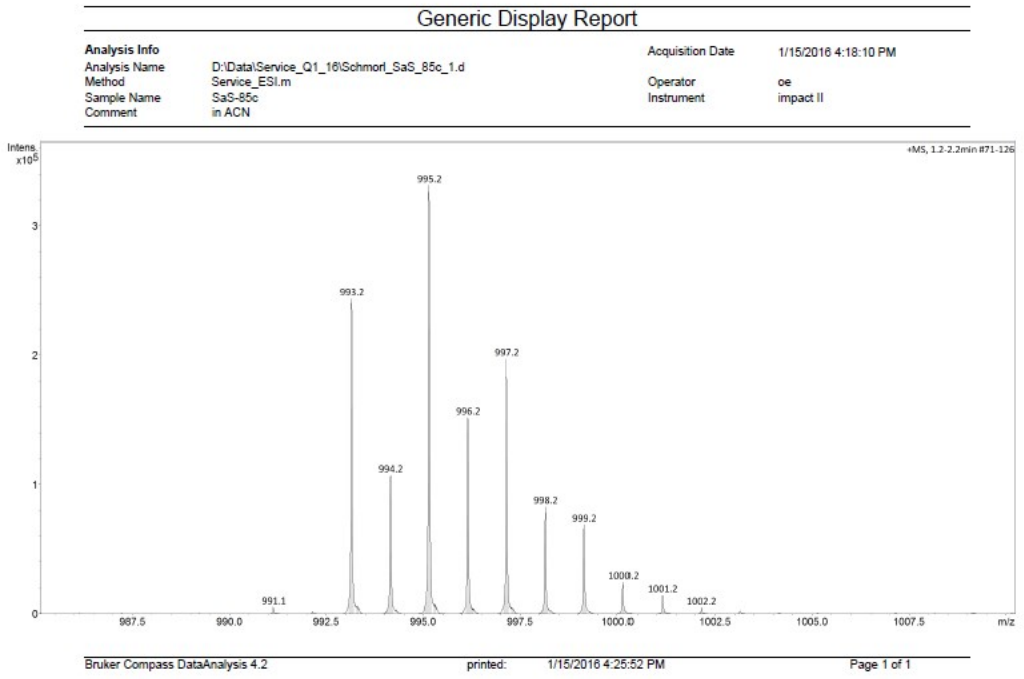

Figure S14. Section of the ESI-MS spectrum of a dilute solution of $[LNi_2(\mu\text{-}F)(CuI_2)]$ (**6**) in MeCN ($c \sim 10^{-3}$ M)

3) Characterization of compounds 3-6 by infrared spectroscopy

All compounds have been investigated by FT-IR spectroscopy. The ATR-FTIR spectra of **3**-**6** are shown in Figures S15-S18. Overlays of the FT-IR spectra are provided in Figure 1 (for **1** and **3**), Figure 3 and Figure S18 (for **2** and **6**), and Figure S19 (for **4**-**6**), respectively. Table S1 lists the data and their assignments.

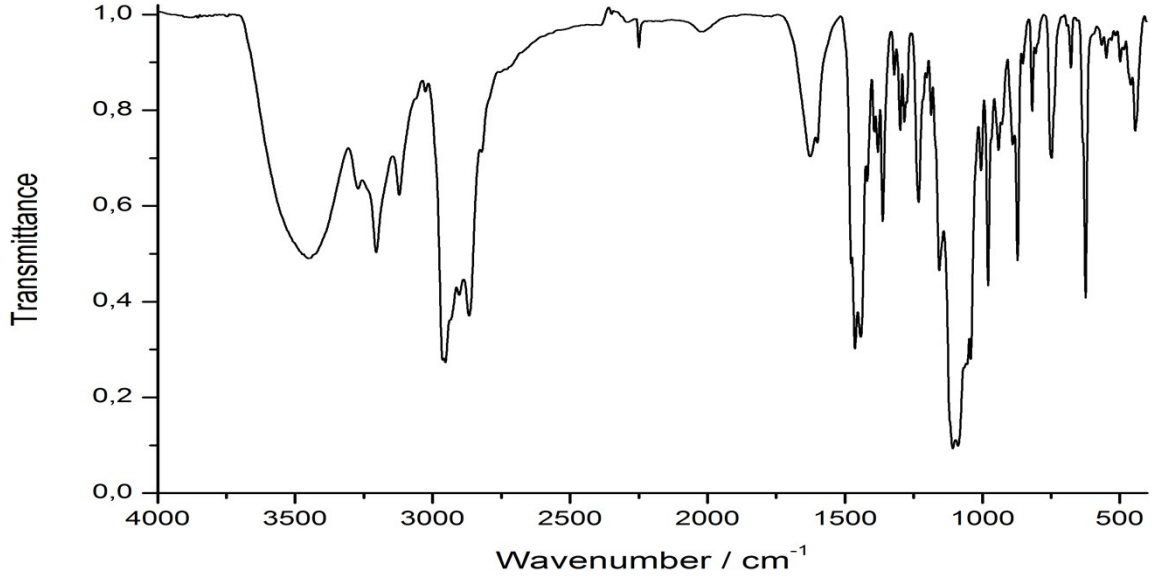

Figure S15. ATR IR spectrum of $[LCo_2(\mu\text{-}F)(CuBr_2)]ClO_4$ (**3**).

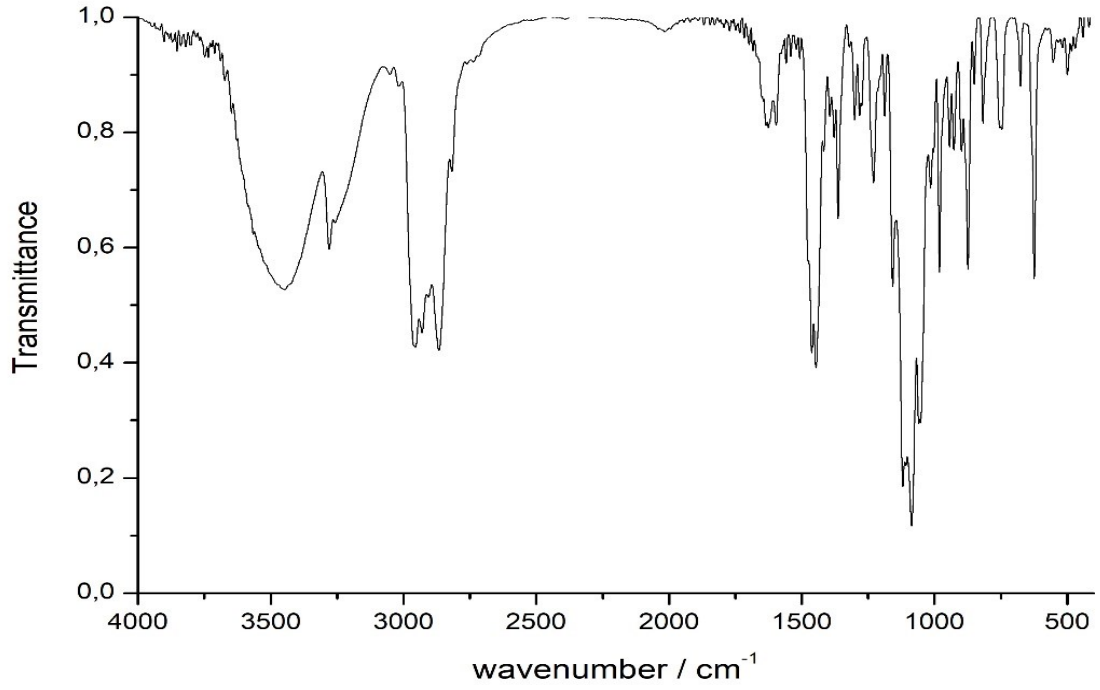

Figure S16. ATR IR spectrum of $[LNi_2(\mu\text{-}F)(CuCl_2)]$ (**4**).

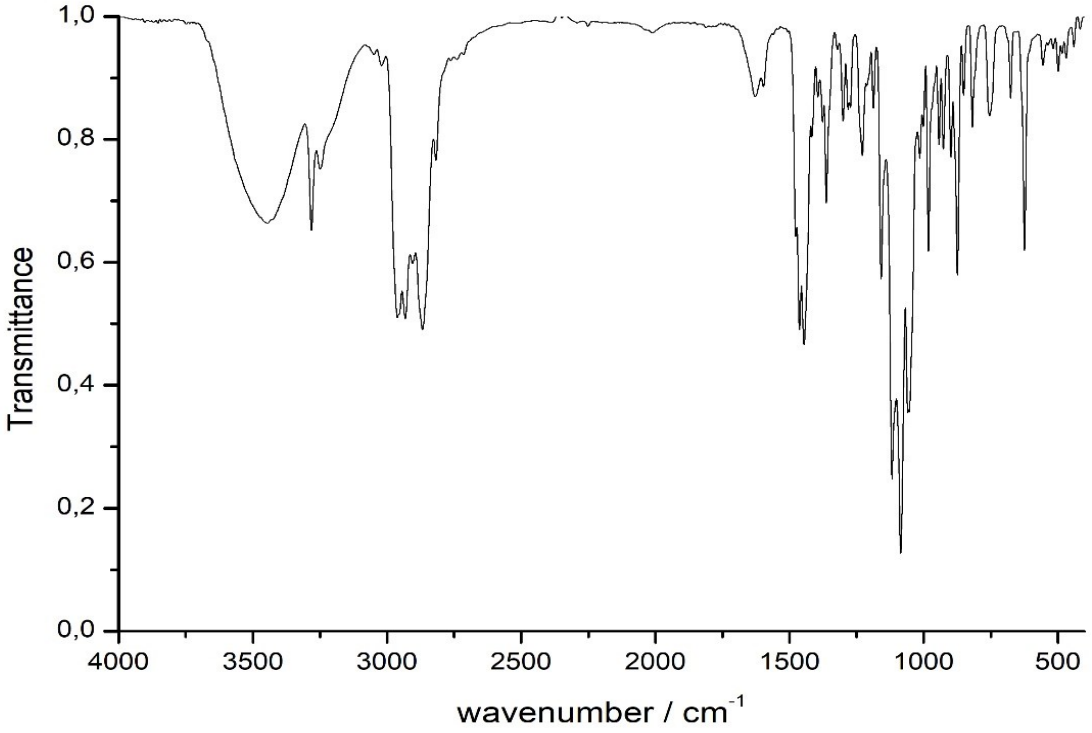

Figure S17. ATR IR spectrum of [$LNi_2(\mu$-F)($CuBr_2$)] (**5**).

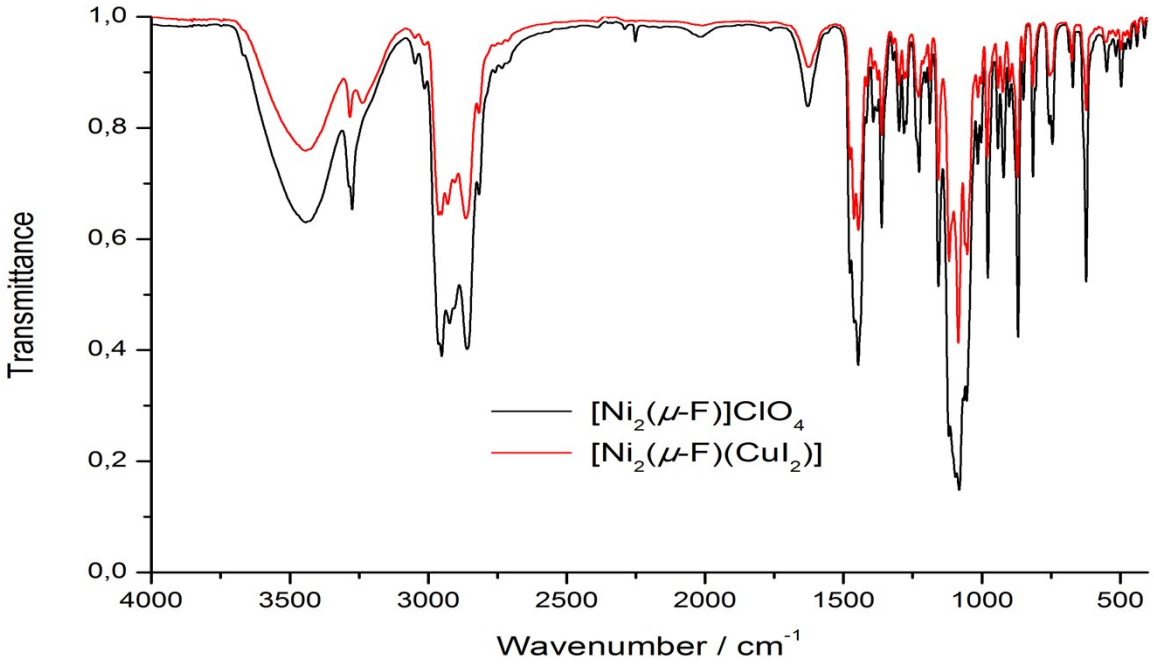

Figure S18. ATR IR spectra for [LNi_2(μ-F)]ClO_4 (**2**) and for [LNi_2(μ-F)(CuI_2)] (**6**).

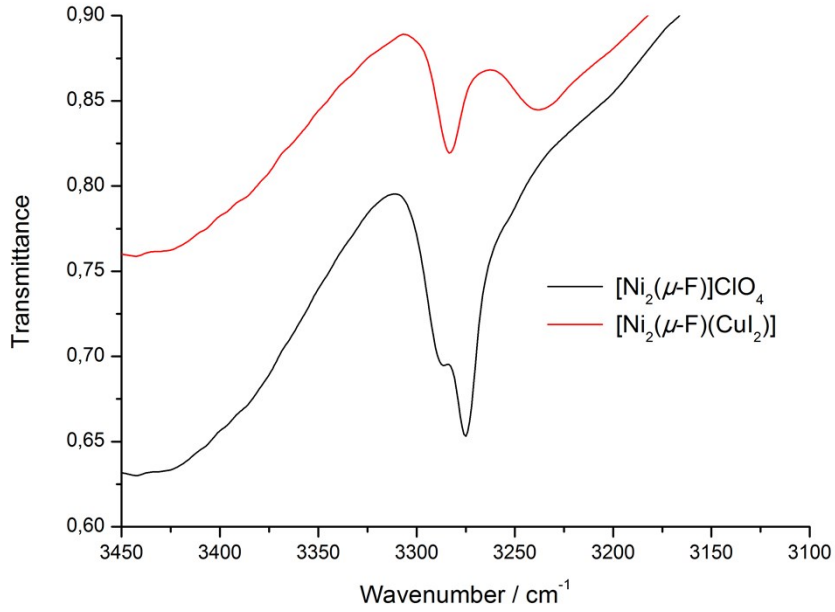

Figure S19. Overlay of ATR IR spectra for $[LNi_2(\mu\text{-}F)]ClO_4$ (**2**) and for $[LNi_2(\mu\text{-}F)(CuI_2)]$ (**6**) (ν(NH) region).

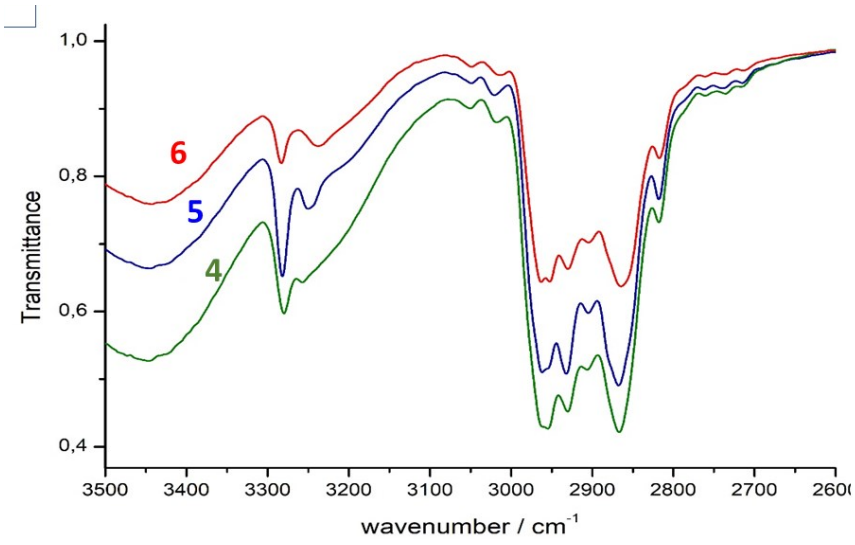

Figure S20. Overlay of ATR-FTIR spectra for $[LNi_2(\mu\text{-}F)(CuCl_2)]$ (**4**), $[LNi_2(\mu\text{-}F)(CuBr_2)]$ (**5**) and $[LNi_2(\mu\text{-}F)(CuI_2)]$ (**6**) in the 3500-2600 cm^{-1} region.

Table S1. Selected analytical data for $[LNi_2(\mu F)]ClO_4$ (**2**) and $[LNi_2(\mu F)(CuX_2)]$ (X = Cl (**4**), Br (**5**), I (**6**)).

	2	**4** (X = Cl)	**5** (X = Br)	**6** (X = I)	assignment
UV-vis [a] λ/nm (ε/$M^{-1}cm^{-1}$)	204 (60326) 283 (15118)	204 (95327) 280 (12173)	205 (158995) 279 (13323)	203 (115108) 280 (19233)	π-π*
	450 (sh)	450 (sh)	450 (sh)	450 (sh)	$RS^- \rightarrow M$ CT
	631 (50)	611 (1194)	614 (744)	618 (248)	ν_2 ($^3A_{2g} \rightarrow {}^3T_{1g}$)
	1021 (50)	1014 (511)	1019 (398)	1021 (152)	ν_1 ($^3A_{2g} \rightarrow {}^3T_{1g}$)
FT-IR [b]	3275	3285	3282	3283	ν(NH)
ν / cm^{-1}	-	3256	3250	3238	ν(NH···X)

a) MeCN/EtOH (1:1 v/v), 10^{-3} M (vis-NIR region), 10^{-5} M (UV region). b) ATR mode.

4) Characterization of compounds 3 and 6 by X-ray crystallography. Single crystals of $[LCo^{II}Co^{III}(\mu\text{-}F)(CuBr_2)](ClO_4)\cdot 2MeCN$ (**3**·2MeCN) and $[LNi^{II}_2(\mu\text{-}F)(CuI_2)]\cdot 2MeCN$ (**6**·2MeCN) were selected and mounted on the tip of a glass fibre using perfluoropolyether oil. The data sets were collected at 180(2) K using a STOE IPDS-2 (for **3**·2MeCN) or STOE IPDS-1 diffractometer (for **6**·2MeCN) both equipped with graphite monochromated Mo-K_α radiation (λ = 0.71073 Å). The data were processed with the programs XAREA and X-RED32.[S2] The structures were solved by direct methods[S3] and refined by full-matrix least-squares techniques on the basis of all data against F^2 using SHELXL-2014/8.[S4] PLATON was used to search for higher symmetry.[S5] All non-hydrogen atoms were refined anisotropically. Graphics were produced with Ortep3 for Windows[S6] and Pov-RAY for Windows.[S7]

Crystallographic data for $[LCo^{II}Co^{III}(\mu\text{-}F)(CuBr_2)]ClO_4\cdot 2MeCN$ (3·2MeCN). The data set was of low quality and can only serve to confirm the atom connectivity. The mean I/σ(I) is only 2.78 and drops to below 3 at ~33° in 2 Θ. The structure could be solved and refined, but the model can only serve to confirm the atom connectivity. The cif file of this structure is available upon request from the corresponding author. **Crystal data:** $C_{42}H_{70}Br_2ClCo_2CuFN_8O_4S_2$, M_r = 1210.85 g/mol, monoclinic space group $P2_1/c$, a = 12.973(3) Å, b = 31.574(6) Å, c = 13.549(3) Å, β = 114.88(3), V = 5035(2) $Å^3$, Z = 4, ρ_{calcd} = 1.597 g/cm^3, T = 180(2) K, μ(Mo K_α) = 2.85 mm^{-1} (λ = 0.71073 Å), 17555 reflections measured, 8789 unique, 2892 with $I > 2\sigma(I)$. Final R_1 = 0.0461, wR_2 = 0.0847 ($I > 2\sigma(I)$), 563 parameters / 0 restraints, min./max. residual electron density = –0.929/0.565 e/$Å^3$.

A perspective view of the central core of **3** showing the immediate coordination environments of the Co and Cu atoms of the $[LCo^{II}Co^{III}(\mu\text{-}F)(Cu^{I}Br_2)]^+$ cation in crystals of **3**·2MeCN is shown in Figure S21. On the basis of the larger metal ligand bond lengths, Co1 may be assigned divalent and Co2 is trivalent. Figure S22 provides a van der Waals representation of the cation with a viewing direction to the thiolate S atom S(1).

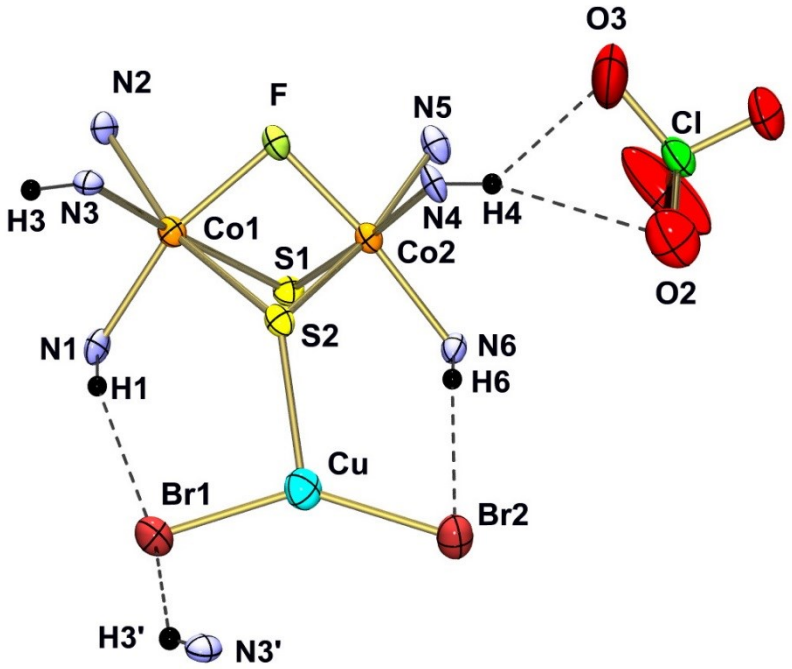

Figure S21. Perspective view of the immediate coordination environments of the Co and Cu atoms of the $[LCo^{II}Co^{III}(\mu\text{-}F)(Cu^{I}Br_2)]^+$ cation in crystals of **3**·2MeCN (C and H atoms, except NH atoms, omitted for clarity). Thermal ellipsoids are drawn at the 50 % probability level. Intra- and intermolecular hydrogen bonding interactions are indicated by dashed lines. Selected bond lengths / Å and angles /°: Given the low quality of the data, all parameters should be taken indicative rather than definitive. Co1–F1 2.075(5), Co1–N1 2.105(8), Co1–N2 2.230(10), Co1–N3 2.138(8), Co1–S2 2.537(3), Co1–S1 2.563(3), Co2–F1 1.993(6), Co2–N4 1.936(7), Co2–N5 2.157(9), Co2–N6 2.095(9), Co2–S1 2.212(3), Co2–S2 2.272(3), Cu–S2 2.465(3), Cu–Br1 2.294(2), Cu–Br2 2.342(2), $Cu^{I}\cdots Ar^{centroid}$ 3.21 ($Ar^{centroid}$ refers to the center of the aryl ring next to the Cu^{I} atom (not shown)); Br1-Cu-Br2 144.35(8), Br1-Cu-S2 99.24(9), Br2-Cu-S2 115.82(8), H1···Br1 3.01, H6···Br2 2.67, H3□···Br1 2.67, H4···O2 2.55, H4···O3 2.72; H1···Br1-Cu 92°, H6···Br2-Cu 74°, Br1···N3 3.555. Symmetry code used to generate equivalent atoms: +*x*, 0.5-*y*, 0.5+*z* (□)

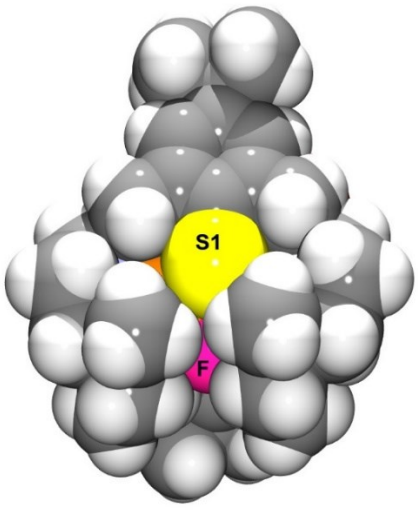

Figure S22. Van der Waals representation of the environment of the thiolate atom S1 in $[LCo^{II}Co^{III}(\mu\text{-}F)(CuBr_2)]ClO_4$ (**3**). In contrast to the environment of the atom S2 (see Figure 2

main text), there are no nearby NH donors that could form hydrogen bonds with a $CuBr_2^-$ moiety (if the latter would bind to this S1 atom).

Crystallographic data for $[Ni^{II}_2L(\mu\text{-}F)(CuI_2)]\cdot 2MeCN$ (6·2MeCN). $C_{42}H_{70}CuFI_2N_8Ni_2S_2$, M_r = 1204.94 g/mol, triclinic space group *P*-1, *a* = 13.171(3) Å, *b* = 13.363(3) Å, *c* = 15.858(3) Å, α = 92.79(3)°, *β* = 108.39(3)°, γ = 110.92(3)°, *V* = 2432.6(12) Å^3, *Z* = 2, ρ_{calcd} = 1.645 g/cm^3, *T* = 180(2) K, μ(Mo K_α) = 2.60 mm^{-1} (λ = 0.71073 Å), 30126 reflections measured, 10418 unique, 9181 with $I > 2\sigma(I)$. Final R_1 = 0.0326, wR_2 = 0.0873 ($I > 2\sigma(I)$), 523 parameters / 0 restraints, min./max. residual electron density = –1.251/1.323 e/Å^3. CCDC-number: 2034011. A perspective view of the central core of **6** showing the immediate coordination environments of the Ni and Cu atoms of the neutral $[LNi^{II}_2(\mu\text{-}F)(Cu^{I}I_2)]$ complex in crystals of **6**·2MeCN is shown in Figure S23. The H1···I1 distance at 2.88 Å is much shorter than the sum (3.18 Å) of the van der Waals radii of r_W(H) = 1.20, r_w(I) = 1.98 Å).[S8] The I2···H6 and I1···H3′ distances at 3.71 Å and 3.34 Å, on the other hand, are much longer than the I1···H1 distance, and the corresponding atoms are thus not connected by a hydrogen bond (taking the sum of the van der Waals radii as the criterion).

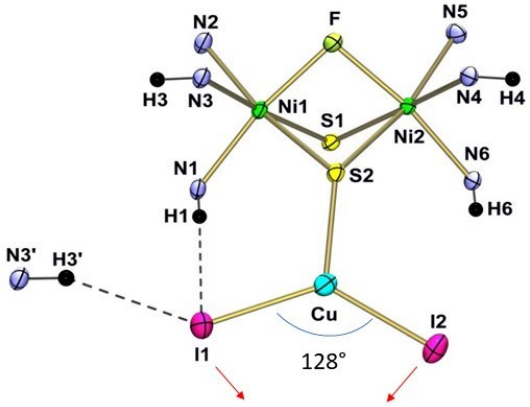

Figure S23. Perspective view of the immediate coordination environments of the Ni and Cu atoms of the neutral $[Ni^{II}_2(L)(\mu\text{-}F)(CuI_2)]$ complex in crystals of **6**·2MeCN (C and H atoms, except NH atoms, omitted for clarity). Thermal ellipsoids are drawn at the 50 % probability level. Hydrogen bonding interactions are indicated by dashed lines. Selected bond lengths / Å and angles /°: Cu-I1 2.547(1), Cu-I2 2.512(1), Cu-S2 2.2968(9), Ni1-F1 2.066(2), Ni1-N1 2.132(2), Ni1-N2 2.189(3), Ni1-N3 2.116(2), Ni1-S1 2.421(1), Ni1-S2 2.448(1), Ni2-F1 2.052(2), Ni2-N4 2.116(2), Ni2-N5 2.181(3), Ni2-N6 2.142(2), Ni2-S1 2.473(1), Ni2-S2 2.482(1); I1-Cu-S2 114.44(3), I2-Cu-S2 116.57(3), I1-Cu-I2 128.03(4); I1···H1 2.88, I1···H3′ 3.34. The red arrows illustrate the strong bending of the $[CuI_2]^-$ unit. This leads to a large I2···H6 distance of 3.71 Å, which is out of the range of a hydrogen bonding interaction. Symmetry code used to generate equivalent atoms: -*x*, -*y*, -*z* (′).

5) Characterization of compounds 3 and 4-6 by variable temperature dc magnetic susceptibility measurements

a) Magnetic susceptibility measurements for $[LCo^{II}Co^{III}(\mu\text{-}F)(CuBr_2)]ClO_4$ (3)

The temperature dependence of the magnetic susceptibility of compound $[LCo^{II}Co^{III}(\mu\text{-}F)(CuBr_2)]ClO_4$ (**3**) was investigated in the temperature range between 2 and 330 K in an applied external field of $B = \mu_0 H$ = 1.0 T using an MPMS 7XL SQUID magnetometer (Quantum

Design). The observed susceptibility data were corrected for underlying diamagnetism. Figure S24 shows the experimental data and the theoretical fit in the form of a μ_{eff} versus T plot.

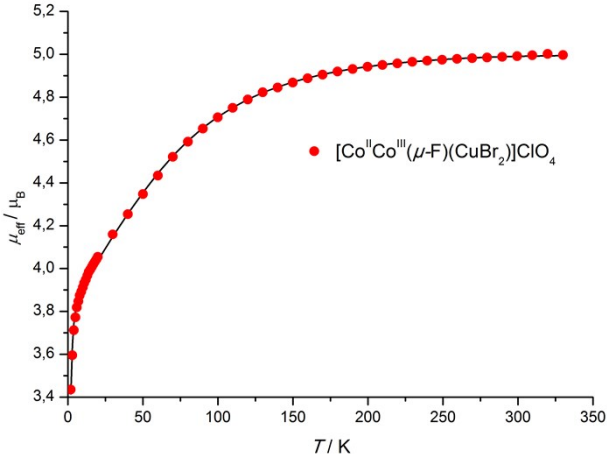

Figure S24. Temperature dependence of the effective magnetic moment μ_{eff} (per dinuclear complex) for **3**. The solid line corresponds to the best fit to eq. 1.

The effective magnetic moment of the mixed-valent $Co^{II}Co^{III}$ complex at 295 K (4.99 μ_B) is in good agreement with the presence of a high-spin Co^{2+} ion (d^7, S = $^3/_2$), a low-spin Co^{3+} ion (d^6, S=0), and a Cu^+ ion (d^{10}, S = 0). The μ_{eff} value is significantly larger than the theoretical spin-only value of 3.87 μ_B for a six-coordinate Co^{2+} ion (S = $^3/_2$, g = 2.00), attributed to an orbital contribution to the magnetic moment, which is typically observed for high-spin Co^{II} complexes with a $^4T_{1g}$ ground state (in O_h symmetry).[S9] The magnetic moment of **3** decreases with decreasing temperature to a value of 3.44 μ_B at 2 K, as a consequence of zero-field splitting and the residual orbital angular momentum of the Co^{2+} ion. The temperature dependence of the magnetic susceptibility for the cobalt complex was analysed by using the spin-Hamiltonian (equation S1) by using a full-matrix diagonalization approach.

$$\hat{H} = [D_i(\hat{S}_{zi}^2 - \frac{1}{3}\hat{S}_i(\hat{S}_i + 1)) + g_i\mu_B\hat{S}_{i\tau}B_\tau)] \ (\tau = x, y, z) \qquad (S1)$$

A reasonable fit to the experimental susceptibility data was possible. The best fit gave the following parameters: g = 2.55, |D| = 88.94 cm^{-1}.

b) Variable-temperature magnetic susceptibility measurements for the complexes [LNi$^{II}_2$(μ-F)(Cu^{I}X$_2$)] (X = Cl (4), Br (5), I (6))

Variable-temperature magnetic susceptibility measurements were performed for powdered samples of the complexes **4**-**6** between 2 and 330 K in an applied external magnetic field of B = 1.0 T by using a SQUID magnetometer. Plots of the temperature dependence of the effective magnetic moment μ_{eff} (per binuclear complex) are displayed in Figure 4 (main manuscript). The data for the precursor **2** have been reported earlier and are included for comparison.[10] The data for complex **6** are representative for the CT adducts **4**-**6** and will be described. As can be seen, the effective magnetic moment increases gradually from ca. 4.4 μ_B at 295 K to 4.9 μ_B at 15 K, and then decreases rapidly to 4 μ_B at 2 K. This behavior indicates an intramolecular ferromagnetic exchange interaction between the two Ni^{2+} (S = 1) ions that leads to an S_t = 2 high-spin ground state. Notice that the precursor complex **2** shows a different behavior. The effective magnetic moment decreases steadily from 4.44 μ_B at 300 K to 4.12 μ_B at 17 K and then drops rapidly to 2.3 μ_B at 2 K, indicative of an antiferromagnetic exchange interaction that leads to a diamagnetic S_t = 0 ground state. The change of the coupling type from

antiferromagnetic in **2** to ferromagnetic in **6** is ascribed to the RS→Cu^+ CT interaction in **6** that reduces the e^- density on the thiolate sulfur atom S2, thereby altering the magnetic coupling through the thiolato bridges.

The temperature dependence of the magnetic susceptibility for the dinuclear nickel complexes was analyzed by using the spin Hamiltonian (eq S2) utilizing a full matrix diagonalization approach.[S11] The magnetic interaction is represented by an isotropic Heisenberg-Dirac-van Vleck exchange interaction term where J is the magnetic exchange coupling constant,[S12] and D_i and g_i are the local axial zero field splitting parameters and g values (isotropic average), respectively.[S13] The D and g values were considered to be identical for the two nickel ions.

$$\hat{H} = -2J\hat{S}_1\hat{S}_2 + \sum_{i=1}^{2}[D_i(\hat{S}_{zi}^2 - \frac{1}{3}\hat{S}_i(\hat{S}_i+1)) + g_i\mu_B\hat{S}_{i\tau}B_\tau)]\ (\tau = x,y,z) \qquad (S2)$$

A reasonable fit of the experimental data was possible by taking into account the zero-field splitting and temperature independent paramagnetism (TIP), yielding J = +15.7 cm^{-1}, $|D|$ = 6.0 cm^{-1}, g = 2.0 for **4**, J = +7.9 cm^{-1}, $|D|$ = 5.7 cm^{-1}, g = 2.06 for **5**, and J = +10.3 cm^{-1}, $|D|$ = 3.7 cm^{-1}, and g = 2.18 for **6**. Thus, in all cases a weak ferromagnetic exchange interaction is present in **4-6** that leads to a paramagnetic S_t = 2 ground state. It should be noted that temperature dependent magnetic susceptibility measurements are not very appropriate for the determination of the sign and magnitude of D,[S14] and the D value should therefore be taken indicative rather than definitive.[S15] On the other hand, the value of J is not influenced markedly by the value (or sign) of D and represents an accurate measure of the magnetic coupling in this complex.

The conversion of the S=0 spin ground state in **2** to a S=2 spin ground state in **4-6** can be traced to the attachment of the cuprate ions to one of the bridging thiophenolato groups. If it can be assumed that the coupling in these compounds is the arithmetic sum of the individual coupling constants through the RS1→CuX_2, RS2, and F bridges and that the coupling through the F and the RS groups in **4-6** is identical to that in **2** (as determined by broken-symmetry DFT calculations,[S10] i.e. $J(\mu$-$F^-)$ = 54.20 cm^{-1}, $J(\mu$-SR) = -27.38 cm^{-1}), then the coupling through the triply bridging μ-SR→CuX_2 bridges is less antiferromagnetic in nature (-11.12 cm^{-1} (**4**), - 19.12 cm^{-1} (**5**), and -16.52 cm^{-1} (**7**)) than through a μ_2-bridging thiophenolato group. A similar behavior was observed for a related thiolate→Br_2 CT complex.[S16]

$$J_{tot}(\mathbf{2}) = J(\mu\text{-}F^-) + 2 \times J(\mu\text{-}SR^-) = -0.56\ cm^{-1} \qquad (S3)$$

$$J_{tot}(\mathbf{4\text{-}6}) = J(\mu\text{-}F^-) + J(\mu\text{-}SR^-) + J(\mu\text{-SR}\rightarrow CuX_2) \qquad (S4)$$

Table S2. Magnetic properties and selected metrical data for complexes **2**, **4-6**.

	g	$\|D\|$/ cm^{-1}	J_t / cm^{-1}	χ_{TIP} / $cm^3 \cdot mol^{-1}$	$\mu_{eff,330K}$ / μ_B	Ni-S-Ni angles / °	Ni-F-Ni angle / °	Ni-S /Å
2	2.18	8.65	– 0.56	$502.3 \cdot 10^{-6}$	4.40	76.30	95.6(1)	2.482(1) 2.487(1) 2.436(1) 2.479(1)
4	2.00	6.0	+15.7	$1565 \cdot 10^{-6}$	4.35	*n.d.*	-	-
5	2.06	5.7	+ 7.9	$242.7 \cdot 10^{-6}$	4.16	*n.d.*	-	-
6	2.18	3.7	+10.3	$1298 \cdot 10^{-6}$	4.48	77.72 (S1) 77.03 (S2)	96.41	2.421(1) 2.448(1) 2.473(1) 2.482(1)

6) Characterization of complexes by UV-vis-Spectroscopy

a) UV-vis Spectroscopy for $[LCo_2(\mu\text{-}F)(CuBr_2)]ClO_4$ (3)

The electronic absorption spectrum of complex **3** has been recorded in acetonitrile solution at ambient temperature. Figure S25a displays the 190-450 nm region of the spectrum. The 450-1000 nm range of the spectrum is shown in Figure S25b. The UV-vis spectrum of the mixed-valent $Co^{III}Co^{II}$ complex is dominated by intense π-π* (190-300 nm) and thiophenolate-to-cobalt(III) charge transfer transitions (300-500 nm) characteristic of thiolato-bridged cobalt(III)-complexes.[S17] The spectrum displays also several weak features in the visible region, attributable to spin-allowed but Laporte-forbidden *d-d* transitions of a Co^{2+} ion. The features at 557 (sh), 620 (sh), 650 (sh), and 680 (sh) nm are attributable to components of the parent octahedral ligand field transitions ($^4T_{1g}(F) \rightarrow {}^4T_{1g(P)}$, $^4T_{1g}(F) \rightarrow {}^4A_{2g}$) split by lower symmetry.

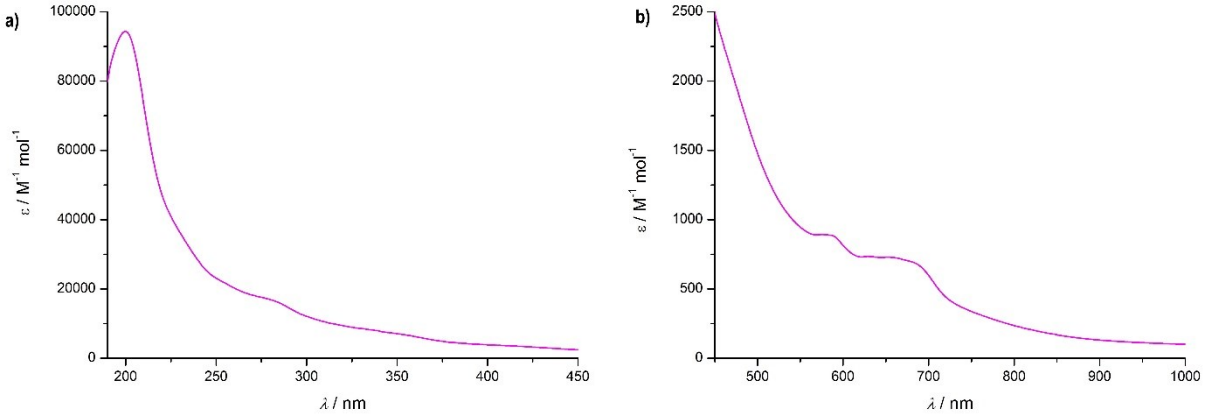

Figure S25. UV-vis-NIR spectra of $[LCo^{II}Co^{III}(\mu\text{-}F)(CuBr_2)]ClO_4$ (**3**) in CH_3CN at 298 K. Concentration of solutions: 1×10^{-3} M (vis-NIR range, left figure) and 1×10^{-5} M (UV range, left figure).

b) UV/vis Spectroscopy for the complexes $[LNi_2(\mu\text{-}F)(CuX_2)]$ (X = Cl (4), Br (5), I (6))

Figure S26 shows the electronic absorption spectra of 10^{-3} M and 10^{-5} M solution of compounds **4**-**6** in the vis-NIR (400-1350 nm) and UV region (190-400 nm), respectively. The electronic absorption spectra of the free ligand and of compound **2** are shown for comparative purposes. Table S1 lists the data and assignments. The two bands around 600 and 1050 nm are attributable to *d–d* transitions and are typical for Ni^{II} complexes with a distorted octahedral $Ni^{II}N_3S_2X$ coordination environment.[S1] The ν_2 ($^3A_{2g} \rightarrow {}^3T_{1g}$ in O_h symmetry) transition occurs in the 580-630 nm range and the ν_1 transition ($^3A_{2g} \rightarrow {}^3T_{2g}$) is seen between 950 and 1200 nm. Complexes **4**-**6** exhibit a weak shoulder at ~450 nm which may be due to the ν_3($^3A_{1g} \rightarrow {}^3T_{1g}$(P)) transition of the octahedral $Ni^{II}N_3S$(S-CuX)F chromophore. The UV region is dominated by more intense π-π* transitions within the aromatic rings of the supporting ligand. The features at 325 nm are tentatively assigned to thiolate to Ni^{2+} or thiolate to Cu^+ charge transfer transition.

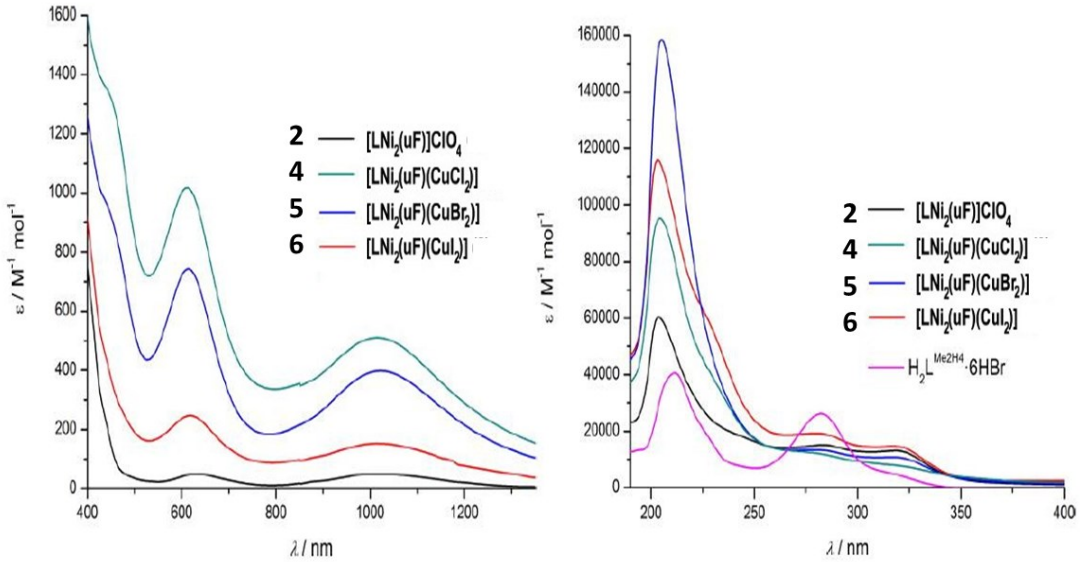

Figure S26. UV-vis-NIR spectra of the complexes $[LNi^{II}_2(\mu\text{-F})(CuX_2)]$ (X = Cl (**4**), Br (**5**), I (**6**)) in CH_3CN at 298 K. Concentration of solutions: 1×10^{-3} M (vis-NIR range, left figure) and 1×10^{-5} M (UV range, right figure).

7) EPR spectrum for 3

The continuous wave (cw) EPR measurements for **3** were performed at X-band frequency (9.4 GHz) with a Bruker EMX micro spectrometer equipped with a high sensitivity ER 4119 HS cylindrical cavity and an Oxford Instruments He cryostat ESR 900. The EPR spectrum of **3** (Figure S27) reveals a strong signal centered at $g_{av} \sim 4.0$ typical for high-spin Co^{II} ions with an $S = {}^3/_2$ spin ground state.[S17]

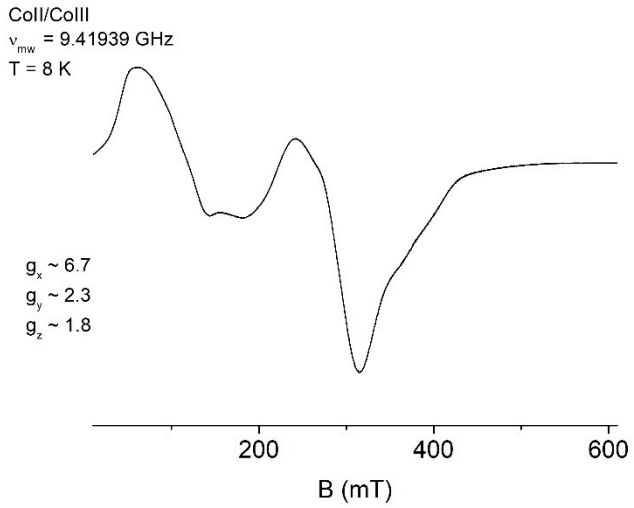

Figure S27. EPR powder spectrum of $[LCo^{II}Co^{III}(\mu\text{-F})(CuBr_2)]ClO_4$ (**3**) at 8 K. Conditions: microwave frequency, ν = 9.41939 GHz, microwave power, 2 mW; modulation frequency, 100 kHz, modulation amplitude: 4 G.

8) Characterization of Compounds by DFT calculations

Density functional theoretical calculations (DFT) calculations on the cobalt and nickel complexes $[LCo_2(\mu\text{-}F)]^{2+}$, **3**, **5** and **6**, respectively, were carried out using the Jaguar program package (version 10.3).[S18] The geometry optimizations were performed using the M06-D3 density functional. The MO6-D3 functional is parameterized for organometallic and non-covalent interactions[S19] and includes physically and chemically important London dispersion interactions.[S20] The same computational model was successfully utilized for calculation of the bonding situation of other nickel thiolate→iodine charge-transfer complexes.[S21] The molecular geometries and energies of the studied structures were calculated at the M06-D3/LACVP*/PBF level of theory as implemented in the Jaguar program package. The LACVP* basis set uses the standard 6-31G(d) basis set for light elements and the LAC pseudopotential for heavier elements,[S22] such as Co, Ni, Br and I in this case.

All geometry optimizations were carried out starting from the crystallographically determined atom coordinates of either **2**, **3** or **6**. The geometry of the complex $[LCo^{II}Co^{III}(F)]^{2+}$ (which has not yet been synthesized) was optimized starting from the coordinates of the $[LCo^{II}Co^{III}(F)CuBr_2)]^{2+}$ cation in **3** (with the $CuBr_2$-moiety omitted). The geometry of the complex $[LNi^{II}_2(F)(CuBr_2)]$ **5** (synthesized but not yet crystallographically characterized) was optimized starting from the coordinates of the $[LNi^{II}_2(F)(CuI_2)]$ complex in **6** (with the two I substituents replaced by Br atoms). Frequency calculations were done at the same level of theory to characterize the stationary points on the potential surface and to obtain total enthalpy (H_{tot}) and Gibbs free energy (G) at a standard temperature of 298.15 K. The calculated frequencies were scaled by a factor of 0.94.
To take solvent effects (acetonitrile and THF in our case) into account the calculation were done using Jaguar's dielectric continuum Poisson-Boltzmann solver, which fits the field produced by the solvent dielectric continuum to another set of point charges.[S23] Counterions and/or solvent molecules were neglected. The quartet state ($M^S = 4$) for **3** was found to be 10.6 kcal mol^{-1} more stable than the doublet ($M^S = 2$) state, while the quintet state for **6** ($M^S = 5$) is 36.5 kcal mol^{-1} and 48.5 kcal mol^{-1} more stable than the triplet ($M^S = 3$) and singlet ($M^S = 1$) states, respectively. Consequently, the analysis of quantum chemical data was further done for the quartet states of **3** and the quintet states of **5** and **6**, respectively.

a) DFT calculations for $[LCo^{II}Co^{III}(\mu\text{-}F)]^{2+}$

Figure S28 displays the optimized geometry of the $[LCo^{II}Co^{III}(\mu\text{-}F)]^{2+}$ dication in the gas phase. The optimized geometry of the fluorido-bridged complex (in MeCN) was found to be very similar to the structure of the hydroxido-bridged $[LCo^{II}Co^{III}(\mu\text{-}OH)]^{2+}$ dication in **1**, which is taken as the reference compound. The average Co^{III}-S bond distances are ca. 0.02 Å longer and the average Co^{II}-S bonds are 0.003 Å longer in the calculated structure (Table S3). The average Co^{III}-N bond distances and the average Co^{II}-N bond distances (not listed in Table S3) in the calculated structure and the experimental structure are virtually identical. The main difference between the calculated structure of the $[LCo^{II}Co^{III}(\mu\text{-}F)]^{2+}$ dication and the experimental structure of the $[LCo^{II}Co^{III}(\mu\text{-}OH)]^{2+}$ dication in **1** is an increase in the Co^{II}–F distance of ca. 0.08 Å in the calculated relative to the Co^{II}-OH distance of the experimental structure of **1** [Co^{II}–F = 2.136 Å and Co^{II}-OH = 2.083(4) Å). This is not surprising in view of the different bridging groups.

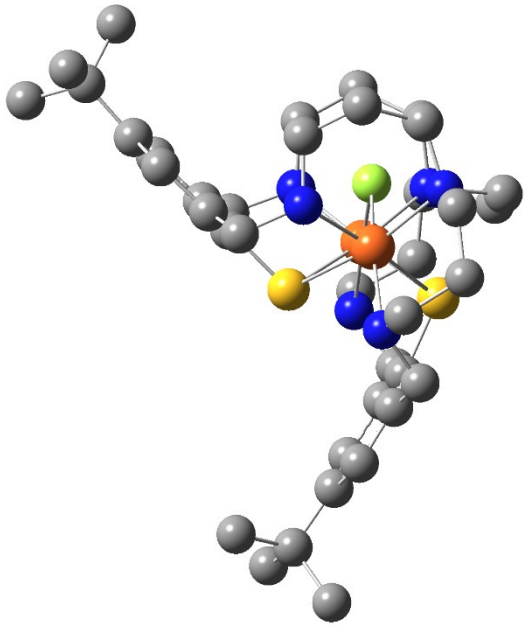

Figure S28. DFT optimized geometry of the $[LCo^{II}Co^{III}(\mu\text{-}F)]^{2+}$ (M06-D3/LACVP*/PBF) in the gas phase (the structures in THF and MeCN are very similar and not shown). The cartesian coordinates of the calculated structures are provided in Tables S5a-c.

b) DFT calculations for $[LCo^{II}Co^{III}(\mu\text{-}F)(CuBr_2)]^+$ (3)

Figure S29 displays the optimized geometry for the $[LCo^{II}Co^{III}(\mu\text{-}F)(\mu\text{-}CuBr_2]^+$ cation in **3** for the gas phase, and in THF and MeCN solution. The structure of the $[LCo^{II}Co^{III}(\mu\text{-}F)]^{2+}$ fragment in **3** is very similar to the structure of the $[LCo^{II}Co^{III}(\mu\text{-}OH)]^+$ cation in **1**. Table S3 lists the computed parameters. The DFT calculations show that 0.11 negative charges (0.11 e^-) are transferred from the RS^- donor to the $[CuBr_2]^-$ acceptor.

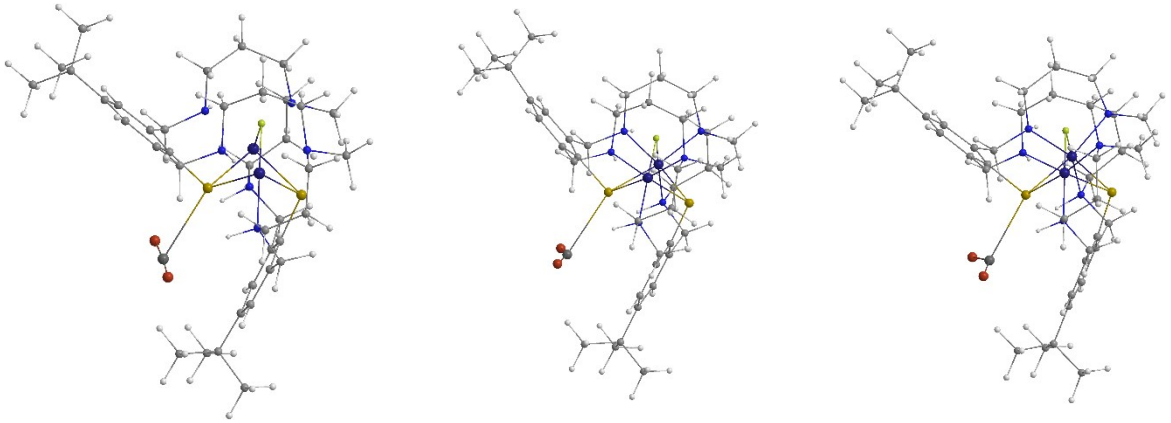

Figure S29. DFT optimized geometry of $[LCo^{II}Co^{III}(\mu\text{-}F)(Cu^{I}Br_2)]^+$ (**3**, $M^S = 4$, quartet state, M06-D3/LACVP*/PBF) in the gas phase (left), THF (middle) and MeCN (right). The cartesian coordinates of the calculated structures are provided in Tables S6a-S6c.

Table S3. Experimental and calculated bond lengths and charge shift δQ / e^- for the dication $[LCo^{II}Co^{III}(\mu\text{-}F)]^{2+}$ and the cation $[LCo^{II}Co^{III}(\mu\text{-}F)(CuBr_2)]^+$ in **3** resulting from DFT calculations at the M06-D3/LACVP* level of theory.

Complex	DFT / Solvation			
$[LCo^{II}Co^{III}(\mu\text{-}F)]^{2+}$ ($M^S = 4$) Co1 = Co^{2+}, Co2 = Co^{3+}.	gas phase[a)]	THF[a)]	MeCN[a)]	crystallographic data for **1**[b]
Co1-S1	2.512	2.493	2.504	2.526
Co1-S2	2.580	2.564	2.577	2.529
Co2-S1	2.334	2.302	2.311	2.310
Co2-S2	2.312	2.317	2.321	2.304
Co1-F1	2.069	2.137	2.136	2.058 (Co^{II}-O1)
Co2-F1	1.909	1.927	1.921	1.939 (Co^{III}-O1)
Co1-S1-Co2	75.8	79.5	80.0	78.1
Co1-S2-Co2	76.7	77.7	78.3	78.0
Co1-F1-Co2	98.3	97.9	99.4	99.4 (Co-OH-Co)
Complex	DFT / Solvation			
$[LCo^{II}Co^{III}(\mu\text{-}F)(CuBr_2)]^+$ (3) Co1 = Co^{2+}, Co2 = Co^{3+}.	gas phase	THF	MeCN	
Co1-S1	2.513	2.526	2.537	
Co1-S2	2.515	2.562	2.590	
Co2-S1	2.327	2.329	2.330	
Co2-S2	2.261	2.298	2.310	
Co1-F	2.084	2.102	2.101	
Co2-F	1.926	1.924	1.925	
Co1-S1-Co2	76.2	78.1	78.4	
Co1-S2-Co2	77.3	77.9	77.7	
Co1-F-Co2	96.3	98.9	99.8	
Cu-S2	2.788	2.790	2.736	
Cu-Br1	2.401	2.392	2.393	
Cu-Br2	2.375	2.392	2.403	
Br1-Cu-Br2	176.9°	163.0°	156.8°	
$Q(CuBr_2)$	-0.815	-1.023	-1.078	
$\delta Q(CuBr_2)$	+0.185	-0.023	-0.078	

a) The geometry of the $[LCo^{II}Co^{III}(\mu\text{-}F)]^{2+}$ dication was optimized starting from the coordinates of the $[LCo^{II}Co^{III}(\mu\text{-}F)(CuBr_2)]^+$ cation in **3** (with the $[CuBr_2]^-$-moiety omitted). The cartesian coordinates of the calculated structures are provided in Tables S5a-c (for the $LCo^{II}Co^{III}(\mu\text{-}F)]^{2+}$ dication) and S6a-c (for **3**). b) Given the absence of an X-ray crystal structure, we provide here the bond lengths of the hydroxido-bridged $[LCo^{II}Co^{III}(\mu\text{-}OH)]^{2+}$ dication in **1**. The comparison should be taken indicative rather than definitive.

Figure S30 lists the caculated N-H stretching frequencies for complex **3** at the M06-D3/LACVP*/PBF level of theory (solvation model: THF). The data are discussed in the main text.

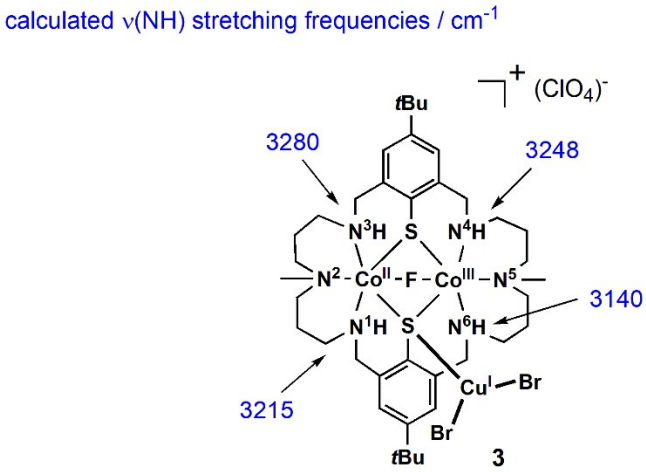

Figure S30. Drawing of complex **3** showing the scaled calculated N-H stretching frequencies (cm^{-1}) at the M06-D3/LACVP*/PBF level of theory (solvation model: THF). The indexes refer to atom numbers utilized in the crystallographic analysis. Note that N2 and N5 are methylated and show no NH frequencies.

c) DFT calculations for the $[LNi^{II}_2(\mu\text{-}F)]^+$ cation in $[LNi^{II}_2(\mu\text{-}F)]ClO_4$ (2)

Figure S31 displays the optimized geometry of the $[LNi^{II}_2(\mu\text{-}F)]^+$ cation in the gas phase. The optimized geometry of the fluorido-bridged complex (in MeCN) was found to be in excellent agreement to the experimental structure. The average Ni^{II}-S bond distances are identical in the calculated and experimental structure. The average Ni^{II}-F distances are ca. 0.02 Å longer and the average Ni^{II}-N bonds are 0.01 Å longer (not listed in Table 4) in the calculated structure (Table S3).

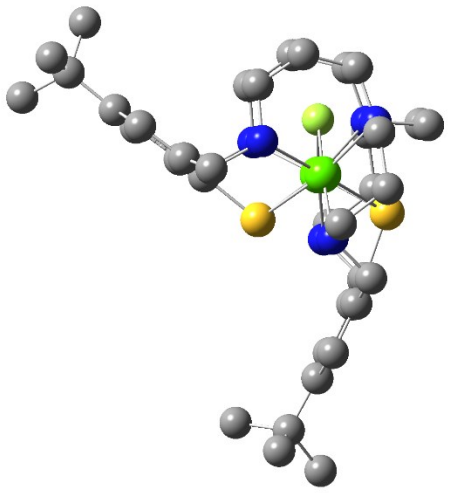

Figure S31. DFT optimized geometry of the $[LNi^{II}_2(\mu\text{-}F)]^+$ cation in **2** (M06-D3/LACVP*/PBF) in the gas phase (the structures in THF and MeCN are very similar and not shown). The cartesian coordinates of the calculated structures are provided in Tables S7a-c.

d) Characterization of $[LNi^{II}_2(\mu\text{-}F)(CuBr_2)]$ (5) by DFT calculations

The geometry of the $[LNi^{II}_2(CuBr_2)]$ complex was optimized starting from the X-ray coordinates of the $[LNi^{II}_2(\mu\text{-}F)(CuI_2)]$ complex in **6** (with the iodides replaced by bromides). Figure S32 displays the optimized geometry of the neutral complex $[LNi^{II}_2(\mu\text{-}F)(CuBr_2)]$ **(**the gas phase. Table S4 lists the computed bond lengths and angles. The Ni^{II}-N, Ni^{II}-S, and Ni^{II}-F distances are in excellent agreement with those in **6**. The DFT calculations show that 0.24 negative charges are transferred from the RS^- donor to the $[CuBr_2]^-$ acceptor.

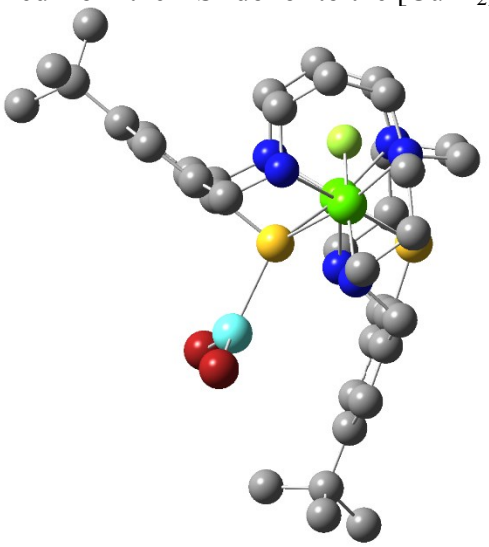

Figure S32. DFT optimized geometry of the $[LNi^{II}_2(\mu\text{-}F)(CuBr_2)]$ complex **5** (M06-D3/LACVP*/PBF) in the gas phase (the structures in THF and MeCN are very similar and not shown). The cartesian coordinates of the calculated structures are provided in Tables S8a-c.

Figure S33 lists the caculated N-H stretching frequencies for complex **5** at the M06-D3/LACVP*/PBF level of theory (solvation model: THF). The data are discussed in the main text.

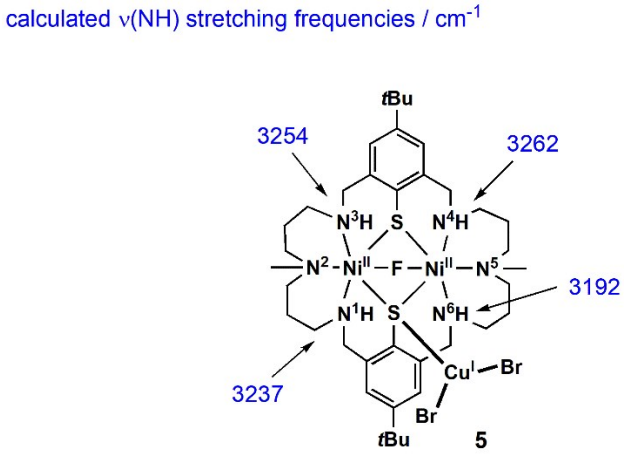

Figure S33. Drawing of complex **5** showing the scaled calculated N-H stretching frequencies (cm^{-1}) at the M06-D3/LACVP*/PBF level of theory (solvation model: THF). The indexes refer to atom numbers utilized in the crystallographic analysis. Note that N2 and N5 are methylated and show no NH frequencies.

e) Characterization of [LNi$^{II}_2$(μ-F)(CuI$_2$)] (6) by DFT calculations

Figure S34 displays the optimized geometry of the neutral complex [LNi$^{II}_2$(μ-F)(CuI$_2$)] **(6)** in gas phase, THF and MeCN. The optimized geometry of complex **6** in various solvents was found to be similar with the experimental crystal structure, with the diiodocuprate located in the cleft formed by the macrocycle. The calculated and experimental metal-ligand bond lengths match reasonably well (Table S4), particularly in case of MeCN as the medium. A good match is also seen for the Cu–S and Cu–I bond lengths as well as the I–Cu–I angle (in MeCN as a medium). In contrast to the crystal structure, the computed structure of **6** reveals two N-H···I hydrogen bonding interactions. This is attributed to the absence of intermolecular interactions. The DFT calculations reveal that 0.24 negative charges are transferred from the RS$^-$ donor to the [CuI$_2$]$^-$ acceptor (in MeCN medium).

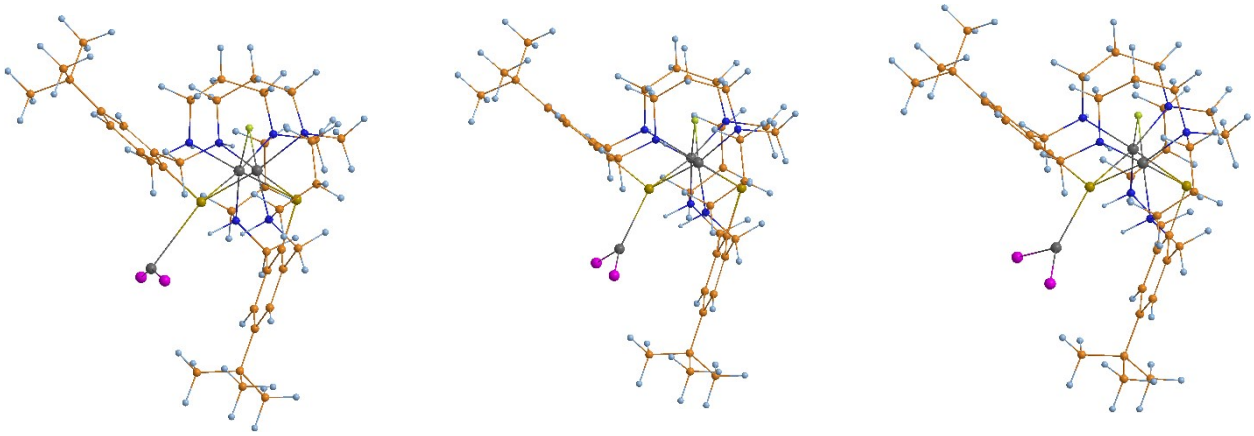

Figure S34. DFT optimized geometries of [LNi$^{II}_2$(μ-F)(Cu^{I}I$_2$)] (**6**, M^S = 5, quintet state, M06-D3/LACVP*/PBF level of theory) with and without solvation (gas phase (left), THF (middle) and MeCN (right)). The cartesian coordinates of the calculated structures are provided in Tables S9a-S9c.

Figure S35 lists the caculated N-H stretching frequencies for complex **6** at the M06-D3/LACVP*/PBF level of theory (solvation model: THF). The data are discussed in the main text.

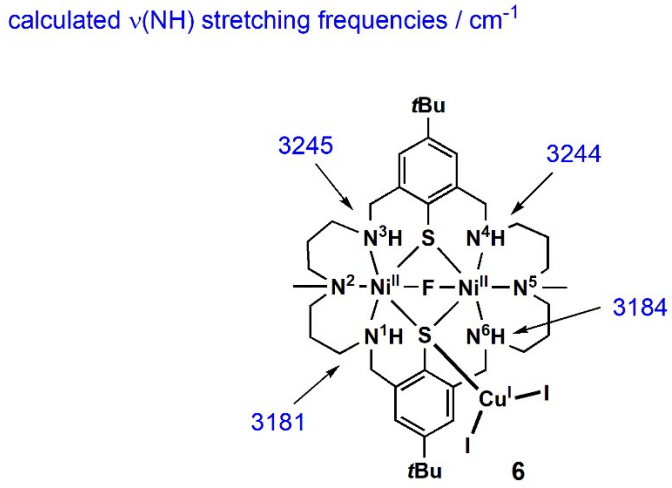

Figure S35. Drawing of complex **5** showing the scaled calculated N-H stretching frequencies (cm^{-1}) at the M06-D3/LACVP*/PBF level of theory (solvation model: THF). The indexes refer to atom numbers utilized in the crystallographic analysis. Note that N2 and N5 are methylated and show no NH frequencies.

Table S4. Selected parameters calculated for the complexes $[LNi_2(\mu\text{-}F)]^+$ (**2**, quintet state), $[LNi_2(\mu\text{-}F)(CuBr_2)]^+$ (**5**, quintet state) and $[LNi_2(\mu\text{-}F)(CuI_2)]$ (**6**, $M^S = 5$, quintet state) with and without solvation (gas phase, THF, and MeCN) at the M06-D3/LACVP*/PBF level of theory. Where appropriate corresponding data from the X-ray crystal structures for $[LNi_2(\mu\text{-}F)]BPh_4$ (**2**)[S10] and $[LNi_2(\mu\text{-}F)(CuI_2)]$ (**6**) are included for comparison (bond lengths / Å, angles /°). The parameter Q represents the calculated Mulliken charge on the $[CuX_2]^-$ moiety in **5** and **6**. δQ is the calculated charge shift from the thiolate complex **2** to the $[CuX_2]^-$ moiety in **5** and **6**.

Complex **$[LNi_2(\mu\text{-}F)]^+$ (2)** ($M^S = 5$)	DFT / Solvation[a]			
	gas phase	THF	MeCN	Crystallographic data for $[LNi_2(\mu\text{-}F)]ClO_4$ (**2**),[S10]
Ni1-S1	2.467	2.517	2.486	2.466
Ni1-S2	2.474	2.459	2.500	2.550
Ni2-S1	2.468	2.510	2.475	2.472
Ni2-S2	2.475	2.462	2.498	2.465
Ni1-F1	2.049	2.076	2.061	2.042
Ni2-F1	2.051	2.080	2.065	2.047
Ni1-S1-Ni2	73.9	75.2	75.7	76.4
Ni1-S2-Ni2	73.6	77.1	75.0	75.0
Ni1-F1-Ni2	92.6	95.2	94.9	96.6
Complex $[LNi_2(\mu\text{-}F)(CuBr_2)]$ **(5)** ($M^S = 5$)	DFT / Solvation[a]			
	gas phase	THF	MeCN	
Ni1-S1	2.456	2.482	2.504	
Ni1-S2	2.411	2.444	2.468	
Ni2-S1	2.480	2.498	2.515	
Ni2-S2	2.457	2.449	2.499	
Ni1-F	2.103	2.096	2.094	
Ni2-F	2.088	2.095	2.093	
Ni1-S1-Ni2	75.5	77.0	77.7	
Ni1-S2-Ni2	76.8	78.6	78.9	
Ni1-F-Ni2	92.3	95.4	97.5	
Cu-S2	2.797	2.364	2.351	
Cu-Br1	2.401	2.497	2.491	
Cu-Br2	2.397	2.485	2.491	
Br-Cu-Br	173.3	142.7	130.1	
$Q(CuBr_2)$	-0.904	-1.152	-1.241	
$\delta Q(CuBr_2)$	+0.096	-0.152	-0.241	
Complex **$[LNi_2(\mu\text{-}F)(CuI_2)]$ (6)** ($M^S = 5$)	DFT / Solvation			
	gas phase	THF	MeCN	Crystallographic data for **6**

Ni1-S1	2.459	2.459	2.478	2.421
Ni1-S2	2.413	2.449	2.470	2.449
Ni2-S1	2.455	2.486	2.499	2.473
Ni2-S2	2.482	2.456	2.467	2.482
Ni1-F	2.079	2.088	2.073	2.066
Ni2-F	2.080	2.079	2.076	2.052
Ni1-S1-Ni2	75.0	76.6	77.2	77.7
Ni1-S2-Ni2	75.3	77.3	76.5	77.0
Ni1-F-Ni2	92.0	94.6	95.8	96.4
Cu-S2	2.826	2.384	2.349	2.296
Cu-I1	2.541	2.612	2.622	2.547
Cu-I2	2.546	2.607	2.621	2.511
I-Cu-I	164.0°	140.4°	131.5°	128.0°
$Q(CuI_2)$	-0.958	-1.161	-1.242	-1.222
$\delta Q(CuI_2)$	+0.042	-0.161	-0.242	-0.222

a) The cartesian coordinates of the calculated structures are provided in Tables S7a-c (for **2**), Tables S8a-c (for **5**), and S9a-c (for **6**).

Table S5a. Cartesian coordinates of geometry optimized $[LCo^{II}Co^{III}(\mu\text{-}F)]^{2+}$ ($M^S = 4$, quartet state, gas phase).

final geometry: angstroms

atom	x	y	z
H1	-1.4739354700	9.9234891613	5.1580763002
H8B	0.8510235949	9.5353509991	4.6858686159
H9A	1.2635457710	11.7012892245	3.4111334970
H9B	1.7999299140	10.2439060883	2.6191358040
H10A	0.7511089844	11.5684100446	0.9268866519
H10B	-0.1930146929	10.1283514557	1.2228744903
H11A	-1.4895065427	14.0082820858	2.0490027468
H11B	-0.0193168990	13.6083857450	1.1280468479
H11C	-0.0457714920	13.4534099289	2.9080228251
H12A	-1.2828348529	12.3002546276	-0.2195583347
H12B	-2.7478199335	12.5851532413	0.7446920285
H3	-1.6633789933	9.3671503793	2.2518873423
H13A	-3.0344467801	10.7001237693	-0.7395122197
H13B	-1.6199256603	9.8760636380	-0.1608839811
H14A	-4.2420369077	10.3547074232	1.3593457864
H14B	-3.5874206083	8.8201586033	0.7617048043
H15A	-2.9508693128	7.5383683533	2.6973804544
H15B	-2.6541638151	8.4196416730	4.2095969676
H19	-8.4371666717	9.2725590251	3.3969593586
H21	-5.0628380253	6.9497062968	2.1495367931
H22A	-8.2518183201	11.0508293517	4.7060758785
H22B	-6.8226185250	11.3626462921	5.7064604275
H4	-7.4275834116	13.1378444647	4.2082589179
H23A	-6.3375932493	11.5857655550	1.9921610304
H23B	-8.0782832916	11.6812033123	2.3003938897
H24A	-7.4765662513	13.3316463543	0.6537002730
H24B	-8.0343290433	14.1462913030	2.0837423592
H25A	-6.0583454746	15.2192508800	0.9671509866
H25B	-5.1217102638	13.7268131344	1.1861796962
H26A	-3.4140804577	14.8442323710	2.1468439168
H26B	-3.6424859885	15.9343868159	3.5278284875
H26C	-4.2928662680	16.3829039108	1.9239389681
H27A	-7.3234830687	15.3977462211	3.4695422360
H6	-5.7405624799	13.2400296483	6.6133803755
H27B	-6.3126706911	16.7242900625	2.9150866942
H28A	-5.0172386049	16.5375987239	5.1323522031

H28B	-6.6837013735	17.0360226840	5.2180236398
H29A	-6.5241462711	15.5220090057	6.9877157321
H29B	-7.3349365185	14.6065678779	5.7240460661
H30A	-4.5688302121	14.9562234601	7.8145951756
H30B	-3.6897851336	15.2949761426	6.3175724732
H32A	-4.6177704270	11.3270693198	10.3362966492
H32B	-3.9157988552	10.0754310316	11.3711149401
H32C	-4.0188986824	9.8150312043	9.6169017582
H45	-3.9345460017	13.2132651474	9.2244927747
H33A	-2.9314058032	13.0478180859	11.2748728794
H33B	-1.1934696956	12.6871179490	11.2206688402
H33C	-2.2596905690	11.7821064420	12.3138062072
H34A	-0.3662862322	10.4318074069	10.3581399338
H34B	-1.5290275135	9.2524949654	9.6896134888
H34C	-1.5172095307	9.6147645564	11.4194004411
H36A	-6.5727811304	5.2679560876	2.1454558824
H36B	-8.2282903235	4.9817158662	1.5925530351
H36C	-7.9307397308	5.4803928485	3.2699185035
H37A	-6.2568082352	6.9363278957	0.1962777019
H5	-0.6393734593	10.6819224761	8.1596798455
H37B	-7.3841045354	8.3007847638	0.0193744084
H37C	-7.9235923174	6.6436955652	-0.3211157194
H38A	-9.4081302688	8.5030221541	1.5340227001
H38B	-9.6279562458	7.3790074557	2.9035451109
H38C	-9.8234720675	6.8111437003	1.2404784079
H7A	0.0895017069	12.3900205124	5.1074561524
H7B	0.4554304096	10.9984488554	6.1474849213
H8A	-0.2428729892	9.0122863411	3.4274281163
Co1	-2.4449839485	11.3915481147	3.4842130104
Co2	-4.8402663952	13.0817348713	4.1719532842
S1	-2.3887489773	13.4579457288	4.5680458692
S2	-4.0489023711	10.7821114010	5.0334070193
F1	-3.9072921368	12.1909299013	2.5539164438
N1	-0.9528785054	10.6201777913	4.6146304247
N2	-1.1063028707	11.9350860729	1.8536229720
N3	-2.6254944977	9.6215026070	2.4730672633
N4	-6.8254154931	12.3848185651	3.8672050069
N5	-5.3638094550	14.8403994678	2.9290411839
N6	-5.3443740912	14.0183038665	6.0782397766
C1	-2.3096337718	12.9455743949	6.2659692134
C2	-3.2234312602	13.4072238500	7.2213820498
C3	-3.2156702513	12.8411335981	8.4918376832
C4	-2.3290101038	11.8201583380	8.8602382914
C5	-1.3841226843	11.4375705865	7.9120359583
C6	-1.3599017813	11.9949900722	6.6354542950
C7	-0.3555569861	11.5405214329	5.6386399997
C8	0.1549358731	9.9099770229	3.9215164390
C9	0.8960139752	10.7845361912	2.9306459313
C10	0.1029225081	11.0825720089	1.6751875300
C11	-0.6354423910	13.3279352768	1.9964575485
C12	-1.9114616974	11.8962768984	0.5922802340
C13	-2.4377807250	10.5347517467	0.1677745270
C14	-3.3151792851	9.8068276451	1.1677842321
C15	-3.1769138875	8.4665523331	3.2437566399
C16	-4.6484709471	8.6215357424	3.4065135917
C17	-5.1517616466	9.7241491213	4.1145220022
C18	-6.5356529664	9.9478244557	4.0903170437
C19	-7.3672550551	9.0656944113	3.3961315201
C20	-6.8833056349	7.9757115797	2.6764999104
C21	-5.5014385095	7.7760784834	2.7117273828
C22	-7.1591779192	11.1782477227	4.6770711168
C23	-7.1243291360	12.2187870855	2.4228891435
C24	-7.1973660437	13.5470036215	1.6943226703
C25	-5.9076649263	14.3503772152	1.6334266925
C26	-4.1105926729	15.5457938014	2.6182145526
C27	-6.3083777154	15.8099467475	3.5352782021
C28	-6.0442480616	16.1734208177	4.9867636656
C29	-6.3767307742	15.0792360287	5.9898956322
C30	-4.1893930578	14.4999089764	6.8862022330
C31	-2.4257106146	11.1758312193	10.2370115050
C32	-3.8258717346	10.5684239943	10.3941047968
C33	-2.1911454794	12.2380917720	11.3172449118
C34	-1.3985688285	10.0606187899	10.4238546639

C35	-7.7579323229	7.0884659405	1.8010847009
C36	-7.6076956108	5.6248423670	2.2304394145
C37	-7.2983161488	7.2535656757	0.3442667001
C38	-9.2321420095	7.4750956066	1.8831703890

Table S5b. Cartesian coordinates of geometry optimized $[LCo^{II}Co^{III}(\mu\text{-}F)]^{2+}$ ($M^S = 4$, quartet state, THF solution).

final geometry:		angstroms	
atom	x	y	z
H1	-1.1708113977	9.8379326148	5.2916801623
H8B	1.1478145794	9.6335325947	4.7272109680
H9A	1.2870354070	11.8044593046	3.3524070289
H9B	1.9847804792	10.3646981745	2.6614058068
H10A	0.8651736440	11.4073434559	0.8586689540
H10B	-0.0021273204	9.9394464967	1.2906109106
H11A	-1.6173235471	13.7530209542	1.8277319440
H11B	-0.0766767164	13.4802566412	0.9668415546
H11C	-0.1474744943	13.3761698143	2.7500780823
H12A	-1.1878287651	11.9606653629	-0.3748509320
H12B	-2.6842879398	12.2150816260	0.5481050797
H3	-1.7147030533	8.9077896139	2.2832824897
H13A	-2.7557732920	10.2287741754	-0.8675035818
H13B	-1.3968896050	9.4874045700	-0.0685008725
H14A	-4.1259524429	10.1300513030	1.1846129514
H14B	-3.5472843748	8.5337215561	0.6615989652
H15A	-3.2402039186	7.3243497490	2.8383219300
H15B	-2.9525377642	8.3406598692	4.2594471733
H19	-8.6179817970	9.4927948622	2.8645602132
H21	-5.2524122587	6.9679423060	2.0081105335
H22A	-8.4250831512	11.3332571727	4.1408895649
H22B	-7.1636226206	11.4147234019	5.3847072485
H4	-7.3050428356	13.2777229210	3.8941084399
H23A	-6.0717754017	11.7144842033	1.7783988396
H23B	-7.8327951265	11.9342742271	1.8927016685
H24A	-6.7891021488	13.5815633236	0.3785285873
H24B	-7.6700458035	14.3305627378	1.6798872134
H25A	-5.5701337257	15.5102280659	1.2183048891
H25B	-4.6283836029	14.0106368934	1.3784966732
H26A	-3.1970757145	15.2135916666	2.7129675945
H26B	-3.7390286706	15.9939776738	4.2122205924
H26C	-4.2520163935	16.6465532451	2.6301275821
H27A	-7.3095019780	15.1761653371	3.4551346966
H6	-5.7344910222	12.7249764232	6.4405450946
H27B	-6.3527978764	16.6266970992	3.2584757616
H28A	-5.4723431126	16.3312075481	5.6170779174
H28B	-7.2050325803	16.4877656394	5.4935314018
H29A	-6.8373620012	14.7384651361	7.0697599266
H29B	-7.4872420656	13.9929375518	5.6288537510
H30A	-4.8916911476	14.5144540304	7.8170150896
H30B	-3.9642238881	15.0565308446	6.4095504966
H32A	-4.0499866143	11.4304523071	10.8056100187
H32B	-3.0289165203	10.5369772948	11.9475522655
H32C	-3.2699682418	9.9161231593	10.2974813142
H45	-3.8557789435	13.1346900859	9.3209368888
H33A	-2.6107433822	13.5339790862	11.2004378949
H33B	-0.8525013675	13.4518646654	10.9546762603
H33C	-1.6014357141	12.6158856043	12.3350868710
H34A	0.2668137971	11.2413215662	10.3904735054
H34B	-0.7188899371	9.7850700601	10.0933608525
H34C	-0.5946801927	10.4614052893	11.7282310488
H36A	-6.8003436648	5.3767092483	1.8208790197
H36B	-8.4190666108	5.1433577812	1.1359200997
H36C	-8.2370851175	5.6443927116	2.8328653183
H37A	-6.2637967750	7.0377569482	-0.0903153237
H5	-0.2770444686	11.0131459623	8.2279754163
H37B	-7.3400953748	8.4247496944	-0.3677322774
H37C	-7.8918349080	6.7762978030	-0.7491594977
H38A	-9.4669544401	8.6969709521	0.9729954842
H38B	-9.8260887782	7.5972586775	2.3296055495
H38C	-9.9106107416	7.0118962734	0.6566877187

H7A	0.0702228535	12.4776930373	5.0466029922
H7B	0.6396386534	11.2315886931	6.1615253930
H8A	0.0224148425	9.0007763985	3.5288034939
Co1	-2.3957727294	11.2200912010	3.4025341056
Co2	-4.8158456236	12.9477266367	4.1634174543
S1	-2.6023904409	13.3825830223	4.6246730933
S2	-4.3945055339	10.8120065370	4.9565248759
F1	-4.0494947058	12.2590781643	2.5346589754
N1	-0.7516347781	10.5660022241	4.7016300920
N2	-1.0309241532	11.7316426474	1.7225548599
N3	-2.6422928170	9.3186303149	2.4216638993
N4	-6.7278733403	12.4825490181	3.6139608310
N5	-5.2254246787	14.8465879102	3.1940425274
N6	-5.4323878331	13.5974163859	5.9908139473
C1	-2.3745159711	12.8211276481	6.2861750458
C2	-3.2919263047	13.2225336086	7.2646025644
C3	-3.1292081597	12.7983315661	8.5779386478
C4	-2.0518194365	11.9946276822	8.9677634672
C5	-1.1459566452	11.6211498260	7.9745839325
C6	-1.2892209644	12.0162733749	6.6427225482
C7	-0.2540005123	11.6102150066	5.6379915464
C8	0.3854850092	9.9323169102	3.9891932509
C9	1.0226802579	10.8224821710	2.9330749021
C10	0.2315233776	10.9523584361	1.6423604021
C11	-0.6933295206	13.1625460498	1.8252148296
C12	-1.8012815639	11.5671532577	0.4568446758
C13	-2.2527409828	10.1566504782	0.1079731848
C14	-3.2285011690	9.5066040517	1.0720966123
C15	-3.3918768094	8.3337743982	3.2510435352
C16	-4.8619249549	8.6394104405	3.2681218878
C17	-5.4008308151	9.7626776232	3.9225664658
C18	-6.7642639031	10.0389660523	3.7654237098
C19	-7.5693283313	9.2159725539	2.9786010208
C20	-7.0617640321	8.0956332601	2.3272382778
C21	-5.7016114555	7.8278628920	2.5103099134
C22	-7.3368802273	11.3063875900	4.3043297794
C23	-6.8585434661	12.3865795527	2.1341878023
C24	-6.7638699932	13.7443014808	1.4656572896
C25	-5.5063198311	14.5466963783	1.7527985280
C26	-4.0358600285	15.7253949774	3.1946336235
C27	-6.3612562121	15.6398337229	3.7518101525
C28	-6.3713350727	15.8115837597	5.2568849159
C29	-6.6048722400	14.5199885495	6.0171490995
C30	-4.3847533185	14.1706071283	6.9026801624
C31	-1.8914118794	11.6030449683	10.4330189752
C32	-3.1338694315	10.8303947572	10.8929553500
C33	-1.7334277001	12.8768939522	11.2750156868
C34	-0.6640819250	10.7237785095	10.6635726816
C35	-7.8883125672	7.2343081765	1.3794548563
C36	-7.8269394266	5.7675146380	1.8204674365
C37	-7.3079263502	7.3763404837	-0.0358553027
C38	-9.3524887988	7.6665583004	1.3398687340

Table S5c. Cartesian coordinates of geometry optimized $[LCo^{II}Co^{III}(\mu\text{-}F)]^{2+}$ ($M^S = 4$, quartet state, MeCN solution).

final geometry: angstroms			
atom	x	y	z
H1	-1.2185787811	9.7266777055	5.3646248711
H8B	1.0843249864	9.4953314033	4.7868640034
H9A	1.2756526853	11.6869132376	3.4553233961
H9B	1.9503751757	10.2445021280	2.7480380844
H10A	0.8889249729	11.3511818614	0.9516976148
H10B	-0.0155646202	9.8929130422	1.3338114345
H11A	-1.5649369698	13.7291537967	1.9177575272
H11B	-0.0249294834	13.4374363837	1.0594852862
H11C	-0.1061521106	13.3103732382	2.8416110105
H12A	-1.1604895446	11.9727021728	-0.3078943922
H12B	-2.6596747588	12.2206916824	0.6117938756
H3	-1.7104849244	8.8720296212	2.2748552524
H13A	-2.7426271982	10.2645701964	-0.8450976113

H13B	-1.3869752895	9.4986704218	-0.0614233489
H14A	-4.1218361324	10.1100932314	1.1944035158
H14B	-3.5289870716	8.5262367908	0.6478692730
H15A	-3.2243511706	7.2912833954	2.8276120360
H15B	-2.9279757093	8.2995209606	4.2539603083
H19	-8.5981781379	9.4728694591	2.8740873919
H21	-5.2276385268	6.9671749056	1.9688961928
H22A	-8.4145179005	11.2708660303	4.2160347637
H22B	-7.1442356221	11.3319782134	5.4535899604
H4	-7.3155227952	13.2157824175	3.9895375517
H23A	-6.0705818417	11.6870717968	1.8536698362
H23B	-7.8318671832	11.9063050929	1.9738987525
H24A	-6.7854701741	13.5640797659	0.4728495965
H24B	-7.6706560394	14.3011461073	1.7805599693
H25A	-5.5758892226	15.4917985371	1.3377713498
H25B	-4.6276385965	13.9936223261	1.4808409358
H26A	-3.2117253809	15.1996353731	2.8246909683
H26B	-3.7561269808	15.9421713130	4.3434902172
H26C	-4.2819678191	16.6231020280	2.7769917468
H27A	-7.3244715183	15.1054926108	3.5667030303
H6	-5.6925632970	12.6610068938	6.5546388479
H27B	-6.3830992018	16.5682564092	3.3856037041
H28A	-5.5156658517	16.2727431514	5.7446317583
H28B	-7.2518324346	16.3872595116	5.6145578779
H29A	-6.8323364917	14.6367388984	7.1828504718
H29B	-7.4816466010	13.8921249969	5.7400386109
H30A	-4.8562805557	14.5070189841	7.8750875402
H30B	-3.9530206052	15.0156165268	6.4398346572
H32A	-3.9144026304	11.6118041764	10.9867427147
H32B	-2.8540443220	10.8113031723	12.1641948394
H32C	-3.1392249716	10.0671271637	10.5719191270
H45	-3.7773094956	13.2132909337	9.4015260397
H33A	-2.4724901883	13.7422475230	11.1986069243
H33B	-0.7233582791	13.6492969877	10.8957286187
H33C	-1.4175012512	12.9082270554	12.3575044190
H34A	0.3858551460	11.4060897042	10.4415794416
H34B	-0.6036996240	9.9302856029	10.2921184386
H34C	-0.4198672055	10.7261242518	11.8675809602
H36A	-6.7878699616	5.3945126412	1.7172470507
H36B	-8.3830166858	5.1966470395	0.9662282523
H36C	-8.2588055928	5.6351768259	2.6867923755
H37A	-6.1861971359	7.0988751579	-0.1240109742
H5	-0.2479071086	11.0016349243	8.3158838573
H37B	-7.2239422390	8.5193348189	-0.3753270894
H37C	-7.8009709892	6.8994653770	-0.8380502706
H38A	-9.3939504102	8.7706026910	0.9107453914
H38B	-9.8075571434	7.6255898048	2.2120840283
H38C	-9.8492749960	7.1036240959	0.5155277788
H7A	0.0722735832	12.3453375723	5.1043118245
H7B	0.6095957998	11.0933073702	6.2271936470
H8A	-0.0423918570	8.9013642690	3.5713707282
Co1	-2.3792001800	11.1637832364	3.4290509045
Co2	-4.8122102836	12.8949748882	4.2508555624
S1	-2.5831417327	13.3188135727	4.6868729347
S2	-4.3766683777	10.7432184531	5.0026265335
F1	-4.0465520727	12.2257360224	2.6209940749
N1	-0.7998380498	10.4554125644	4.7753492190
N2	-1.0170781892	11.7001230226	1.7859062736
N3	-2.6350398603	9.2889394544	2.4239398000
N4	-6.7253562342	12.4328294066	3.6994969021
N5	-5.2346699708	14.8029565189	3.3051794347
N6	-5.4156114225	13.5323190939	6.0840106987
C1	-2.3613061641	12.7672358416	6.3522766546
C2	-3.2586579442	13.2080917423	7.3331869300
C3	-3.0670120910	12.8418412154	8.6593596620
C4	-1.9798658698	12.0570813053	9.0586142742
C5	-1.1122841179	11.6144038655	8.0591454167
C6	-1.2864970923	11.9493687815	6.7136308666
C7	-0.2753568088	11.4929935043	5.7042858038
C8	0.3310484403	9.8192607822	4.0501771211
C9	0.9948778863	10.7188594141	3.0154902162
C10	0.2306273424	10.8927343000	1.7126231535
C11	-0.6520836400	13.1217143708	1.9112373920

C12	-1.7821086032	11.5662986067	0.5114625301
C13	-2.2409727594	10.1661864165	0.1289684199
C14	-3.2196208818	9.4943132963	1.0764504398
C15	-3.3763792558	8.2965891838	3.2500188464
C16	-4.8457663012	8.6014181820	3.2774557328
C17	-5.3866015327	9.7092524883	3.9573519895
C18	-6.7507748617	9.9879803039	3.8048550498
C19	-7.5510620014	9.1891506651	2.9880687941
C20	-7.0377408509	8.0916811087	2.3035143560
C21	-5.6811915201	7.8120713603	2.4926902275
C22	-7.3254634282	11.2419547290	4.3728789612
C23	-6.8567802988	12.3550660708	2.2185572151
C24	-6.7635395174	13.7186107928	1.5615376109
C25	-5.5090929401	14.5212069723	1.8593632904
C26	-4.0535432199	15.6924732839	3.3210256939
C27	-6.3821141936	15.5766476435	3.8696535292
C28	-6.4002434616	15.7341458938	5.3764509380
C29	-6.6060513241	14.4316493200	6.1261151698
C30	-4.3610662242	14.1410947106	6.9628637015
C31	-1.7692895673	11.7654197757	10.5404998421
C32	-2.9923298549	11.0240124476	11.0938393044
C33	-1.5891366110	13.0949829699	11.2871552297
C34	-0.5306416798	10.9080069302	10.7894097441
C35	-7.8471530372	7.2730828205	1.3055070344
C36	-7.8121077736	5.7911068531	1.6943909629
C37	-7.2242315224	7.4576566523	-0.0860959412
C38	-9.3042589537	7.7249211033	1.2396417379

Table S6a. Cartesian coordinates of geometry optimized $[LCo^{II}Co^{III}(\mu\text{-}F)(Cu^{I}Br_2)]^+$ (**4**, M^S = 4, quartet state, gas phase).

final geometry: angstroms			
atom	x	y	z
Co1	-2.3969529441	11.4020649407	3.4438263315
Co2	-4.7830878016	13.0505174545	4.1669730998
S1	-2.5766116095	13.5835680677	4.6773380570
S2	-4.3558880329	10.9776021597	4.9632212798
F1	-3.9894779806	12.3956445944	2.5385968965
Cu1	-4.8057181396	9.9938182571	7.5328086674
Br1	-2.9405506965	8.5700661521	7.0261781382
Br2	-6.7170972138	11.2962653386	8.0705155513
N1	-0.8365509500	10.6587460926	4.7338844895
N2	-1.0209623140	11.8151112343	1.7395795842
N3	-2.6690080898	9.4957904097	2.4759645703
N4	-6.6829002015	12.5163365896	3.6101270462
N5	-5.2474871961	14.9333864732	3.1259711642
N6	-5.4329328067	13.6683480007	5.9701469191
C1	-2.3691144657	12.9488396651	6.3225429009
C2	-3.3271272347	13.2619544957	7.2906717131
C3	-3.2366497595	12.6981968424	8.5602463358
C4	-2.1949898592	11.8354136418	8.9173342698
C5	-1.2264553081	11.5855314337	7.9465793914
C6	-1.3019986423	12.1134864056	6.6598486057
C7	-0.2857903068	11.6976829516	5.6455325658
C8	0.2563428428	9.9464712618	4.0441539953
C9	0.9564899047	10.7827191887	2.9801900337
C10	0.1943165229	10.9709629826	1.6768146870
C11	-0.6203429133	13.2242792674	1.8396627537
C12	-1.8080035541	11.6781546029	0.4854307092
C13	-2.3234441457	10.2867102591	0.1431115325
C14	-3.2819067598	9.6573220109	1.1383381754
C15	-3.3423892657	8.4631019977	3.3122217333
C16	-4.8167747716	8.7094815793	3.3839176452
C17	-5.3603469209	9.8574135825	3.9902564877
C18	-6.7353171716	10.0815649739	3.8589979436
C19	-7.5454789479	9.1755251289	3.1756914041
C20	-7.0378704160	8.0105886631	2.6075097290
C21	-5.6603343628	7.8124825556	2.7341778600
C22	-7.3160620336	11.3693755039	4.3299642907
C23	-6.8016868939	12.3834312058	2.1377787052
C24	-6.7731048849	13.7336810437	1.4492953944

C25	-5.5455848287	14.5933091136	1.7038991408
C26	-4.0627296748	15.8071412277	3.0912396948
C27	-6.3713788185	15.7184497658	3.6949034267
C28	-6.3627664089	15.8773222389	5.2031557173
C29	-6.5971916516	14.5873497221	5.9677085493
C30	-4.4305904247	14.2053886818	6.9503154047
C31	-2.1567367135	11.2031638461	10.3047635218
C32	-3.4804388681	10.4811080223	10.5884935611
C33	-1.9464430387	12.3121440086	11.3425228425
C34	-1.0272171708	10.1829792192	10.4371772180
C35	-7.8874835050	7.0145336941	1.8243641836
C36	-7.8204278140	5.6422379976	2.5049018458
C37	-7.3444028330	6.9086725689	0.3926242973
C38	-9.3514007791	7.4433979477	1.7459390281
H1	-1.3388323810	9.9884102769	5.3422389904
H3	-1.7173467986	9.1562328236	2.3298496644
H4	-7.2362491172	13.3309669876	3.8719881585
H6	-5.7691779447	12.7965042275	6.4205031861
H57	-4.0214184047	12.9276270305	9.2823447291
H5	-0.4000835323	10.9114378007	8.1687518440
H7A	0.0492897414	12.5511853662	5.0410545629
H7B	0.6011505061	11.2903438277	6.1582275352
H8A	-0.1535776172	9.0251552937	3.6014349952
H8B	0.9979918590	9.6126927433	4.7882080467
H9A	1.2779683303	11.7465079937	3.3997156807
H9B	1.8894055415	10.2639223061	2.7182492721
H10A	0.8716471497	11.3900245742	0.9087129713
H10B	-0.0889366190	9.9764321363	1.3086784484
H11A	-1.5172351276	13.8539001296	1.8552031091
H11B	0.0064261811	13.5183092218	0.9791565703
H11C	-0.0644860331	13.4086161105	2.7644089414
H12A	-1.1919040458	12.0433189444	-0.3581719857
H12B	-2.6639913942	12.3585921714	0.5902681265
H13A	-2.8565944895	10.3821532309	-0.8132679076
H13B	-1.4957715083	9.5929771713	-0.0705409916
H14A	-4.1775512282	10.2805693713	1.2572428546
H14B	-3.6158005790	8.6785129820	0.7546333658
H15A	-3.1682655734	7.4706668572	2.8675056080
H15B	-2.8843827103	8.4661330133	4.3118717003
H19	-8.6057640671	9.4108370078	3.0842545325
H21	-5.2059887845	6.9293297188	2.2814990233
H22A	-8.3979803125	11.3875369168	4.1264127436
H22B	-7.1782179512	11.5080567182	5.4122818082
H23A	-5.9815329734	11.7453109015	1.7950954207
H23B	-7.7471679109	11.8726931268	1.8970455567
H24A	-6.8115460321	13.5587796458	0.3650986872
H24B	-7.6995420597	14.2845937208	1.6740694057
H25A	-5.6545690022	15.5391754918	1.1435140601
H25B	-4.6571546678	14.0760679152	1.3269281981
H26A	-3.2264203242	15.2725125944	2.6302233771
H26B	-3.7605389699	16.1006216635	4.0996705586
H26C	-4.2744378344	16.7111094767	2.4964887897
H27A	-7.3191154165	15.2464871228	3.4060615108
H27B	-6.3792779777	16.7102138187	3.2091133110
H28A	-5.4463077103	16.3755388656	5.5481166916
H28B	-7.1785788174	16.5685538960	5.4555245248
H29A	-6.8541400095	14.8078027952	7.0143994286
H29B	-7.4741719539	14.0519196530	5.5761763809
H30A	-4.9832916661	14.4567814940	7.8677496910
H30B	-4.0211393769	15.1353778430	6.5341463667
H32A	-4.3484282668	11.1517399140	10.5527303158
H32B	-3.4515341611	10.0313572900	11.5905717106
H32C	-3.6491543519	9.6692006395	9.8644679275
H33A	-2.7625389773	13.0472225941	11.3270333570
H33B	-1.0036205307	12.8480617209	11.1639438071
H33C	-1.9060453489	11.8813490573	12.3525089245
H34A	-0.0367670865	10.6443387131	10.3165409718
H34B	-1.1315748037	9.3683004026	9.7062493047
H34C	-1.0557036049	9.7341632457	11.4385513956
H36A	-6.7949640523	5.2534002904	2.5551614307
H36B	-8.4240567810	4.9142890330	1.9449686279
H36C	-8.2115677302	5.6901015279	3.5299646317
H37A	-6.3069472479	6.5492407946	0.3644489989

H37B	-7.3795117988	7.8826268232	-0.1162360515
H37C	-7.9511976528	6.2022758650	-0.1904296747
H38A	-9.4702284922	8.4103748115	1.2361907213
H38B	-9.8126875942	7.5152034939	2.7404195888
H38C	-9.9225057984	6.7009915922	1.1733369895

Table S6b. Cartesian coordinates of geometry optimized $[LCo^{II}Co^{III}(\mu\text{-}F)(Cu^{I}Br_2)]^+$ (**4**, M^S = 4, quartet state, THF solution).

final geometry:			angstroms
atom	x	y	z
Co1	-2.3379192217	11.3097729187	3.4087237507
Co2	-4.7660272983	13.0086862711	4.1742044530
S1	-2.5405933738	13.5109551581	4.6317574941
S2	-4.2956508358	10.9223308795	5.0145266153
F1	-4.0055834964	12.2731759235	2.5666009904
Cu1	-4.8448872732	10.0659292668	7.6119076470
Br1	-3.2827089608	8.2748407597	7.3372171775
Br2	-6.7507686944	11.3596311189	8.2563906311
N1	-0.7341336458	10.6046285971	4.6873506248
N2	-1.0500598685	11.7713720862	1.6891698902
N3	-2.5914212826	9.3690412023	2.4967114870
N4	-6.6740290884	12.4828150942	3.6545178693
N5	-5.2102871776	14.8581805666	3.1302302262
N6	-5.3926803265	13.6794688537	5.9694169427
C1	-2.3347424327	12.8943146819	6.2817443600
C2	-3.2777792130	13.2463946905	7.2529645016
C3	-3.1888591436	12.7018442859	8.5315226862
C4	-2.1683493366	11.8148959212	8.8908593675
C5	-1.2169322146	11.5176117978	7.9141745199
C6	-1.2819267138	12.0381201119	6.6224343299
C7	-0.2358453317	11.6467653198	5.6249121288
C8	0.3998373543	9.9774410567	3.9653263691
C9	1.0143527514	10.8708825040	2.8963433144
C10	0.2117277399	10.9880891337	1.6101536554
C11	-0.7173628272	13.2050391335	1.7404887619
C12	-1.8541570047	11.5595652061	0.4497924010
C13	-2.2959785751	10.1341408771	0.1485403637
C14	-3.2225540298	9.4867112229	1.1627660820
C15	-3.2780754801	8.3964469633	3.3923354399
C16	-4.7532068302	8.6581925309	3.4425550630
C17	-5.3047729281	9.7994908341	4.0530632810
C18	-6.6748789860	10.0418878101	3.9010385985
C19	-7.4727260170	9.1664304977	3.1628166360
C20	-6.9526987171	8.0241459790	2.5610598525
C21	-5.5863125485	7.7923180238	2.7402515332
C22	-7.2654607063	11.3223531818	4.3868561752
C23	-6.8214244994	12.3382220802	2.1823466153
C24	-6.7652074122	13.6754871540	1.4712079876
C25	-5.5144913832	14.5041800502	1.7078738983
C26	-4.0235064289	15.7365421875	3.0782641273
C27	-6.3364857011	15.6663204592	3.6814746832
C28	-6.3147981755	15.8828917041	5.1809203792
C29	-6.5511537360	14.6157596198	5.9782705950
C30	-4.3592082846	14.2180117336	6.9156428767
C31	-2.1001715231	11.2528150589	10.3072933519
C32	-3.4630245746	10.6914588718	10.7294378380
C33	-1.7013836714	12.3876312592	11.2597401703
C34	-1.0725643316	10.1281450992	10.4250046300
C35	-7.7671431043	7.1014501055	1.6607587617
C36	-7.6900617017	5.6615899531	2.1807969166
C37	-7.1842300965	7.1706372428	0.2404697328
C38	-9.2367924024	7.5121335156	1.5928535989
H1	-1.1707781428	9.8820007836	5.2715563957
H3	-1.6592431119	8.9763479102	2.3403730448
H4	-7.2583277081	13.2784072410	3.9184702694
H6	-5.7319598328	12.8184559775	6.4247204739
H57	-3.9460542139	12.9879987026	9.2636491699
H5	-0.3946435530	10.8395116611	8.1428851054

H7A	0.0902747212	12.5144079126	5.0360307554
H7B	0.6533490272	11.2628986623	6.1526446426
H8A	0.0458089515	9.0369677089	3.5162237417
H8B	1.1752184050	9.6937960317	4.6957291876
H9A	1.2696778322	11.8578692464	3.3092497292
H9B	1.9792111676	10.4233138731	2.6172583109
H10A	0.8395730624	11.4343374377	0.8170697254
H10B	-0.0244462775	9.9723766001	1.2696467296
H11A	-1.6454713037	13.7881252397	1.7572346847
H11B	-0.1292712475	13.5008828001	0.8545406305
H11C	-0.1450695715	13.4444763591	2.6428238769
H12A	-1.2684004912	11.9392178237	-0.4078898468
H12B	-2.7427376147	12.1979814513	0.5506318347
H13A	-2.8352624879	10.1784020224	-0.8091532618
H13B	-1.4352549398	9.4765165920	-0.0472070611
H14A	-4.1376012399	10.0830098247	1.2783783802
H14B	-3.5214131014	8.4907604085	0.7932815988
H15A	-3.1073917956	7.3746606435	3.0177755417
H15B	-2.8183697802	8.4624986319	4.3889987250
H19	-8.5269839152	9.4200199544	3.0465348042
H21	-5.1247978892	6.9188838101	2.2739332196
H22A	-8.3535584536	11.3268583691	4.2184586392
H22B	-7.0971179857	11.4694772675	5.4626480185
H23A	-6.0258994100	11.6716638684	1.8357673306
H23B	-7.7884981770	11.8569115534	1.9686674082
H24A	-6.8123866595	13.4812573151	0.3898352298
H24B	-7.6755263412	14.2534434004	1.6911547578
H25A	-5.6003052259	15.4467479178	1.1394099114
H25B	-4.6373253802	13.9644695902	1.3359888938
H26A	-3.1905359980	15.2031871677	2.6096051322
H26B	-3.7151830643	16.0468629002	4.0803016099
H26C	-4.2461543369	16.6328227018	2.4765362637
H27A	-7.2887686846	15.1886512658	3.4203281298
H27B	-6.3414812086	16.6368276001	3.1559296523
H28A	-5.3983664575	16.3943129162	5.5082431311
H28B	-7.1324765312	16.5791068411	5.4149082942
H29A	-6.7756880881	14.8628650308	7.0270369408
H29B	-7.4432081602	14.0861366505	5.6134024220
H30A	-4.8834630994	14.5138546598	7.8373510131
H30B	-3.9331880830	15.1264311235	6.4692619777
H32A	-4.2513091719	11.4557262594	10.7410354239
H32B	-3.3937001857	10.2725728773	11.7437504550
H32C	-3.7831297595	9.8862872597	10.0498366671
H33A	-2.4355769314	13.2052812934	11.2436091311
H33B	-0.7223266052	12.8054500150	10.9830992461
H33C	-1.6339582655	12.0140454845	12.2923798870
H34A	-0.0493673513	10.4782006638	10.2261263428
H34B	-1.3024213237	9.3047730318	9.7328527961
H34C	-1.0864356568	9.7243685695	11.4467866037
H36A	-6.6581099908	5.2868233775	2.2137529780
H36B	-8.2661203580	4.9924469075	1.5250404262
H36C	-8.1083026969	5.5881091677	3.1945686162
H37A	-6.1388367568	6.8332269822	0.2053930458
H37B	-7.2194574393	8.1998267104	-0.1468832453
H37C	-7.7641318249	6.5310314929	-0.4413328476
H38A	-9.3607302116	8.5187035515	1.1682181951
H38B	-9.7134212367	7.4931076209	2.5832469150
H38C	-9.7849292573	6.8132536523	0.9460336087

Table S6c. Cartesian coordinates of geometry optimized $[LCo^{II}Co^{III}(\mu\text{-}F)(Cu^{I}Br_2)]^+$ (**4**, M^S = 4, quartet state, MeCN solution).

final geometry: angstroms			
atom	x	y	z
Co1	-2.3155708664	11.3209038823	3.4243555878
Co2	-4.7642024649	13.0235229665	4.1987469573
S1	-2.5340053359	13.5323326190	4.6481028610
S2	-4.2860601318	10.9369123822	5.0613630270
F1	-4.0029357135	12.2640997089	2.6024733877

Cu1	-4.9134870034	10.0683235138	7.5793294681
Br1	-3.5128982732	8.1348137082	7.4139143187
Br2	-6.7985844074	11.3761161296	8.2944818463
N1	-0.6972767979	10.6368582671	4.6960019518
N2	-1.0545716347	11.7877120867	1.6929498777
N3	-2.5712110716	9.3675194696	2.5373680404
N4	-6.6732669176	12.4986048142	3.6807413751
N5	-5.2009647998	14.8592895580	3.1389807343
N6	-5.3930646220	13.7068065103	5.9885152329
C1	-2.3291260802	12.9105229391	6.2963339325
C2	-3.2771238951	13.2540324291	7.2664827781
C3	-3.1971565325	12.6924577889	8.5385550475
C4	-2.1812181500	11.7970993287	8.8913779147
C5	-1.2213847099	11.5129472457	7.9182560248
C6	-1.2764089628	12.0522497321	6.6334214200
C7	-0.2175870053	11.6812451147	5.6406645896
C8	0.4489843331	10.0355591926	3.9678185436
C9	1.0349889652	10.9408302955	2.8937606151
C10	0.2230917211	11.0286113971	1.6114232283
C11	-0.7486807768	13.2285223004	1.7259565063
C12	-1.8603958339	11.5467991586	0.4591224892
C13	-2.2805017046	10.1104730475	0.1803364634
C14	-3.2031719440	9.4689256767	1.2013428596
C15	-3.2637301777	8.4072220609	3.4425173143
C16	-4.7395923098	8.6719328002	3.4885515237
C17	-5.2939405762	9.8134619256	4.0972154250
C18	-6.6631576344	10.0587065593	3.9388027899
C19	-7.4595007598	9.1819284434	3.2001983778
C20	-6.9379782200	8.0375252230	2.6037579721
C21	-5.5715744273	7.8050213681	2.7851390795
C22	-7.2589937638	11.3399807889	4.4173679789
C23	-6.8202537268	12.3417786027	2.2090549171
C24	-6.7603233054	13.6727102991	1.4876436750
C25	-5.5059651117	14.4964559018	1.7178797352
C26	-4.0139529371	15.7386441158	3.0766209996
C27	-6.3261196013	15.6761607254	3.6827736371
C28	-6.2950770591	15.9128866479	5.1786698191
C29	-6.5419738833	14.6577842589	5.9912341153
C30	-4.3544449573	14.2338097092	6.9359200479
C31	-2.1173283304	11.2205292546	10.3024872572
C32	-3.4915189386	10.6925142110	10.7300955838
C33	-1.6826763159	12.3354190404	11.2629877464
C34	-1.1184928053	10.0681503197	10.4034321657
C35	-7.7532285210	7.1158652484	1.7031956929
C36	-7.6627667354	5.6727330682	2.2109973309
C37	-7.1804700822	7.1984533067	0.2802120317
C38	-9.2260135255	7.5172937503	1.6475145627
H1	-1.1077788859	9.8975806976	5.2767014550
H3	-1.6426666193	8.9625062585	2.3836123457
H4	-7.2688332931	13.2897692568	3.9365841760
H6	-5.7404574764	12.8488773702	6.4416420200
H57	-3.9535849234	12.9780828575	9.2720152401
H5	-0.3974953248	10.8351533504	8.1436837624
H7A	0.0988942407	12.5565326528	5.0576577380
H7B	0.6742597369	11.3078283959	6.1710933688
H8A	0.1140978877	9.0859271516	3.5235921533
H8B	1.2326410475	9.7735410700	4.6970998365
H9A	1.2635447999	11.9368919498	3.3011607762
H9B	2.0106919746	10.5183225526	2.6128222593
H10A	0.8350272893	11.4823973186	0.8105085675
H10B	0.0061662732	10.0049499195	1.2822165947
H11A	-1.6876031154	13.7941383647	1.7443788883
H11B	-0.1752624983	13.5248624553	0.8306603313
H11C	-0.1709489727	13.4880006450	2.6195342791
H12A	-1.2821295148	11.9234818826	-0.4048106965
H12B	-2.7580667681	12.1739836612	0.5521658345
H13A	-2.8167677417	10.1305914037	-0.7800476746
H13B	-1.4102339887	9.4608082865	0.0018065550
H14A	-4.1215070860	10.0619140566	1.3102038469
H14B	-3.4950627185	8.4671128911	0.8425698667
H15A	-3.0934520628	7.3813817894	3.0793199720
H15B	-2.8035612031	8.4819349816	4.4381025989
H19	-8.5128101647	9.4381329315	3.0787636137

H21	-5.1079138774	6.9321829470	2.3189887835
H22A	-8.3468556019	11.3415930885	4.2484179312
H22B	-7.0910304023	11.4940230175	5.4916666582
H23A	-6.0266152267	11.6698124917	1.8681996695
H23B	-7.7898789059	11.8633548836	2.0011144077
H24A	-6.8093167771	13.4702624042	0.4077011297
H24B	-7.6671598480	14.2560220573	1.7067051934
H25A	-5.5886753293	15.4367407565	1.1455735557
H25B	-4.6301797255	13.9525335780	1.3485557031
H26A	-3.1814188937	15.2021551267	2.6105991440
H26B	-3.7049561809	16.0621430844	4.0743643903
H26C	-4.2410677849	16.6266397617	2.4647698429
H27A	-7.2809390147	15.1977883995	3.4321864656
H27B	-6.3293007188	16.6389969242	3.1436346082
H28A	-5.3722482859	16.4190788012	5.4965094677
H28B	-7.1054387305	16.6194386703	5.4071036277
H29A	-6.7586888447	14.9198315956	7.0382623699
H29B	-7.4406210023	14.1345823626	5.6325911228
H30A	-4.8748340377	14.5301917788	7.8598874180
H30B	-3.9244360777	15.1423839923	6.4932462798
H32A	-4.2534549136	11.4820251432	10.7717768925
H32B	-3.4227865364	10.2458766890	11.7327262330
H32C	-3.8459389153	9.9168460717	10.0329002326
H33A	-2.3923781316	13.1747598839	11.2513945232
H33B	-0.6916201009	12.7247024176	10.9871967579
H33C	-1.6261460037	11.9520542524	12.2929815430
H34A	-0.0870740279	10.3943506120	10.2074676318
H34B	-1.3688692645	9.2602945705	9.6999013046
H34C	-1.1415523652	9.6519692070	11.4203068600
H36A	-6.6276655772	5.3059103220	2.2320026006
H36B	-8.2397183330	5.0046124326	1.5548856049
H36C	-8.0725684792	5.5894131528	3.2276612147
H37A	-6.1325433081	6.8699484744	0.2381241455
H37B	-7.2258725308	8.2299821609	-0.0996612296
H37C	-7.7607458120	6.5586048453	-0.4012663729
H38A	-9.3596986333	8.5247266772	1.2279547140
H38B	-9.6947386486	7.4922322200	2.6416669328
H38C	-9.7735408859	6.8170383886	1.0013884843

Table S7a. Cartesian coordinates of geometry optimized $[LNi^{II}_2(\mu\text{-}F)]^+$ (**2**, $M^S = 5$, quintet state, gas phase).

final geometry: angstroms			
atom	x	y	z
Ni1	2.4083658414	-0.9233790466	3.1299530222
Ni2	4.4143278581	0.7355864987	4.5498280458
S3	3.1368505459	-1.1623969022	5.4743998154
S4	2.2209578856	1.4815858464	3.6786379112
F5	4.3804099951	-0.4347768299	2.8654009943
N6	0.3516566846	-1.4194975427	3.6639903283
H7	-0.1030809156	-0.5231484015	3.4716898009
N8	2.8486794526	-2.9941673951	2.3865056041
N9	1.8290532518	-0.5381405242	1.0908205196
H10	1.1774911024	-1.2892855551	0.8609772591
N11	5.4002305631	2.3930375946	3.6026136735
H12	6.0626394780	2.7342465994	4.2997505875
N13	6.5001510567	0.0380576054	5.0002274619
N14	4.2665531185	1.8356025809	6.4259069579
H15	3.6564138155	2.6043564673	6.1356835244
C16	1.8346290511	-0.2412836753	6.2498656567
C17	0.4895379879	-0.5204914978	5.9649535682
C18	-0.5110770639	0.3071969728	6.4606256899
H19	-1.5462672896	0.0697204038	6.2042069509
C20	-0.2370552490	1.4224472155	7.2583640303
C21	1.0979182405	1.6328254170	7.5947672133
H22	1.3703047749	2.4607526046	8.2503788048
C23	2.1243479662	0.8186073357	7.1144746086
C24	0.1284483128	-1.6892507760	5.1066981621
H25	0.7325841222	-2.5632464422	5.3839711114
H26	-0.9318681637	-1.9529824879	5.2643695432

C27	-0.2960088689	-2.4601262459	2.8455277120
H28	-0.4147960451	-2.0764640172	1.8199591754
H29	-1.3180180449	-2.6406684069	3.2206420083
C30	0.4688267127	-3.7759070718	2.8199537239
H31	-0.2131381462	-4.5480446157	2.4369450407
H32	0.7190663071	-4.0951703398	3.8414877095
C33	1.6936793166	-3.7879470084	1.9202102940
H34	2.0267826057	-4.8310512104	1.7589076706
H35	1.3873288346	-3.4190027203	0.9322479137
C36	3.5112784827	-3.7255412756	3.4740788090
H37	2.8482200959	-3.8368084291	4.3365885077
H38	4.3907239577	-3.1610806259	3.8014718250
H39	3.8358117451	-4.7241588667	3.1305898456
C40	3.8509316743	-2.8594511465	1.2978809657
H41	4.2038583178	-3.8714765640	1.0213884122
H42	4.6921120895	-2.3094764408	1.7361689350
C43	3.4032782192	-2.1382328413	0.0354295842
H44	4.2591871246	-2.1660769678	-0.6537090204
H45	2.6079019929	-2.6928937020	-0.4877577135
C46	2.9986011767	-0.6848241085	0.1986183814
H47	3.8199811511	-0.1062986965	0.6377145148
H48	2.7766320002	-0.2576121749	-0.7945950044
C49	1.0923187234	0.7344082678	0.8761096024
H50	0.3039018844	0.7970174525	1.6401782990
H51	0.6030169381	0.7126486605	-0.1115918408
C52	2.6681795415	2.2498810042	2.1404569737
C53	2.0201936156	1.9057377875	0.9400925114
C54	2.3321744733	2.5691829323	-0.2407501852
H55	1.8119002933	2.2622655500	-1.1507370487
C56	3.3015789179	3.5706140876	-0.3116915710
C57	3.9532857450	3.8792232738	0.8771303686
H58	4.7416809324	4.6320474924	0.8825944056
C59	3.6612326181	3.2382682667	2.0820552900
C60	4.5181097054	3.5410417186	3.2699368816
H61	5.1370586568	4.4274837837	3.0541322702
H62	3.9122454125	3.7641598164	4.1602718374
C63	6.1873938282	1.9141817302	2.4466724506
H64	6.4955295836	2.7666223586	1.8177272833
H65	5.5309100750	1.2715212159	1.8487593434
C66	7.4228965896	1.1475523566	2.8827708283
H67	8.1246423418	1.8258244394	3.3939395451
H68	7.9540256142	0.8353007357	1.9724638491
C69	7.1839232836	-0.1199138986	3.6901924377
H70	6.5488549657	-0.7956094590	3.1048480005
H71	8.1570789686	-0.6186692985	3.8616688001
C72	6.4135757313	-1.3035122729	5.5910876624
H73	7.4223423666	-1.7260434215	5.7471844702
H74	5.8565001054	-1.9604318816	4.9148644955
H75	5.8788822473	-1.2816419338	6.5449016312
C76	7.3041868429	0.8945895237	5.8960103527
H77	7.6277863559	1.7838624145	5.3390237687
H78	8.2333016182	0.3533115943	6.1584594239
C79	6.6141131920	1.3685754582	7.1645354219
H80	7.3890015141	1.8305217620	7.7923993987
H81	6.2334724306	0.5229629900	7.7545260483
C82	5.5198756705	2.4045292533	6.9517073009
H83	5.3180431845	2.9208011549	7.9059803436
H84	5.8708993668	3.1830163334	6.2561011330
C85	3.5368060786	1.1157323697	7.4994425634
H86	4.0773438217	0.1835678410	7.7102675400
H87	3.5515664922	1.7264170890	8.4190009136
C88	-1.3688526349	2.3423035778	7.7009117493
C89	-2.3902023369	1.5518127620	8.5263096314
H90	-1.9275711882	1.1357014070	9.4318348229
H91	-2.8262960871	0.7186333129	7.9595190334
H92	-3.2158754492	2.2069517069	8.8378985082
C93	-2.0478631624	2.9195856185	6.4519591517
H94	-2.8527465495	3.6112816876	6.7381445525
H95	-2.4933156396	2.1351750869	5.8255801327
H96	-1.3257281179	3.4717422492	5.8339651043
C97	-0.8655034173	3.5072473855	8.5501895942
H98	-0.3852577001	3.1628056989	9.4768618798
H99	-1.7102279826	4.1471752906	8.8378295608

H100	-0.1502294761	4.1355441420	8.0005193107
C101	3.6550779023	4.1989046648	-1.6546604263
C102	4.7432989585	5.2614331860	-1.5229023552
H103	4.9602760943	5.6937854874	-2.5085206937
H104	5.6828333781	4.8404847283	-1.1370435879
H105	4.4348651070	6.0837530591	-0.8624953356
C106	4.1735863473	3.0990906731	-2.5913721312
H107	4.4552085214	3.5250134864	-3.5647753209
H108	3.4186685018	2.3226431039	-2.7759797175
H109	5.0615989668	2.6095864874	-2.1661766097
C110	2.4123811688	4.8543210175	-2.2660951082
H111	2.0314315434	5.6558880632	-1.6186635243
H112	1.5981422323	4.1345990070	-2.4228838679
H113	2.6566121636	5.2946163276	-3.2430459257

Table S7b. Cartesian coordinates of geometry optimized $[LNi^{II}_2(\mu\text{-}F)]^+$ (**2**, $M^S = 5$, quintet state, THF solution).

final geometry: angstroms			
atom	x	y	z
Ni1	2.3414236717	-0.9360808128	3.0802520940
Ni2	4.4280350117	0.7729514954	4.5426503126
S3	3.1216394409	-1.1629134864	5.4624207978
S4	2.2223857896	1.4461511290	3.6790863897
F5	4.3440230622	-0.4383031907	2.8535429412
N6	0.2859242547	-1.4175357360	3.6413989403
H7	-0.1868592429	-0.5270796507	3.4610513763
N8	2.7534076039	-2.9945214713	2.3394717266
N9	1.7368706310	-0.5266487745	1.0708277173
H10	1.0662996148	-1.2543130325	0.8135589325
N11	5.3840599992	2.4321020688	3.6028379514
H12	6.0514996747	2.8087520310	4.2794605462
N13	6.4896521810	0.0841152030	4.9945739429
N14	4.2431366431	1.8753365672	6.4146052900
H15	3.6430834528	2.6564399551	6.1332441638
C16	1.8108264983	-0.2374474973	6.2308861741
C17	0.4658362522	-0.5162476953	5.9347694729
C18	-0.5365324789	0.3350677124	6.3888743988
H19	-1.5685222360	0.0988528731	6.1146007433
C20	-0.2646319061	1.4748153257	7.1529144216
C21	1.0662421331	1.6815679626	7.5111947252
H22	1.3391984805	2.5291992503	8.1422552899
C23	2.0949930500	0.8437724627	7.0744614834
C24	0.0980452469	-1.6934382355	5.0875990199
H25	0.7135537638	-2.5634330420	5.3518417038
H26	-0.9565093388	-1.9663493195	5.2694833259
C27	-0.3848956187	-2.4562184753	2.8329415777
H28	-0.5225025442	-2.0673756355	1.8119068895
H29	-1.3999611675	-2.6293840086	3.2301168415
C30	0.3724483484	-3.7753645271	2.7860162743
H31	-0.3179695904	-4.5377313100	2.3968727868
H32	0.6278978140	-4.1120219998	3.8013779046
C33	1.5884541853	-3.7798542985	1.8730265742
H34	1.9189993459	-4.8211868375	1.6954967537
H35	1.2711698575	-3.3976511132	0.8937841847
C36	3.4202621077	-3.7366993434	3.4178332283
H37	2.7605209692	-3.8515211835	4.2834478654
H38	4.3065597817	-3.1792667234	3.7402903927
H39	3.7343776756	-4.7365991251	3.0671845916
C40	3.7501046612	-2.8559881545	1.2442958126
H41	4.0993287748	-3.8677593161	0.9617559673
H42	4.5940554391	-2.3085544584	1.6817650208
C43	3.2941854554	-2.1280272598	-0.0123104994
H44	4.1453042460	-2.1551215116	-0.7085560480
H45	2.4899820474	-2.6755216067	-0.5294164059
C46	2.8971518328	-0.6730287163	0.1645576000
H47	3.7262649406	-0.1019099253	0.6001500306
H48	2.6640321141	-0.2393260391	-0.8233084414
C49	1.0187125628	0.7609073800	0.8836615031
H50	0.2400779427	0.8240418514	1.6579855918

H51	0.5132796242	0.7564065341	-0.0961038901
C52	2.6326697082	2.2488880344	2.1446545408
C53	1.9611470309	1.9222900012	0.9505902014
C54	2.2456089365	2.6085224012	-0.2256744209
H55	1.7064957057	2.3109870404	-1.1288342456
C56	3.2055048588	3.6202200573	-0.2973941563
C57	3.8775662703	3.9154574408	0.8848846124
H58	4.6584886579	4.6768783446	0.8926857410
C59	3.6157388421	3.2502246442	2.0851524496
C60	4.4813679332	3.5640057357	3.2664506229
H61	5.0886224374	4.4572019084	3.0452535532
H62	3.8796227379	3.7864222514	4.1601258411
C63	6.1713028189	1.9595403077	2.4432756773
H64	6.4742680554	2.8152452968	1.8161199114
H65	5.5174310973	1.3122861817	1.8461314426
C66	7.4119774186	1.2003516975	2.8782054063
H67	8.1053846364	1.8826583273	3.3949137580
H68	7.9467139910	0.8927887724	1.9675677129
C69	7.1747434113	-0.0697084133	3.6826944955
H70	6.5389676321	-0.7456789624	3.0973623650
H71	8.1482462855	-0.5679409959	3.8544947723
C72	6.4110106912	-1.2599719942	5.5826403983
H73	7.4232581860	-1.6774792564	5.7342342792
H74	5.8547848859	-1.9171991705	4.9049870062
H75	5.8834354457	-1.2407028451	6.5415265119
C76	7.2884251489	0.9464377633	5.8947874685
H77	7.6028813304	1.8419883241	5.3428815312
H78	8.2216190373	0.4100712201	6.1530284206
C79	6.5926675485	1.4084136506	7.1661749035
H80	7.3645674482	1.8725900776	7.7972259246
H81	6.2167816982	0.5578361085	7.7535283976
C82	5.4952438525	2.4420047873	6.9561193806
H83	5.2825902800	2.9507222166	7.9121965201
H84	5.8469385132	3.2268784583	6.2684233361
C85	3.5029342512	1.1513753991	7.4778128811
H86	4.0474281184	0.2237897724	7.6992116210
H87	3.5007969875	1.7620200106	8.3981289804
C88	-1.3940547468	2.4300590765	7.5265720436
C89	-2.4575145315	1.6892232074	8.3449112688
H90	-2.0307156696	1.2951649528	9.2784274292
H91	-2.8902154910	0.8457134602	7.7898105810
H92	-3.2794414508	2.3717767105	8.6073948224
C93	-2.0266748168	2.9732322617	6.2376549463
H94	-2.8278125792	3.6886851605	6.4766504038
H95	-2.4646873516	2.1723052359	5.6265513974
H96	-1.2753781720	3.4896865101	5.6230726956
C97	-0.8973646226	3.6187125032	8.3478149513
H98	-0.4510112776	3.3012586905	9.3011994806
H99	-1.7405955146	4.2839479866	8.5816848841
H100	-0.1513668559	4.2104248818	7.7979851043
C101	3.5219022801	4.2811625249	-1.6350074841
C102	4.5823166327	5.3721859600	-1.5019188953
H103	4.7704282132	5.8273045383	-2.4845824333
H104	5.5380543626	4.9706404509	-1.1354367546
H105	4.2608633318	6.1719991663	-0.8193608774
C106	4.0531270169	3.2130708240	-2.6011996721
H107	4.2985711544	3.6623637092	-3.5752646718
H108	3.3180252010	2.4150732956	-2.7758854910
H109	4.9648958633	2.7468206012	-2.2007806918
C110	2.2525411821	4.9125989779	-2.2172490229
H111	1.8529279753	5.6839349296	-1.5433328148
H112	1.4630371263	4.1671721459	-2.3820911857
H113	2.4715264131	5.3859684871	-3.1857958414

Table S8c. Cartesian coordinates of geometry optimized $[LNi^{II}_2(\mu\text{-}F)]^+$ (**2**, $M^S = 5$, quintet state, MeCN solution).

final geometry:	angstroms		
atom	x	y	z
Ni1	5.1584838319	2.6877754652	2.1686121621
Ni2	5.2675060456	4.3861600594	-0.3518599202

S2	6.1870929961	4.9506759158	1.9007103988
S1	6.3483821831	2.1948249794	0.0421958911
F1	3.8223723119	3.4944577751	0.8228442371
N1	6.7940684856	1.8367576932	3.3374733454
N2	3.8994717120	0.8495278848	2.3302136294
N3	4.1216993630	3.3135931206	3.9507779130
N4	4.2769918614	6.2876446959	-0.4882116615
N5	4.1302544098	3.8991585798	-2.2176839704
N6	6.9993275118	5.1161078687	-1.4629089068
C1	4.9103761144	5.9970272660	2.5650809870
C2	4.4212123142	7.0953501526	1.8400697137
C3	3.4617234876	7.9408760704	2.4033172944
C4	2.9380553997	7.7356827244	3.6768011782
C5	3.4233018719	6.6276129896	4.3758129646
C6	4.3737868783	5.7606559544	3.8458502694
C7	4.7012358879	4.5132848142	4.6099199969
C8	2.6776721873	3.4648776768	3.6652962708
C9	1.9936285952	2.1243711373	3.4733630681
C10	2.4794344829	1.2904866038	2.2979256143
C11	4.1072940256	0.0483378857	1.1162023193
C12	4.1374763727	-0.0108128426	3.5123813053
C13	5.5918721877	-0.3162724989	3.8315169783
C14	6.3909024184	0.8612326838	4.3739133426
C15	7.9103861346	1.2796571745	2.5321487906
C16	8.5812867214	2.2990004034	1.6635169395
C17	7.9726721637	2.7485831594	0.4845529968
C18	8.6675387510	3.6571327094	-0.3318034836
C19	9.9208935636	4.1180404354	0.0589384737
C20	10.5387552498	3.7021206383	1.2434258171
C21	9.8407907414	2.7822741855	2.0262939078
C22	8.0865357907	4.1202484240	-1.6323586037
C23	6.7009838513	5.7596640235	-2.7605814912
C24	5.9327669874	4.8696513127	-3.7276700195
C25	4.4539458381	4.7102910365	-3.4140437447
C26	4.3400686542	2.4823519920	-2.5451503494
C27	2.6889575692	4.0383209981	-1.8757718259
C28	2.1942495108	5.4381852533	-1.5446565882
C29	2.8180046526	6.0989347917	-0.3288344698
C30	4.8209017924	7.3339856738	0.4150038815
C31	1.8302549133	8.5935606586	4.2799144384
C32	1.4685639779	9.7776479885	3.3860192107
C33	0.5773136115	7.7238095163	4.4553715661
C34	2.2737295839	9.1376178303	5.6426295692
C35	11.9222872145	4.2331796818	1.6080885851
C36	12.9239256422	3.8089842946	0.5258919467
C37	12.4115263091	3.6911481045	2.9498182629
C38	11.8770683657	5.7634896318	1.6924792363
H1	7.1742409171	2.6569279866	3.8209884605
H3	4.2085007235	2.5585324538	4.6357313613
H4	4.4276999236	6.6441462086	-1.4351328134
H6	7.3704181814	5.8414507906	-0.8411826898
H3B	3.1064579213	8.7728971912	1.7933524441
H5	3.0244654286	6.3967362335	5.3671968533
H7A	4.2966176620	4.5948589050	5.6320346126
H7B	5.7862342281	4.3546933309	4.6932581739
H8A	2.5839175360	4.0733738892	2.7572009830
H8B	2.1832042718	4.0051974395	4.4910725462
H9A	2.0191786540	1.5529772138	4.4146186990
H9B	0.9268362527	2.3214108753	3.2906907630
H10A	1.8389225076	0.3918036000	2.2108136163
H10B	2.3728683382	1.8792370925	1.3782881265
H11A	3.9029739943	0.6713996119	0.2382180519
H11B	5.1403191679	-0.3069556608	1.0490477753
H11C	3.4248803178	-0.8207857134	1.1040705596
H12A	3.5783221948	-0.9557834536	3.3724021920
H12B	3.6966466116	0.4685838663	4.3960377115
H13A	6.1056469972	-0.7726743733	2.9728699495
H13B	5.5861063316	-1.0942880105	4.6088005646
H14A	5.8044277207	1.3912548088	5.1398491654
H14B	7.2921846142	0.4851420110	4.8874871359
H15A	7.5037333719	0.4696581220	1.9110935099
H15B	8.6539398222	0.8284629954	3.2121386903
H19	10.4315265621	4.8236043009	-0.6020094512

H21	10.2774698264	2.4036403512	2.9519465515
H22A	8.8845130534	4.5600841396	-2.2559255693
H22B	7.6750897608	3.2642711358	-2.1851914724
H23A	7.6461303274	6.0789879595	-3.2321607531
H23B	6.1313360852	6.6812809271	-2.5664707386
H24A	5.9944189439	5.3375238758	-4.7211065826
H24B	6.4301129344	3.8949266811	-3.8393853705
H25A	4.0303074747	5.7152460545	-3.2903078274
H25B	3.9314488071	4.2696266422	-4.2847127769
H26A	4.0624906531	1.8668774741	-1.6823085264
H26B	3.7148538127	2.1870113993	-3.4073581477
H26C	5.3902775213	2.2816652878	-2.7793520116
H27A	2.5281585645	3.3897214336	-1.0053235121
H27B	2.0914200168	3.6417992564	-2.7191381333
H28A	1.1151470630	5.3458154152	-1.3514839543
H28B	2.2690920661	6.1091776810	-2.4149044969
H29A	2.3278251126	7.0728261982	-0.1604851284
H29B	2.6646199693	5.4778685263	0.5620842886
H30A	4.4450546483	8.3188389383	0.0923650641
H30B	5.9142072260	7.3401735421	0.2932284565
H32A	1.0867720375	9.4517013323	2.4076127431
H32B	0.6811159987	10.3758973085	3.8657257141
H32C	2.3329343812	10.4355098545	3.2152307348
H33A	0.7604130964	6.8706831698	5.1238233551
H33B	-0.2455060329	8.3167918962	4.8824321584
H33C	0.2439882910	7.3241293629	3.4861431977
H34A	2.5071614980	8.3320052728	6.3519988837
H34B	3.1695652142	9.7672881837	5.5400794421
H34C	1.4752011388	9.7510094601	6.0857554207
H36A	12.6535998097	4.2079334312	-0.4615921676
H36B	13.9319110878	4.1758279048	0.7710561277
H36C	12.9709975869	2.7128990961	0.4450268166
H37A	12.5042401158	2.5956748403	2.9366819296
H37B	13.4038073487	4.1060141502	3.1766139139
H37C	11.7374454282	3.9687007785	3.7735464931
H38A	11.5815865011	6.2192423262	0.7374900357
H38B	11.1584882255	6.0903140106	2.4581323831
H38C	12.8674972421	6.1603197668	1.9605578411

Table S8a. Cartesian coordinates of geometry optimized [$LNi^{II}_2(\mu\text{-}F)(Cu^{I}Br_2)$] (**5**, $M^S = 5$, quintet state) gas phase.

final geometry: angstroms			
atom	x	y	z
Br1	-1.5476477594	1.8080761388	3.2689418726
Br2	1.5999938122	4.4882580597	5.6898553843
Ni3	2.3278558000	-0.8566977410	2.9679000903
Ni4	4.3916289634	0.8377727284	4.3854443969
Cu5	0.1206061150	3.0438939355	4.4767828426
S6	3.1066897398	-1.0830648826	5.2860041397
S7	2.2185604896	1.5028093411	3.4525758959
F8	4.3758104676	-0.4396385507	2.7338537550
N9	0.2896286418	-1.2519549838	3.5370759445
H10	-0.1576318960	-0.3311143312	3.3969420824
N11	2.6833198208	-2.9845447341	2.2906567279
N12	1.8319459207	-0.5186261155	0.9094554477
H13	1.1532327283	-1.2467323446	0.6861779089
N14	5.3816831734	2.4775583414	3.4646100977
H15	6.0156288924	2.8297710679	4.1807572766
N16	6.4897914633	0.2244389038	4.9638648110
N17	4.1583328793	1.9360849348	6.2574907602
H18	3.4605872049	2.6565298906	6.0097674722
C19	1.8143071776	-0.2134243683	6.1505179935
C20	0.4615707350	-0.4907457585	5.9028169678
C21	-0.5282550512	0.2533424280	6.5402550103
H22	-1.5687180088	0.0324480203	6.2936657499
C23	-0.2366587734	1.2788479057	7.4443320652
C24	1.1113825454	1.5127464331	7.6983410554
H25	1.4066352750	2.3096051628	8.3801288413
C26	2.1256531195	0.7927773260	7.0704413385
C27	0.0693049169	-1.5880013686	4.9649323496

H28	0.6441089148	-2.4964590444	5.1959447951
H29	-0.9998773965	-1.8246000338	5.1104435981
C30	-0.4168498420	-2.2205109437	2.6873294181
H31	-0.4961012401	-1.7999075353	1.6720687605
H32	-1.4570003589	-2.3294374683	3.0426544119
C33	0.2399951071	-3.5958458081	2.6409643103
H34	-0.4885116927	-4.2974359548	2.2085170492
H35	0.4244715670	-3.9655023846	3.6598115664
C36	1.4952986586	-3.6979031995	1.7867152354
H37	1.7589605085	-4.7650357186	1.6410821159
H38	1.2512598337	-3.3142183723	0.7873228459
C39	3.2482957438	-3.7360912590	3.4152516181
H40	2.5482923709	-3.7767951998	4.2546657977
H41	4.1542100859	-3.2317340357	3.7685234052
H42	3.5081990802	-4.7657048310	3.1033795899
C43	3.7395583525	-2.9169821653	1.2525309736
H44	4.0697523313	-3.9488656204	1.0167315795
H45	4.5750044893	-2.3813293785	1.7205548494
C46	3.3811555090	-2.2117358060	-0.0472740209
H47	4.2705809889	-2.2859171283	-0.6901538753
H48	2.5935856118	-2.7535911478	-0.5956810940
C49	3.0206365823	-0.7402574736	0.0627654431
H50	3.8502362682	-0.1830563669	0.5143199415
H51	2.8502702071	-0.3351104887	-0.9507809054
C52	1.1470875408	0.7723771311	0.6256632886
H53	0.3207389348	0.8887201227	1.3434509988
H54	0.7137182295	0.7340672753	-0.3881493377
C55	2.6947720634	2.2845519025	1.9261289206
C56	2.1056798783	1.9185187992	0.7020955181
C57	2.5045709699	2.5365706004	-0.4793379316
H58	2.0397987445	2.1991846201	-1.4089157477
C59	3.4931613810	3.5215436961	-0.5236372104
C60	4.0477997022	3.8862605656	0.6974793262
H61	4.8315060195	4.6433892382	0.7353147674
C62	3.6793190312	3.2839482364	1.9009802237
C63	4.4813605811	3.6114963214	3.1186040181
H64	5.0902283075	4.5095922087	2.9201359835
H65	3.8402961755	3.8233252813	3.9873535881
C66	6.2025519178	1.9939140347	2.3383297210
H67	6.5198284790	2.8375275669	1.7005131069
H68	5.5698892036	1.3329852517	1.7325952032
C69	7.4366434849	1.2456311840	2.8163758062
H70	8.1327021888	1.9438818287	3.3087144489
H71	7.9771882439	0.8968446474	1.9243896792
C72	7.1910890671	0.0113305215	3.6744693888
H73	6.5604255812	-0.6871296879	3.1095330279
H74	8.1654321117	-0.4773712591	3.8770580347
C75	6.4111256654	-1.0797991152	5.6278163932
H76	7.4245063553	-1.4729275464	5.8356521149
H77	5.8793402553	-1.7856879189	4.9809507963
H78	5.8523586231	-1.0094822422	6.5658427019
C79	7.2499646717	1.1510361955	5.8261137746
H80	7.5692415199	2.0120188305	5.2245136387
H81	8.1855551644	0.6489755968	6.1450261838
C82	6.5225809330	1.6918070053	7.0487203222
H83	7.2669881041	2.2597247189	7.6263380799
H84	6.2025746939	0.8776897283	7.7144395599
C85	5.3545036339	2.6271981800	6.7592859937
H86	5.0999240179	3.1788121731	7.6816642391
H87	5.6513367504	3.3981526540	6.0308258030
C88	3.5456232764	1.1485265503	7.3566745361
H89	4.1430491213	0.2386435211	7.5069194999
H90	3.5950772216	1.7385553883	8.2893018070
C91	-1.3567454597	2.0884557946	8.0924092239
C92	-2.2490604952	1.1478219651	8.9107576159
H93	-1.6722883308	0.6418308285	9.6985099256
H94	-2.7139768148	0.3747197094	8.2839488473
H95	-3.0586902806	1.7154997774	9.3925455099
C96	-2.1968106220	2.7766601957	7.0105200376
H97	-3.0181193480	3.3411834981	7.4766639121
H98	-2.6352051985	2.0672467394	6.2966650040
H99	-1.5850459641	3.4854151368	6.4311397097
C100	-0.8143182297	3.1719017555	9.0234837231

H101	-0.2351108170	2.7467717843	9.8564320748
H102	-1.6527552033	3.7332365006	9.4587560263
H103	-0.1796181062	3.8880220446	8.4820611113
C104	4.0001704615	4.0510744438	-1.8604863987
C105	5.0445834839	5.1518343894	-1.6887225635
H106	5.3678712870	5.5120162101	-2.6750061156
H107	5.9401213468	4.7893778580	-1.1637467563
H108	4.6443764720	6.0114856026	-1.1337144574
C109	4.6596768172	2.8896861082	-2.6178004529
H110	5.0585401032	3.2328501050	-3.5839505715
H111	3.9493051038	2.0755247052	-2.8176222894
H112	5.4928899192	2.4697595546	-2.0350575720
C113	2.8433659506	4.6137166649	-2.6903643896
H114	2.3606069377	5.4533683197	-2.1724073197
H115	2.0737157584	3.8575701165	-2.8911299318
H116	3.2119648566	4.9770454478	-3.6608366376

Table S8b. Cartesian coordinates of geometry optimized [$LNi^{II}_2(\mu\text{-}F)(Cu^{I}Br_2)$] (**5**, $M^S = 5$, quintet state, THF solution).

final geometry: angstroms			
atom	x	y	z
Br1	-1.5731075590	2.0105299292	3.2252356454
Br2	1.4918847665	4.6457917455	5.6627626538
Ni3	2.3539057609	-0.9526493207	3.0648093098
Ni4	4.4388982175	0.7943157335	4.5523854607
Cu5	0.5299719593	2.7837442325	4.3270540004
S6	3.0845217561	-1.1119412430	5.4315969422
S7	2.3098480314	1.4461603719	3.5327849665
F8	4.3879423184	-0.4795333998	2.8904618437
N9	0.2838933716	-1.2894629472	3.6117711222
H10	-0.1424956967	-0.3677087487	3.4468686681
N11	2.6749603271	-3.0489981733	2.4107039142
N12	1.8603434613	-0.6007232106	0.9997399356
H13	1.1795382055	-1.3172503031	0.7401444064
N14	5.4263721580	2.4416406842	3.5764847332
H15	6.0708584645	2.8398620111	4.2623227260
N16	6.4904145194	0.1590608961	5.1000645553
N17	4.1699550536	1.9083105114	6.3955865451
H18	3.5034501317	2.6417925770	6.1195947802
C19	1.7857323051	-0.2120375760	6.2431800209
C20	0.4344958044	-0.4831038273	5.9673650537
C21	-0.5608065235	0.2787896931	6.5756345156
H22	-1.5991364497	0.0552007681	6.3192464347
C23	-0.2766606977	1.3087178797	7.4788636728
C24	1.0686455785	1.5399684838	7.7556310577
H25	1.3575164722	2.3346226975	8.4436974996
C26	2.0914667572	0.8030863984	7.1580666372
C27	0.0458692061	-1.5974865947	5.0443902082
H28	0.6115338643	-2.5059033176	5.2957609268
H29	-1.0245554843	-1.8298090097	5.1857260870
C30	-0.4287218351	-2.2674368290	2.7655499043
H31	-0.4968449263	-1.8594557893	1.7450911467
H32	-1.4700939039	-2.3652454997	3.1193559105
C33	0.2199562140	-3.6458226514	2.7367408927
H34	-0.5091392668	-4.3426043394	2.2973641269
H35	0.3879670915	-4.0158195110	3.7587947829
C36	1.4813269309	-3.7555480315	1.8931743659
H37	1.7421263373	-4.8223500231	1.7511080275
H38	1.2473720113	-3.3727700763	0.8913765057
C39	3.2232306231	-3.8130179130	3.5392709422
H40	2.5114347520	-3.8563539818	4.3696148720
H41	4.1330296882	-3.3206238089	3.9006534900
H42	3.4749746767	-4.8426288100	3.2243696530
C43	3.7437447610	-3.0007959308	1.3771681212
H44	4.0569582210	-4.0387756379	1.1517327173
H45	4.5860934700	-2.4806264129	1.8509245077
C46	3.4095134059	-2.2996486177	0.0678532165
H47	4.3060498222	-2.3872941842	-0.5637326984
H48	2.6216579735	-2.8347490074	-0.4857898884

C49	3.0606138829	-0.8245210249	0.1669534502
H50	3.8863286438	-0.2687572083	0.6283716887
H51	2.8999258722	-0.4225353597	-0.8486942718
C52	1.1850410587	0.6930603579	0.7192414436
H53	0.3648658239	0.8123402560	1.4428218313
H54	0.7394998605	0.6545278929	-0.2889173205
C55	2.7537570999	2.2257168280	1.9911185068
C56	2.1372462467	1.8479577913	0.7854227402
C57	2.4798666327	2.4964075339	-0.3974929899
H58	1.9859722299	2.1682203295	-1.3155248213
C59	3.4383290697	3.5112849790	-0.4539361813
C60	4.0499577241	3.8531333262	0.7490676434
H61	4.8254883300	4.6192422739	0.7698228586
C62	3.7343486709	3.2254550896	1.9568269411
C63	4.5407794915	3.5674382693	3.1724505934
H64	5.1613891135	4.4528507615	2.9557992569
H65	3.8929599994	3.8129353703	4.0275594777
C66	6.2482470213	1.9225976899	2.4625667626
H67	6.5746817741	2.7523832498	1.8123031636
H68	5.6102987170	1.2547986125	1.8703144110
C69	7.4730392138	1.1748238202	2.9603974890
H70	8.1613341666	1.8739657549	3.4611893794
H71	8.0256935419	0.8217954956	2.0770355345
C72	7.2089142355	-0.0564408826	3.8154929515
H73	6.5860558164	-0.7563324096	3.2441104613
H74	8.1762303768	-0.5484721810	4.0356279221
C75	6.4031711940	-1.1529403203	5.7549806650
H76	7.4134026426	-1.5541565004	5.9567940929
H77	5.8688882510	-1.8482975082	5.0979008642
H78	5.8502361359	-1.0872458112	6.6973421930
C79	7.2565143803	1.0795519757	5.9712441927
H80	7.5770048958	1.9455584320	5.3781466340
H81	8.1886058714	0.5690555247	6.2824209811
C82	6.5287006914	1.6061336682	7.1981400621
H83	7.2762486187	2.1507337321	7.7937378907
H84	6.1891893676	0.7863970872	7.8479631430
C85	5.3844202908	2.5698544318	6.9120184537
H86	5.1355621129	3.1185567472	7.8372185535
H87	5.7026401051	3.3339377318	6.1859161501
C88	3.5107627619	1.1435433657	7.4849312801
H89	4.0938077680	0.2300753232	7.6650943726
H90	3.5408223971	1.7413872621	8.4128110852
C91	-1.4059630064	2.1289653339	8.0954410327
C92	-2.3575559154	1.1999381008	8.8586499288
H93	-1.8298072336	0.6737444663	9.6676970979
H94	-2.8083740983	0.4436250424	8.2016159693
H95	-3.1768990806	1.7809973230	9.3078267330
C96	-2.1773798084	2.8480331953	6.9818758280
H97	-2.9829918214	3.4600825134	7.4160034840
H98	-2.6276561665	2.1456146435	6.2675515891
H99	-1.5076377442	3.5075119334	6.4090347587
C100	-0.8841763719	3.1855631201	9.0682256098
H101	-0.3286124472	2.7344298766	9.9036767635
H102	-1.7305532556	3.7428417742	9.4944562975
H103	-0.2275208529	3.9087353028	8.5631621261
C104	3.8122388530	4.1344674772	-1.7951922651
C105	4.8628883491	5.2332830736	-1.6485360931
H106	5.0919497562	5.6588556966	-2.6356997700
H107	5.8035450400	4.8472170916	-1.2297762236
H108	4.5100700825	6.0524266925	-1.0057412974
C109	4.3901201157	3.0444392705	-2.7086679859
H110	4.6751470874	3.4726061510	-3.6815343526
H111	3.6676653592	2.2382409150	-2.8970489668
H112	5.2869004140	2.5936702827	-2.2589543456
C113	2.5670343416	4.7432795903	-2.4497856052
H114	2.1385202311	5.5331410187	-1.8165907318
H115	1.7851724233	3.9925098332	-2.6270960605
H116	2.8278773792	5.1890820807	-3.4211967295

Table S8c. Cartesian coordinates of geometry optimized [$LNi^{II}_2(\mu\text{-}F)(Cu^{I}Br_2)$] (**5**, $M^S = 5$, quintet state, MeCN solution).

final geometry: angstroms			
atom	x	y	z
Br1	-1.6277497992	2.6322302406	3.2252758381
Br2	1.6161808098	4.8521704767	5.4513914205
Ni3	2.2311743746	-1.1607135142	3.1432772765
Ni4	4.4195308076	0.7649731285	4.3323634669
Cu5	0.6022642433	2.8870438577	4.3054751249
S6	3.2090191394	-1.1363346671	5.4479663274
S7	2.1232455772	1.2757416643	3.5202341651
F8	4.2075763384	-0.5898080011	2.7510970352
N9	0.2468015345	-1.5488736919	3.9226062162
H10	-0.2314298263	-0.6677586663	3.7094990004
N11	2.6092805633	-3.2520138430	2.5872291111
N12	1.4902680439	-0.9307702667	1.1493062579
H13	0.8054118007	-1.6730766495	0.9847994792
N14	5.2433683265	2.3667633842	3.1742355050
H15	5.9388674446	2.8370273758	3.7581743304
N16	6.5269369683	0.2268682771	4.7121870583
N17	4.3013375867	2.0078161266	6.0971765044
H18	3.5992377442	2.7107956983	5.8347758135
C19	1.9642082011	-0.1901013084	6.2960315410
C20	0.5998336596	-0.5035651141	6.1595079140
C21	-0.3611219697	0.3090734816	6.7571612995
H22	-1.4119341500	0.0428112526	6.6156459188
C23	-0.0270647728	1.4336962067	7.5213866280
C24	1.3315777095	1.7023386840	7.6718824849
H25	1.6589140630	2.5623456185	8.2568835517
C26	2.3199590605	0.9139752366	7.0813313083
C27	0.1636394096	-1.7170278621	5.3963236908
H28	0.7869890093	-2.5790407765	5.6721583324
H29	-0.8765854221	-1.9668875853	5.6689875107
C30	-0.4846543386	-2.6433379945	3.2479435691
H31	-0.6923060139	-2.3362254853	2.2115527551
H32	-1.4685498863	-2.7754790466	3.7299840169
C33	0.2606642960	-3.9714022457	3.2560415833
H34	-0.4596960937	-4.7531875343	2.9736120446
H35	0.5801089822	-4.2307796867	4.2761064883
C36	1.4140048761	-4.0686292336	2.2694882363
H37	1.7315337626	-5.1240690573	2.1687761847
H38	1.0351172046	-3.7759085905	1.2817618586
C39	3.3462925583	-3.9032511201	3.6803191316
H40	2.7417307396	-3.9491000033	4.5916290841
H41	4.2509493018	-3.3243406758	3.8987394921
H42	3.6399665602	-4.9282490959	3.3898946733
C43	3.5371181576	-3.2173133629	1.4230410468
H44	3.8777270486	-4.2511043876	1.2219660683
H45	4.4017493030	-2.6277403450	1.7535821844
C46	2.9995581524	-2.6197483326	0.1313701879
H47	3.8098832740	-2.7093717968	-0.6074817164
H48	2.1735400374	-3.2210682530	-0.2798686594
C49	2.5958219893	-1.1574918188	0.1913258553
H50	3.4432488617	-0.5416181685	0.5171105605
H51	2.2962380311	-0.8243786585	-0.8173906107
C52	0.7530273241	0.3358192511	0.8897607173
H53	0.0235591215	0.4812339985	1.7003157872
H54	0.1904335523	0.2354998507	-0.0529288470
C55	2.4069165879	1.9697037475	1.8967771405
C56	1.6796398509	1.5087401620	0.7857451262
C57	1.8949103186	2.0772060637	-0.4660706419
H58	1.3235640050	1.6784447758	-1.3082309619
C59	2.8296654525	3.0925269252	-0.6825084672
C60	3.5437234717	3.5272081482	0.4298032746
H61	4.3045025919	4.3011613251	0.3230973889
C62	3.3575007399	2.9811397892	1.7020856867
C63	4.2721102643	3.4285649714	2.8008884615
H64	4.8278566238	4.3207743860	2.4681723143
H65	3.7076835416	3.7042370725	3.7041156903
C66	5.9703061909	1.8093532259	2.0124943800
H67	6.2033665620	2.6113907188	1.2915322644

H68	5.3012150458	1.0902550195	1.5235731636
C69	7.2629336605	1.1289946972	2.4283947897
H70	7.9711433721	1.8770867307	2.8178031480
H71	7.7384648943	0.7377374513	1.5166415040
C72	7.1232305799	-0.0529073533	3.3773393443
H73	6.4707995109	-0.8050934135	2.9149814916
H74	8.1221134341	-0.5051550931	3.5303643696
C75	6.5532838292	-1.0400309305	5.4562092248
H76	7.5926519247	-1.3947488077	5.5817636148
H77	5.9851082264	-1.7962218457	4.9028347207
H78	6.0937250958	-0.9255057671	6.4432441570
C79	7.3477326056	1.2224957974	5.4429016672
H80	7.5792579768	2.0573102830	4.7693497591
H81	8.3214952198	0.7565570450	5.6877895508
C82	6.7290402037	1.8073981603	6.7026719480
H83	7.5147749693	2.4059541876	7.1869391307
H84	6.4767979139	1.0240983486	7.4327639644
C85	5.5385035030	2.7263984118	6.4681475259
H86	5.3536610496	3.3206382079	7.3799909684
H87	5.7710802375	3.4544195091	5.6755531194
C88	3.7514802936	1.2996863606	7.2794922669
H89	4.3702065650	0.4117201568	7.4665044246
H90	3.8384723363	1.9526592228	8.1657973439
C91	-1.1175248338	2.2959405752	8.1512883223
C92	-1.9570685713	1.4420148858	9.1090369579
H93	-1.3340811948	1.0316411371	9.9174660838
H94	-2.4384250815	0.6000762122	8.5925226470
H95	-2.7509335736	2.0518397358	9.5663652788
C96	-2.0163767439	2.8631901337	7.0478088546
H97	-2.7893213964	3.5133029349	7.4855318890
H98	-2.5218332701	2.0729854871	6.4766284049
H99	-1.4255642987	3.4536112329	6.3309247402
C100	-0.5388468902	3.4707124636	8.9382706717
H101	0.1021729441	3.1343281143	9.7665424639
H102	-1.3587185358	4.0612644193	9.3719598082
H103	0.0500884355	4.1370768774	8.2908091147
C104	3.0910801041	3.6053617503	-2.0953152990
C105	4.0880267693	4.7626964285	-2.1160829306
H106	4.2273122230	5.1100640975	-3.1495805049
H107	5.0746418921	4.4627275188	-1.7343923565
H108	3.7344353384	5.6163385441	-1.5199628547
C109	3.6759605471	2.4574230781	-2.9304830875
H110	3.8848447974	2.7968187572	-3.9563630837
H111	2.9872458034	1.6030063673	-2.9908695643
H112	4.6185914780	2.0981937019	-2.4916511414
C113	1.7830710169	4.0871846717	-2.7318817983
H114	1.3439587412	4.9092552027	-2.1486583276
H115	1.0361941653	3.2848211796	-2.7999063038
H116	1.9701706173	4.4544066481	-3.7519193558

Table S9a. Cartesian coordinates of geometry optimized [$LNi^{II}_2(\mu\text{-}F)(Cu^{I}I_2)$] (**6**, $M^S = 5$, quintet state) gas phase.

final geometry: angstroms			
atom	x	y	z
I1	-1.7659573141	1.8161891965	3.1129588840
I2	1.4782744373	4.8094186311	5.5384917715
Ni3	2.4125114411	-0.8489059938	3.1039824006
Ni4	4.4290624163	0.8099688608	4.5645660236
Cu5	0.0874747409	3.2737880611	4.0592227012
S6	3.1521209518	-1.0979036851	5.4355389756
S7	2.2451878317	1.5040541581	3.6118491214
F8	4.4357391044	-0.4234629823	2.8892204932
N9	0.3667612850	-1.2860289879	3.6669871137
H10	-0.0890242383	-0.3750618346	3.5035251568
N11	2.7802255554	-3.0116097909	2.4530155357
N12	1.9210010018	-0.5649073103	1.0538746164
H13	1.2515486560	-1.3047650112	0.8426149472
N14	5.4492786381	2.4093580017	3.6205222701
H15	6.0910983615	2.7650314266	4.3285205445

N16	6.5131221381	0.1184652214	5.1243958281
N17	4.2245733030	1.8958189443	6.4290177226
H18	3.5481302218	2.6307446233	6.1743550854
C19	1.8593049474	-0.2216770908	6.2852002270
C20	0.5086517169	-0.4986311834	6.0303221632
C21	-0.4824331369	0.2351255694	6.6751497154
H22	-1.5231110367	0.0063805392	6.4363091232
C23	-0.1924227491	1.2516796405	7.5891306448
C24	1.1535908068	1.4959793000	7.8409615542
H25	1.4454728780	2.2823553172	8.5365795062
C26	2.1686943948	0.7798912326	7.2103439589
C27	0.1238580263	-1.6008951128	5.0965314362
H28	0.6895597600	-2.5104920431	5.3456762875
H29	-0.9485512529	-1.8298217844	5.2291974486
C30	-0.3274777512	-2.2731727634	2.8264181290
H31	-0.4061834687	-1.8689123743	1.8046973974
H32	-1.3685679936	-2.3846884288	3.1781243308
C33	0.3419501830	-3.6422646762	2.8023167286
H34	-0.3782029178	-4.3571792455	2.3780526560
H35	0.5277793720	-3.9962053138	3.8265373540
C36	1.5999114426	-3.7400825096	1.9520840760
H37	1.8735445342	-4.8058874265	1.8157596472
H38	1.3532412468	-3.3677810339	0.9490096295
C39	3.3449750678	-3.7524079998	3.5842709226
H40	2.6426682325	-3.7929490350	4.4216707616
H41	4.2468479126	-3.2412664163	3.9383099974
H42	3.6126497949	-4.7822859075	3.2797197796
C43	3.8392436170	-2.9465877458	1.4190729628
H44	4.1753616010	-3.9782645744	1.1908162738
H45	4.6717808713	-2.4050009100	1.8861671016
C46	3.4820246277	-2.2512908736	0.1135313751
H47	4.3725335895	-2.3263543623	-0.5272188954
H48	2.6970604418	-2.8000085799	-0.4317441432
C49	3.1135473091	-0.7812662316	0.2128294585
H50	3.9377377618	-0.2148922868	0.6631288474
H51	2.9425085863	-0.3833089636	-0.8031006407
C52	1.2205622987	0.7129366415	0.7670962482
H53	0.3860579477	0.8123324824	1.4751715473
H54	0.7929303465	0.6719939658	-0.2486813253
C55	2.7531473102	2.2456834040	2.0751287895
C56	2.1629517322	1.8700200191	0.8540405966
C57	2.5523218349	2.4852479519	-0.3289310489
H58	2.0797036453	2.1459401966	-1.2529919399
C59	3.5389722356	3.4691528017	-0.3825845786
C60	4.1202440147	3.8205054017	0.8298869951
H61	4.9146924310	4.5661727370	0.8569723462
C62	3.7568015641	3.2254532473	2.0388820342
C63	4.5707451827	3.5520600243	3.2502653045
H64	5.1966013134	4.4343699315	3.0367591172
H65	3.9351147327	3.7928455993	4.1150336224
C66	6.2598941486	1.8956062361	2.4991925634
H67	6.5931195057	2.7276537937	1.8551360852
H68	5.6121599339	1.2425415344	1.9026861983
C69	7.4781153554	1.1247067770	2.9797253540
H70	8.1864278278	1.8093431782	3.4737601818
H71	8.0129038852	0.7667095834	2.0880666227
C72	7.2105615115	-0.1060877494	3.8348803247
H73	6.5676486072	-0.7922012864	3.2692767134
H74	8.1750152445	-0.6130757866	4.0383252528
C75	6.4090457330	-1.1878415185	5.7815959362
H76	7.4145540483	-1.6032405701	5.9828231488
H77	5.8617472855	-1.8789896753	5.1319039126
H78	5.8537757798	-1.1144976251	6.7212368777
C79	7.2949990178	1.0240257143	5.9879365818
H80	7.6289430099	1.8816314865	5.3896906658
H81	8.2208454458	0.5009903933	6.3011721346
C82	6.5805950240	1.5699473669	7.2148561644
H83	7.3390231130	2.1058379756	7.8041160109
H84	6.2333931303	0.7562919219	7.8673990712
C85	5.4432045153	2.5452512525	6.9336374252
H86	5.2079213877	3.0964093550	7.8608342221
H87	5.7643095366	3.3089853901	6.2082313212
C88	3.5882320163	1.1146790016	7.5189427848

H89	4.1710143151	0.1958787603	7.6712548074
H90	3.6349356133	1.6996672967	8.4545672549
C91	-1.3174821812	2.0305426977	8.2601884375
C92	-2.1762195279	1.0633881396	9.0853681072
H93	-1.5782273428	0.5760388393	9.8694770011
H94	-2.6212186927	0.2742678665	8.4642012676
H95	-2.9993633613	1.6053236269	9.5738028364
C96	-2.1778447161	2.7068825546	7.1865121057
H97	-2.9789825419	3.2943777655	7.6589945647
H98	-2.6474325545	1.9828391067	6.5072988491
H99	-1.5712421933	3.3858673914	6.5682285258
C100	-0.7841597457	3.1139072480	9.1960345325
H101	-0.1793878519	2.6903810790	10.0117520757
H102	-1.6263308013	3.6489528929	9.6558695496
H103	-0.1769054416	3.8525899483	8.6536865855
C104	3.9962433176	4.0163542142	-1.7285177137
C105	5.0671688886	5.0926841817	-1.5762864251
H106	5.3571948177	5.4719661274	-2.5655171281
H107	5.9744540869	4.6992114733	-1.0960380991
H108	4.7057166967	5.9445490569	-0.9839142862
C109	4.5920634232	2.8611315695	-2.5448460982
H110	4.9475342523	3.2199054801	-3.5217523901
H111	3.8561623025	2.0660107013	-2.7275752407
H112	5.4445690253	2.4104324540	-2.0157644343
C113	2.8057526114	4.6199738870	-2.4783286722
H114	2.3650294599	5.4484393047	-1.9076559845
H115	2.0148158568	3.8801738357	-2.6560071302
H116	3.1245669705	5.0081752089	-3.4565101141

Table S9b. Cartesian coordinates of geometry optimized [$LNi^{II}_2(\mu\text{-}F)(Cu^{I}I_2)$] (**6**, $M^S = 5$, quintet state, THF solution).

final geometry: angstroms			
atom	x	y	z
I1	-1.7232978616	2.1624602514	3.1424331727
I2	1.5057654446	4.7945006552	5.7420149655
Ni3	2.3670005248	-0.9181876475	3.0595332087
Ni4	4.4239166722	0.8145663897	4.5244486929
Cu5	0.5214875882	2.8833487492	4.2676406049
S6	3.0740714336	-1.0742852698	5.4096618973
S7	2.2962261532	1.4895549584	3.5003388614
F8	4.3931248336	-0.4485097799	2.8737206058
N9	0.2972262808	-1.2481587314	3.5973480099
H10	-0.1117590366	-0.3204669712	3.4281935412
N11	2.6783241009	-3.0235752536	2.4241735524
N12	1.8972918065	-0.5875034849	0.9822590287
H13	1.2240877694	-1.3102613761	0.7213788396
N14	5.4273758420	2.4546545213	3.5461376837
H15	6.0723101403	2.8481113681	4.2340878517
N16	6.4765990017	0.1796567874	5.0786941462
N17	4.1609202653	1.9170476874	6.3682783765
H18	3.4892605423	2.6436033504	6.0886797767
C19	1.7778724440	-0.1788193850	6.2276686253
C20	0.4255888868	-0.4524238838	5.9613178362
C21	-0.5668798924	0.2803763018	6.6086425064
H22	-1.6072477568	0.0543418046	6.3630256950
C23	-0.2780029666	1.2814352556	7.5421744407
C24	1.0691151963	1.5199566877	7.8027013626
H25	1.3603376791	2.2946537469	8.5121663523
C26	2.0892073149	0.8177291293	7.1607003254
C27	0.0338617681	-1.5545360640	5.0250371875
H28	0.5810181300	-2.4729590488	5.2822762552
H29	-1.0422364313	-1.7701268669	5.1489870323
C30	-0.4182575153	-2.2132364637	2.7402614517
H31	-0.4689037850	-1.8023514797	1.7201664958
H32	-1.4650509900	-2.2972425323	3.0816052181
C33	0.2151757713	-3.5985600991	2.7185162305
H34	-0.5156548825	-4.2879281311	2.2709284541
H35	0.3667211363	-3.9694991941	3.7428202070
C36	1.4863247693	-3.7216321813	1.8916201199

H37	1.7394857530	-4.7911375737	1.7572108124
H38	1.2688190583	-3.3415175621	0.8852288467
C39	3.2003484370	-3.7886208923	3.5640951251
H40	2.4744855414	-3.8236373635	4.3825842859
H41	4.1079730554	-3.3038042976	3.9407539611
H42	3.4482699993	-4.8211560648	3.2558182650
C43	3.7662430560	-2.9862252522	1.4105021596
H44	4.0793636818	-4.0266681549	1.1964445954
H45	4.6021753081	-2.4675674237	1.8972263522
C46	3.4615276761	-2.2916595458	0.0903065427
H47	4.3718668717	-2.3832116363	-0.5205579289
H48	2.6861854149	-2.8306611405	-0.4768840957
C49	3.1111639034	-0.8159584307	0.1709348430
H50	3.9291456886	-0.2565588985	0.6408166392
H51	2.9663955491	-0.4228120866	-0.8504688754
C52	1.2199197875	0.6980777378	0.6773287058
H53	0.3879745797	0.8173720430	1.3864957520
H54	0.7890522425	0.6472315804	-0.3365215071
C55	2.7626307428	2.2503614922	1.9568489360
C56	2.1643636709	1.8582820928	0.7469919419
C57	2.5277034128	2.4886617868	-0.4389497988
H58	2.0505517875	2.1461588508	-1.3605056092
C59	3.4896370271	3.5002164606	-0.4939245207
C60	4.0849030444	3.8556565898	0.7129576044
H61	4.8651285641	4.6175200831	0.7349898640
C62	3.7480644056	3.2450508616	1.9234619432
C63	4.5517728037	3.5859961184	3.1400487264
H64	5.1781568839	4.4673562251	2.9241291444
H65	3.9058151895	3.8359697044	3.9944929350
C66	6.2490287103	1.9311107534	2.4349168257
H67	6.5811805379	2.7590830972	1.7853937452
H68	5.6105961111	1.2666014407	1.8400684942
C69	7.4685260882	1.1785960704	2.9367493527
H70	8.1593800256	1.8765221771	3.4355773380
H71	8.0198212924	0.8185482481	2.0554370735
C72	7.1966532854	-0.0467860719	3.7974378465
H73	6.5720480319	-0.7467650707	3.2284860373
H74	8.1611434792	-0.5418357224	4.0227340331
C75	6.3814892815	-1.1276111448	5.7410035560
H76	7.3891834013	-1.5325275937	5.9475158035
H77	5.8450741775	-1.8238753508	5.0864527244
H78	5.8266654762	-1.0544898202	6.6817378509
C79	7.2445947784	1.1031921637	5.9449317303
H80	7.5694124201	1.9637871171	5.3462293174
H81	8.1744083382	0.5914952807	6.2606397746
C82	6.5190752333	1.6425966649	7.1679087275
H83	7.2669385306	2.1966056927	7.7539078297
H84	6.1842334360	0.8294471213	7.8284589581
C85	5.3695245622	2.5965033272	6.8720380913
H86	5.1166732247	3.1583465198	7.7884351716
H87	5.6799129499	3.3523873436	6.1339922523
C88	3.5110789954	1.1617996165	7.4701502502
H89	4.0952913566	0.2499023335	7.6549404665
H90	3.5489199102	1.7692016435	8.3915527044
C91	-1.4066648314	2.0565332664	8.2175522389
C92	-2.3158383630	1.0777966500	8.9704898395
H93	-1.7539440424	0.5367196096	9.7461058994
H94	-2.7626456105	0.3332795109	8.2972882799
H95	-3.1382637384	1.6205973310	9.4603791590
C96	-2.2228767311	2.7981385917	7.1527220230
H97	-3.0216343053	3.3848808156	7.6313436543
H98	-2.6900588011	2.1110944781	6.4340094228
H99	-1.5819168759	3.4832126027	6.5775393812
C100	-0.8809726730	3.0876881932	9.2155130658
H101	-0.2974745477	2.6186552349	10.0215892590
H102	-1.7270973768	3.6136636840	9.6803848984
H103	-0.2497526529	3.8411842001	8.7221523565
C104	3.8938618029	4.0948928751	-1.8386575489
C105	4.9499948378	5.1878043544	-1.6904778227
H106	5.2038239110	5.5941097100	-2.6796728809
H107	5.8780836446	4.8021816856	-1.2441064100
H108	4.5899172950	6.0206354161	-1.0696765451
C109	4.4783010146	2.9794260191	-2.7162396975

H110	4.7844126207	3.3815989144	-3.6936892134
H111	3.7518577747	2.1750862242	-2.8974416142
H112	5.3618914635	2.5316183577	-2.2385587897
C113	2.6670916295	4.7003867986	-2.5294848064
H114	2.2346041846	5.5083852619	-1.9224168708
H115	1.8820312247	3.9521297959	-2.7013857364
H116	2.9483948574	5.1197288651	-3.5068943369

Table S9c. Cartesian coordinates of geometry optimized [$LNi^{II}_2(\mu\text{-}F)(Cu^{I}I_2)$] (**6**, $M^S = 5$, quintet state, MeCN solution).

final geometry: angstroms			
atom	x	y	z
I1	-1.7834955524	2.4637615140	3.2532950633
I2	1.6025415003	4.9730084397	5.5102051949
Ni3	2.2992694386	-1.0751060543	3.1403918437
Ni4	4.4447301302	0.8081443363	4.2962667453
Cu5	0.5921442809	2.8922519940	4.2778006180
S6	3.2267045541	-1.0519111880	5.4376618000
S7	2.1888453967	1.3701205496	3.4701615036
F8	4.2617717272	-0.5452613480	2.7324073063
N9	0.2982250733	-1.4536184353	3.8943154261
H10	-0.1708776024	-0.5680623748	3.6771306986
N11	2.6707620552	-3.1783430558	2.5856600625
N12	1.5815285880	-0.8711774383	1.1179567460
H13	0.9068895576	-1.6233504628	0.9587701448
N14	5.3065617758	2.3921068766	3.1175846416
H15	6.0095354823	2.8543588545	3.6984671758
N16	6.5464988727	0.2478012790	4.6925887784
N17	4.3236150167	2.0458450680	6.0630276719
H18	3.6235194415	2.7447406037	5.7868625809
C19	1.9810540702	-0.1112022887	6.2823028444
C20	0.6184582957	-0.4314315212	6.1504536172
C21	-0.3401878290	0.3495521120	6.7927541065
H22	-1.3910263921	0.0817190882	6.6537208470
C23	-0.0031208107	1.4409652971	7.6018456168
C24	1.3540897319	1.7254131054	7.7314648165
H25	1.6812226343	2.5668411693	8.3427546019
C26	2.3399743652	0.9769358941	7.0873329421
C27	0.1854341869	-1.6310926278	5.3638229166
H28	0.7949988111	-2.5013944105	5.6451146139
H29	-0.8617608451	-1.8740929994	5.6150865516
C30	-0.4281397958	-2.5387575966	3.2009931392
H31	-0.6146322300	-2.2253257317	2.1623719283
H32	-1.4227888707	-2.6639477326	3.6625870318
C33	0.3050356601	-3.8734866729	3.2195531125
H34	-0.4180717637	-4.6483228911	2.9256621652
H35	0.6052273439	-4.1359926653	4.2445522161
C36	1.4735766686	-3.9848036992	2.2527851586
H37	1.7826769990	-5.0436613106	2.1625533177
H38	1.1129551826	-3.6948270162	1.2573495110
C39	3.3848811853	-3.8268885290	3.6943064222
H40	2.7645314227	-3.8659022622	4.5952344530
H41	4.2878197914	-3.2505019093	3.9259454548
H42	3.6794217193	-4.8544953950	3.4142659111
C43	3.6170572292	-3.1542788074	1.4375384360
H44	3.9551827528	-4.1907234846	1.2467606832
H45	4.4792440901	-2.5679648401	1.7790479475
C46	3.1046594014	-2.5617133552	0.1333181354
H47	3.9273165425	-2.6572527078	-0.5909121817
H48	2.2840853899	-3.1635466852	-0.2882571669
C49	2.6990958737	-1.0996297254	0.1766752073
H50	3.5412270010	-0.4790073871	0.5072682903
H51	2.4116591060	-0.7759356299	-0.8387201431
C52	0.8338615040	0.3824456792	0.8402003251
H53	0.0966838906	0.5244643595	1.6434283565
H54	0.2786682030	0.2686700248	-0.1055015625
C55	2.4754104328	2.0362983097	1.8387758443
C56	1.7537147806	1.5590194084	0.7312877027
C57	1.9815321671	2.1043025385	-0.5279920636

H58	1.4158235488	1.6919871200	-1.3669798937
C59	2.9270117043	3.1061727758	-0.7560848978
C60	3.6420724959	3.5509943642	0.3513940188
H61	4.4152101879	4.3108840714	0.2343824516
C62	3.4408938082	3.0302933423	1.6319209355
C63	4.3630942576	3.4713709326	2.7263700984
H64	4.9397711389	4.3462528120	2.3839025193
H65	3.8046617091	3.7705350238	3.6254423042
C66	6.0255382444	1.8033797129	1.9669654396
H67	6.2754466339	2.5890670622	1.2339317195
H68	5.3460091681	1.0886647250	1.4866981754
C69	7.3042049318	1.1071947532	2.3982387185
H70	8.0229424025	1.8497887666	2.7789063509
H71	7.7762365962	0.6936827073	1.4946455492
C72	7.1450610892	-0.0575326379	3.3648289617
H73	6.4856784768	-0.8082635147	2.9108760516
H74	8.1377398863	-0.5191436649	3.5288544025
C75	6.5552110127	-1.0090616237	5.4529594048
H76	7.5897644229	-1.3741056318	5.5872302223
H77	5.9807900151	-1.7653924719	4.9064021247
H78	6.0923868150	-0.8781429195	6.4362970033
C79	7.3702482913	1.2469351415	5.4137129579
H80	7.6123330752	2.0703171550	4.7296598569
H81	8.3391576973	0.7772664074	5.6701365810
C82	6.7504816571	1.8540204913	6.6628167931
H83	7.5373986215	2.4574715620	7.1382884992
H84	6.4953834499	1.0823292008	7.4040470548
C85	5.5610668059	2.7709952092	6.4136768117
H86	5.3787193247	3.3867606232	7.3119244084
H87	5.7906466384	3.4804104528	5.6032848499
C88	3.7737395973	1.3683443829	7.2638614899
H89	4.3911008028	0.4837330801	7.4716179120
H90	3.8649680967	2.0446387061	8.1320262148
C91	-1.0903260640	2.2509463245	8.3026289894
C92	-1.8823625430	1.3327948826	9.2414243193
H93	-1.2255298877	0.8961068431	10.0081643768
H94	-2.3616839527	0.5072796390	8.6972008593
H95	-2.6739015594	1.9012777249	9.7530783433
C96	-2.0359780813	2.8480637986	7.2554323370
H97	-2.8060096520	3.4616236677	7.7470916430
H98	-2.5460779128	2.0726324194	6.6679467165
H99	-1.4815703723	3.4810648432	6.5460529007
C100	-0.5108761514	3.3982232268	9.1289475493
H101	0.1633544465	3.0351531721	9.9186685331
H102	-1.3283960480	3.9482846231	9.6170203260
H103	0.0439644262	4.1100068934	8.4995812377
C104	3.2063906565	3.5809839417	-2.1779538537
C105	4.2223748993	4.7206872508	-2.2170950912
H106	4.3769589600	5.0412624871	-3.2569795183
H107	5.1999365902	4.4131526830	-1.8184907549
H108	3.8777400062	5.5936386665	-1.6442210487
C109	3.7769390945	2.4020175959	-2.9788903743
H110	4.0033739702	2.7117642883	-4.0102324322
H111	3.0711450281	1.5609129653	-3.0260767347
H112	4.7066088286	2.0338573851	-2.5203634408
C113	1.9107767371	4.0679617588	-2.8357222649
H114	1.4823346576	4.9126469204	-2.2774188542
H115	1.1503110786	3.2771036195	-2.8865061339
H116	2.1098976582	4.4041768535	-3.8641712932

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