

Hexahalorhenate(IV) salts of metal oxazolidine nitroxides

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Table S1. Crystallographic data for **1a**, **1b**, **2a** and **2a**·150 K.

Parameters	1a	1b	2a	2a ·150 K
formula	C ₃₀ H ₃₂ N ₆ O ₄ Cl ₆ FeRe	C ₃₀ H ₃₂ N ₆ O ₄ Br ₆ FeRe	C ₃₄ H ₃₈ N ₈ O ₄ Cl ₆ CoRe	C ₃₈ H ₄₄ N ₁₀ O ₄ Cl ₆ CoRe
<i>M_r</i>	995.38	1262.12	1080.55	1162.66
cryst. syst.	triclinic	triclinic	triclinic	monoclinic
space group	<i>P</i> $\bar{1}$	<i>P</i> $\bar{1}$	<i>P</i> $\bar{1}$	<i>P</i> 2 ₁ / <i>c</i>
<i>a</i> /Å	7.9831(3)	8.0539(4)	8.09457(16)	13.5159(6)
<i>b</i> /Å	10.5052(5)	10.6650(6)	10.9775(2)	11.1140(4)
<i>c</i> /Å	10.7890(4)	11.0535(7)	11.5719(3)	15.7455(8)
α /deg	106.255(4)	105.576(5)	80.2539(19)	90
β /deg	103.909(3)	101.890(5)	78.1007(19)	110.854(5)
γ /deg	92.852(3)	93.681(4)	88.8645(16)	90
<i>V</i> /Å ³	836.49(6)	887.72(9)	991.53(4)	2210.29(18)
<i>T</i> /K	120.01(10)	120.01(10)	120.01(10)	149.94(13)
<i>Z</i>	1	1	1	2
ρ_{calcd} /g cm ⁻³	1.976	2.361	1.810	1.747
λ^3 /Å	0.71073	0.71073	0.71073	0.71073
no. of indep rflns	3822	4460	10126	5419
no. of params	232	222	260	278
no. of restraints	0	0	0	18
final <i>R</i> 1, <i>wR</i> 2 ^b (<i>I</i> > 2 σ (<i>I</i>))	0.0335, 0.0560	0.0493, 0.0815	0.0222, 0.0453	0.0704, 0.1250
<i>R</i> 1, <i>wR</i> 2 ^b (all data)	0.0378, 0.0575	0.0666, 0.0875	0.0231, 0.0459	0.0931, 0.1311
goodness of fit	1.045	1.069	1.032	1.292
largest residuals/e Å ⁻³	1.14/-0.77	2.01/-1.89	0.77/-0.73	2.29/-0.88

^a Graphite monochromators. ^b $R1 = \sum |F_o| - |F_c| / \sum |F_o|$, $wR2 = \{\sum [w(F_o^2 - \sum F_c^2)^2] / \sum [w(F_o^2)]\}^{1/2}$.

Table S2. Crystallographic data for **2a**·200 K, **2a**·250 K and **2b**.

Parameters	2a ·200 K	2a ·250 K	2b
formula	C ₃₈ H ₄₄ N ₁₀ O ₄ Cl ₆ CoRe	C ₃₈ H ₄₄ N ₁₀ O ₄ Cl ₆ CoRe	C ₃₀ H ₃₂ N ₆ O ₄ Br ₆ CoRe
<i>M_r</i>	1162.66	1162.66	1265.20
cryst. syst.	monoclinic	monoclinic	triclinic
space group	<i>P</i> 2 ₁ / <i>c</i>	<i>P</i> 2 ₁ / <i>c</i>	<i>P</i> $\bar{1}$
<i>a</i> /Å	13.5101(6)	13.4707(5)	8.1009(3)
<i>b</i> /Å	11.2475(4)	11.3978(3)	10.7229(3)
<i>c</i> /Å	15.7037(7)	15.6234(6)	10.9708(3)
α /deg	90	90	106.156(3)
β /deg	110.536(5)	110.044(4)	101.328(3)
γ /deg	90	90	93.673(3)
<i>V</i> /Å ³	2234.61(17)	2253.47(14)	890.36(5)
<i>T</i> /K	199.94(13)	250.00(10)	120.01(10)
<i>Z</i>	2	2	1
ρ_{calcd} /g cm ⁻³	1.728	1.713	2.360
λ^3 /Å	0.71073	0.71073	1.54184
no. of indep rflns	5470	5538	3700
no. of params	278	278	222
no. of restraints	18	18	0
final <i>R</i> 1, <i>wR</i> 2 ^b (<i>I</i> > 2 σ (<i>I</i>))	0.0712, 0.1217	0.0482, 0.1044	0.0423, 0.1073
<i>R</i> 1, <i>wR</i> 2 ^b (all data)	0.0985, 0.1290	0.0742, 0.1131	0.0445, 0.1101
goodness of fit	1.278	1.115	1.052
largest residuals/e Å ⁻³	2.20/-0.85	0.92/-0.72	1.31/-1.77

^a Graphite monochromators. ^b $R1 = \sum ||F_o| - |F_c|| / \sum |F_o|$, $wR2 = \{\sum[w(F_o^2 - F_c^2)^2] / \sum[w(F_o^2)]\}^{1/2}$.

Table S3. Crystallographic data for **3a**, **3b**, **4a** and **4b**.

Parameters	3a	3b	4a	4b
formula	C ₂₃ H ₂₈ N ₇ O ₂ Cl ₆ NiRe	C ₂₇ H ₃₄ N ₉ O ₂ Br ₆ NiRe	C ₃₀ H ₃₂ CN ₆ O ₄ Cl ₆ CuRe	C ₃₀ H ₃₂ N ₆ O ₄ Br ₆ CuRe
<i>M_r</i>	892.13	1241.00	1003.05	1269.81
cryst. syst.	orthorhombic	monoclinic	triclinic	triclinic
space group	<i>Pbca</i>	<i>P2₁/c</i>	<i>P</i> $\bar{1}$	<i>P</i> $\bar{1}$
<i>a</i> /Å	16.0287(5)	11.3999(4)	8.0389(2)	8.07321(20)
<i>b</i> /Å	18.8615(4)	23.9868(8)	10.6038(3)	10.8110(4)
<i>c</i> /Å	22.0793(5)	14.3655(6)	10.8240(3)	11.0629(4)
α /deg	90	90	107.565(3)	107.144(3)
β /deg	90	91.166(3)	102.333(2)	100.370(2)
γ /deg	90	90	93.278(2)	93.917(2)
<i>V</i> /Å ³	6675.1(3)	3927.4(3)	851.99(5)	899.99(5)
<i>T</i> /K	120.01(10)	120.01(10)	120.01(10)	120.01(10)
<i>Z</i>	8	4	1	1
ρ_{calcd} /g cm ⁻³	1.775	2.099	1.955	2.343
λ^3 /Å	0.71073	0.71073	1.54184	0.71073
no. of indep rflns	6101	9632	3525	5554
no. of params	367	423	243	222
no. of restraints	0	0	0	0
final R1, wR2 ^b (<i>I</i> > 2 σ (<i>I</i>))	0.0504, 0.0720	0.0407, 0.0739	0.0195, 0.0499	0.0537, 0.1277
R1, wR2 ^b (all data)	0.0667, 0.0764	0.0795, 0.0783	0.0197, 0.0500	0.0681, 0.1379
goodness of fit	1.208	0.922	1.040	1.025
largest residuals/e Å ⁻³	0.80/-0.67	2.693/-1.596	0.97/-1.10	3.10/-3.42

^a Graphite monochromators. ^b $R1 = \sum |F_o| - |F_c| / \sum |F_o|$, $wR2 = \{\sum [w(F_o^2 - F_c^2)^2] / \sum [w(F_o^2)]\}^{1/2}$.

Table S4. Selected bond lengths (Å) and angles (°) for **1a**, **1b**, **2a**, **2a**·150 K, **2a**·200 K, **2a**·250 K.

	1a (M = Fe)	1b (M = Fe)	2a (M = Co)	2a ·150 K	2a ·200 K	2a ·250 K
Re(1)–Cl(1)	2.3602(9)	-	2.3590(3)	2.3631(17)	2.3639(18)	2.3642(14)
Re(1)–Cl(2)	2.3748(9)	-	2.3714(3)	2.3585(17)	2.3441(19)	2.3435(13)
Re(1)–Cl(3)	2.3547(8)	-	2.3676(3)	2.3427(19)	2.3586(17)	2.3587(15)
Re(1)–Br(1)	-	2.5132(6)	-	-	-	-
Re(1)–Br(2)	-	2.5029(6)	-	-	-	-
Re(1)–Br(3)	-	2.5249(6)	-	-	-	-
M(1)–O(1)	1.872(2)	1.873(4)	1.9103(10)	2.144(5)	2.121(5)	2.093(4)
M(1)–N(1)	1.984(3)	1.963(5)	1.9251(11)	1.978(6)	1.997(6)	2.031(4)
M(1)–N(2)	1.967(3)	1.991(5)	1.9556(10)	1.963(6)	2.018(6)	2.049(4)
O(1)–N(3)	1.323(3)	1.316(6)	1.3137(16)	1.290(8)	1.295(8)	1.305(5)
N(3)–C(11)	1.478(5)	1.472(7)	1.4786(18)	1.466(9)	1.462(9)	1.467(7)
N(3)–C(13)	1.486(5)	1.499(7)	1.471(2)	1.484(9)	1.470(9)	1.466(7)
C(11)–O(2)	1.385(4)	1.396(7)	1.3973(16)	1.412(9)	1.406(8)	1.405(6)
O(2)–C(12)	1.443(12)	1.456(7)	1.4535(18)	1.431(10)	1.415(10)	1.414(8)
C(12)–C(13)	1.547(14)	1.530(9)	1.528(2)	1.549(12)	1.560(13)	1.529(10)
C(13)–C(14)	1.513(6)	1.504(8)	1.520(2)	1.508(13)	1.522(14)	1.511(11)
C(13)–C(15)	1.508(6)	1.536(8)	1.519(2)	1.521(12)	1.505(14)	1.499(11)
Cl(1)–Re(1)–Cl(2)	89.74(3)	-	89.513(13)	90.15(6)	89.91(10)	90.18(6)
Cl(1)–Re(1)–Cl(3)	90.18(3)	-	90.909(13)	89.87(8)	89.78(6)	89.78(5)
Cl(2)–Re(1)–Cl(3)	89.73(3)	-	89.184(12)	90.34(9)	89.64(10)	89.40(7)
Br(1)–Re(1)–Br(2)	-	90.38(2)	-	-	-	-
Br(1)–Re(1)–Br(3)	-	90.19(2)	-	-	-	-
Br(2)–Re(1)–Br(3)	-	89.79(2)	-	-	-	-
M(1)–O(1)–N(3)	118.31(19)	117.9(3)	113.99(9)	113.5(4)	114.5(4)	115.1(3)
M(1)–O(1)–N(3)–C(11)	13.8(3)	-14.9(5)	-29.26(11)	5.0(5)	-3.7(5)	-2.4(6)
M(1)–O(1)–N(3)–C(13)	155.3(2)	-157.3(4)	-168.87(10)	168.6(5)	-169.5(5)	-170.8(4)

Table S5. Selected bond lengths (Å) and angles (°) for **2b**.

2b	
Re(1)–Br(1)	2.5107(5)
Re(1)–Br(2)	2.5226(5)
Re(1)–Br(3)	2.5049(5)
Co(1)–O(1)	2.092(4)
Co(1)–N(1)	1.963(4)
Co(1)–N(2)	1.975(4)
O(1)–N(3)	1.269(6)
N(3)–C(11)	1.485(7)
N(3)–C(13)	1.493(7)
C(11)–O(2)	1.399(6)
O(2)–C(12)	1.412(8)
C(12)–C(13)	1.539(9)
C(13)–C(14)	1.525(8)
C(13)–C(15)	1.518(9)
Br(1)–Re(1)–Br(2)	90.148(17)
Br(1)–Re(1)–Br(3)	90.211(17)
Br(2)–Re(1)–Br(3)	89.856(18)
M(1)–O(1)–N(3)	113.9(3)
M(1)–O(1)–N(3)–C(11)	-5.9(4)
M(1)–O(1)–N(3)–C(13)	-157.1(4)

Table S6. Selected bond lengths (Å) and angles (°) for **3a** and **3b**.

3a		3b	
Re1–Cl(1)	2.3585(15)	Re1–Br(1)	2.5087(5)
Re1–Cl(2)	2.3616(13)	Re1–Br(2)	2.5124(6)
Re1–Cl(3)	2.3546(15)	Re1–Br(3)	2.5072(5)
Re1–Cl(4)	2.3630(13)	Re1–Br(4)	2.5147(7)
Re1–Cl(5)	2.3606(16)	Re1–Br(5)	2.5008(6)
Re1–Cl(6)	2.3603(15)	Re1–Br(6)	2.5208(6)
Ni(1)–O(1)	2.073(4)	Ni(1)–O(1)	2.090(4)
Ni(1)–N(1)	2.068(4)	Ni(1)–N(1)	2.083(4)
Ni(1)–N(2)	2.059(4)	Ni(1)–N(2)	2.076(4)
Ni(1)–N(4)	2.071(5)	Ni(1)–N(4)	2.051(4)
Ni(1)–N(5)	2.058(5)	Ni(1)–N(5)	2.079(4)
Ni(1)–N(6)	2.037(5)	Ni(1)–N(6)	2.047(5)
O(1)–N(3)	1.271(6)	O(1)–N(3)	1.274(6)
N(3)–C(11)	1.496(7)	N(3)–C(11)	1.497(7)
N(3)–C(13)	1.481(7)	N(3)–C(13)	1.467(7)
C(11)–O(2)	1.403(6)	C(11)–O(2)	1.386(7)
O(2)–C(12)	1.452(7)	O(2)–C(12)	1.460(7)
C(12)–C(13)	1.527(8)	C(12)–C(13)	1.512(8)
C(13)–C(14)	1.523(8)	C(13)–C(14)	1.530(7)
C(13)–C(15)	1.509(8)	C(13)–C(15)	1.529(7)
Ni(1)–O(1)–N(3)	115.3(3)	Ni(1)–O(1)–N(3)	115.1(3)
Ni(1)–O(1)–N(3)–C(11)	-4.186	Ni(1)–O(1)–N(3)–C(11)	3.491
Ni(1)–O(1)–N(3)–C(13)	-172.213	Ni(1)–O(1)–N(3)–C(13)	-173.417

Table S7. Selected bond lengths (Å) and angles (°) for **4a** and **4b**.

	4a	4b
Re(1)–Cl(1)	2.3578(5)	-
Re(1)–Cl(2)	2.3727(5)	-
Re(1)–Cl(3)	2.3583(5)	-
Re(1)–Br(1)	-	2.5103(6)
Re(1)–Br(2)	-	2.5082(6)
Re(1)–Br(3)	-	2.5224(6)
Cu(1)–O(1)	2.3021(16)	2.321(5)
Cu(1)–N(1)	2.0135(18)	2.017(5)
Cu(1)–N(2)	2.0116(18)	2.014(5)
O(1)–N(3)	1.270(3)	1.266(7)
N(3)–C(11)	1.491(3)	1.487(8)
N(3)–C(13)	1.485(3)	1.487(8)
C(11)–O(2)	1.392(3)	1.400(8)
O(2)–C(12)	1.463(6)	1.414(9)
C(12)–C(13)	1.492(6)	1.536(11)
C(13)–C(14)	1.433(8)	1.524(11)
C(13)–C(15)	1.506(3)	1.513(10)
Cl(1)–Re(1)–Cl(2)	90.96(2)	-
Cl(1)–Re(1)–Cl(3)	90.135(18)	-
Cl(2)–Re(1)–Cl(3)	89.799(19)	-
Br(1)–Re(1)–Br(2)	-	90.08(2)
Br(1)–Re(1)–Br(3)	-	90.52(2)
Br(2)–Re(1)–Br(3)	-	89.85(2)
Cu(1)–O(1)–N(3)	110.96(13)	110.6(4)
Cu(1)–O(1)–N(3)–C(11)	0.67(16)	-2.0(5)
Cu(1)–O(1)–N(3)–C(13)	-155.94(14)	-160.5(4)

Table S8. Intermolecular distances (Å) and angles (°) found in all complexes. CH $\cdots\pi$ angles (θ) are taken from angle between the plane of the ring and the C-H bond while CH $\cdots\pi$ distances (d) are from the carbon of the CH moiety to the centroid of the ring.

Complex	CH $\cdots\pi$		Cl $\cdots\pi$	Br $\cdots\pi$	Br \cdots O	Cl \cdots Cl	Br \cdots Br
	θ (°)	d (Å)	d (Å)	d (Å)	d (Å)	d (Å)	d (Å)
1a	111.6	3.495	3.688	-	-	4.708	-
	133.1	3.759	-	-	-	-	-
1b	131.1	3.681	-	3.783	-	-	4.569
	115.6	3.619	-	-	-	-	-
2a	127.5	3.912	-	-	-	3.831	-
	120.9	3.388	-	-	-	-	-
2a-150K	-	-	-	-	-	6.455	-
2a-200K	-	-	-	-	-	6.572	-
2a-250K	-	-	-	-	-	6.715	-
2b	114.0	3.613	-	3.791	-	-	4.615
	134.9	3.703	-	-	-	-	-
3a	123.0	3.786	-	-	-	4.548	-
	114.2	3.575	-	-	-	-	-
3b	129.2	3.812	-	-	-	-	3.907
	124.5	3.485	-	-	-	-	-
4a	134.5	3.839	3.645	-	-	4.770	-
	108.1	3.504	-	-	-	-	-
4b	128.1	3.702	-	3.714	-	-	4.578
	112.8	3.608	-	-	-	-	-

Electronic Supporting Information (ESI)

Table S9. Selected bond lengths (Å) for **2a**, **2a**·150 K, **2a**·200 K, **2a**·250 K, **2b**, [Co^{II}(L[•])₂](NO₃)₂ (**A**),¹ [Co^{III}(L⁻)₂](BPh₄) (**B**),¹ [Co^{II}(L[•])₂](B(C₆F₅)₄)₂·CH₂Cl₂ (**C**)² and [Co^{II}(L[•])₂](B(C₆F₅)₄)₂·2Et₂O (**D**)² at temperatures shown. Low-spin (LS), high spin (HS), neutral radical (L[•]) and hydroxylamino anionic (L⁻) assigned forms of the cobalt ion and the ligand are shown in the table below. See Fig. S1 for labelling of atoms.

	2a	2a ·150 K	2a ·200 K	2a ·250 K	2b			
Co spin state	LS Co(II)	LS Co(II)	LS/HS	LS/HS	LS Co(II)			
Co(1)-O(1)	1.9103(10)	2.144(5)	2.121(5)	2.093(4)	2.092(4)			
Co(1)-N(1)	1.9556(10)	1.978(6)	1.997(6)	2.031(4)	1.963(4)			
Co(1)-N(2)	1.9251(11)	1.963(6)	2.018(6)	2.049(4)	1.976(4)			
Ligand form	L [•]	L [•]	L [•]	L [•]	L [•]			
O(1)-N(3)	1.3137(16)	1.290(8)	1.295(8)	1.305(5)	1.269(6)			
O(3)-N(6)	-	-	-	-	-			
	A ·123K	A ·273K	A ·353K	B ·123K	C ·123K	C ·273 K	D ·123 K	D ·273 K
Co spin state	LS Co(II)	LS/HS	LS/HS	LS Co(III)	LS Co(II)	HS Co(II)	HS Co(II)	HS Co(II)
Co(1)-O(1)	2.113(3)	2.117(2)	2.107(3)	1.879(2)	2.117(2)	2.078(3)	2.054(2)	2.075(2)
Co(1)-N(1)	1.959(3)	2.040(2)	2.056(3)	1.930(3)	1.977(2)	2.078(4)	2.114(3)	2.098(3)
Co(1)-N(2)	1.986(3)	2.056(2)	2.073(43)	1.928(3)	1.981(2)	2.084(3)	2.116(3)	2.107(3)
Co(1)-O(3)	-	-	-	1.892(2)	2.126(2)	2.086(3)	-	-
Co(1)-N(4)	-	-	-	1.921(3)	1.987(2)	2.093(3)	-	-
Co(1)-N(5)	-	-	-	1.916(3)	1.992(2)	2.090(3)	-	-
Ligand form	L [•]	L [•]	L [•]	Anionic	L [•]	L [•]	L [•]	L [•]
O(1)-N(3)	1.294(3)	1.285(3)	1.285(4)	1.411(3)	1.274(3)	1.275(4)	1.286(4)	1.290(3)
O(3)-N(6)	-	-	-	1.401(3)	1.276(3)	1.278(4)	-	-

Table S10. Summary of selected octahedral nickel salts containing three coordinated acetonitrile solvate molecules. The loss of coordinated acetonitrile is based on the microanalysis of the relevant complex.

Formula	Loss of coordinated acetonitrile	Reference
$[\{\text{Ni}(\text{CH}_3\text{CN})_3\}_2\{\text{Ni}(\mu\text{-}2\text{-pyS})(\mu_3\text{-}2\text{-pyS})\}_6](\text{PF}_6)_4$	No	3
$[\text{Ni}(\text{L}^1)(\text{CH}_3\text{CN})_3](\text{ClO}_4)_2 \cdot 2\text{CH}_3\text{CN}$	No	4
$[\text{Tpm}^{\text{Me,Me}}\text{Ni}(\text{CH}_3\text{CN})_3](\text{BF}_4)_2$	Yes	5
$[\text{Tpm}^{\text{Ph}}\text{Ni}(\text{MeCN})_3](\text{BF}_4)_2 \cdot \text{MeCN}$	No	5
$[\text{Ni}\{(\text{Me-Tp})_2\text{PMA}\}(\text{CH}_3\text{CN})_3](\text{ClO}_4)_2$	No	6
$[\text{Ni}(\text{P}^{\text{tBu}}_2\text{N}^{\text{Ph}}_2)(\text{CH}_3\text{CN})_3](\text{BF}_4)_2$	No	7
$[\text{Ni}(\text{L})(\text{CH}_3\text{CN})_3](\text{ClO}_4)_2 \cdot 0.5\text{H}_2\text{O}$	No	8
$[\text{Ni}(\text{L1})(\text{CH}_3\text{CN})_3](\text{ClO}_4)_2 \cdot 2\text{CH}_3\text{CN}$	No	9
$[\text{Ni}(\text{L2})(\text{CH}_3\text{CN})_3](\text{ClO}_4)_2 \cdot 2\text{CH}_3\text{CN}$	No	9
$[\text{Ni}(\text{L3})(\text{CH}_3\text{CN})_3](\text{BF}_4)_2$	No	10
$[\text{Ni}(\text{L4})(\text{CH}_3\text{CN})_3](\text{BF}_4)_2$	No	10
$[\text{Tp}^{\text{iPr}_2}\text{Ni}(\text{CH}_3\text{CN})_3]\text{OTf}$	Yes	11
$[\text{Tp}^{\text{Ph,Me}}\text{Ni}(\text{CH}_3\text{CN})_3]\text{OTf}$	No	11

Abbreviations: pyS = 2-mercaptopyridinate; L^1 = $\text{N}_2\text{O}_2\text{S}_2$ macrocycle; $\text{Tpm}^{\text{Me,Me}}$ = tris(3,5-dimethylpyrazol-1-yl)methane; Tpm^{Ph} = tris(3-phenylpyrazol-1-yl)methane; $(\text{Me-Tp})_2\text{PMA}$ = bis(5-methyl-2-thiophenemethyl)(2-pyridylmethyl)amine; $\text{P}^{\text{tBu}}_2\text{N}^{\text{Ph}}_2$ and $\text{P}^{\text{tBu}}_2\text{N}^{\text{Bz}}_2$ = cyclic diphosphine; L = 1,4,7-tris(cyanomethyl)-1,4,7-triazacyclononane; L1 = bis(1-methylbenzimidazolyl-2-methyl)amine; L2 = bis(1-methylbenzimidazolyl-2-methyl)-10-camphorsulfonamide; L3 = 1,3,5-tribenzyl-1,3,5-triazinane; L4 = 1,3,5-tris(2-fluorobenzyl)-1,3,5-triazinane; Tp^{R_2} = hydrotrispyrazolylborato with R group shown.

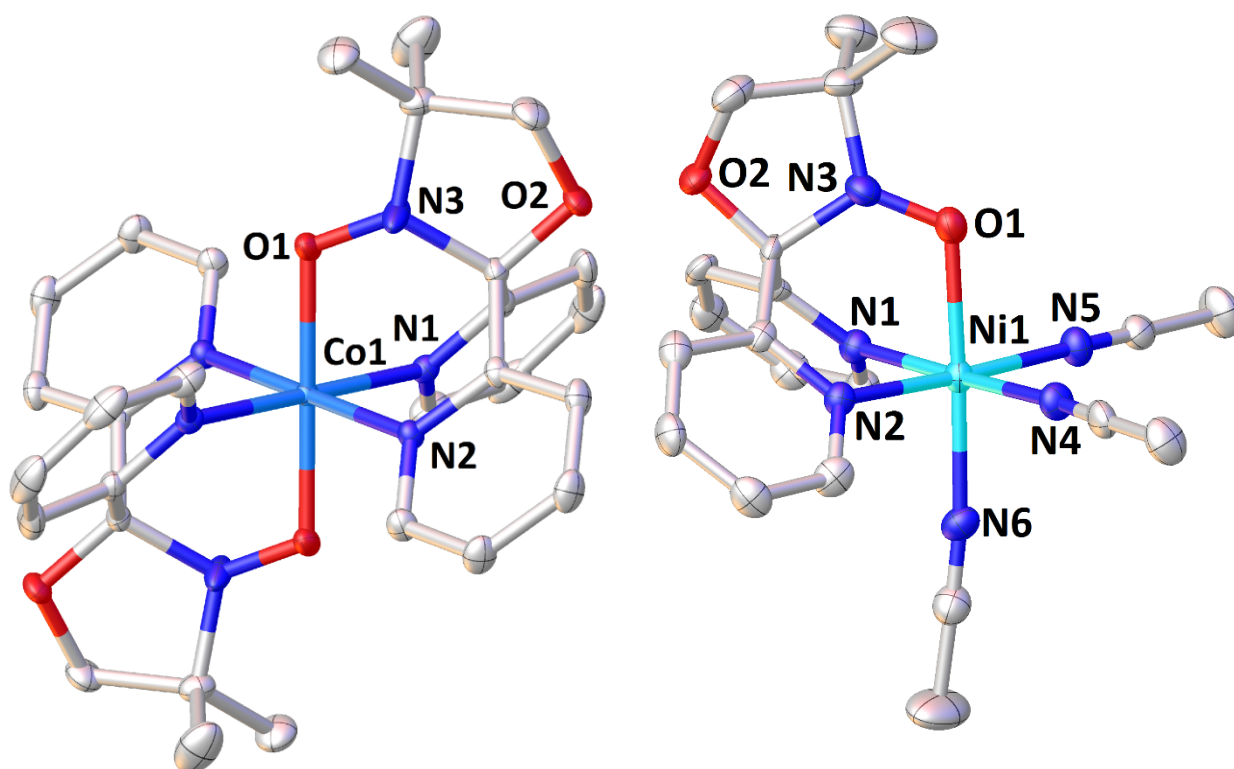


Figure S1. Labelled molecular structure of the $[\text{Co}^{\text{II}}(\text{L}^*)_2]^{2+}$ (left) and $[\text{Ni}^{\text{II}}(\text{L}^*)(\text{MeCN})_3]^{2+}$ cations. The labelling shown for the $[\text{Co}^{\text{II}}(\text{L}^*)_2]^{2+}$ cation (left) is representative of that employed in complexes **1a**, **1b**, **2a**, **2b**, **4a** and **4b**. The labelling shown for the $[\text{Ni}^{\text{II}}(\text{L}^*)(\text{MeCN})_3]^{2+}$ cation (right) is representative of that employed for **3a** and **3b**. Hydrogen atoms removed for clarity. Colour code: Co, light blue; Ni, cyan; N, blue; O, red; C, grey.

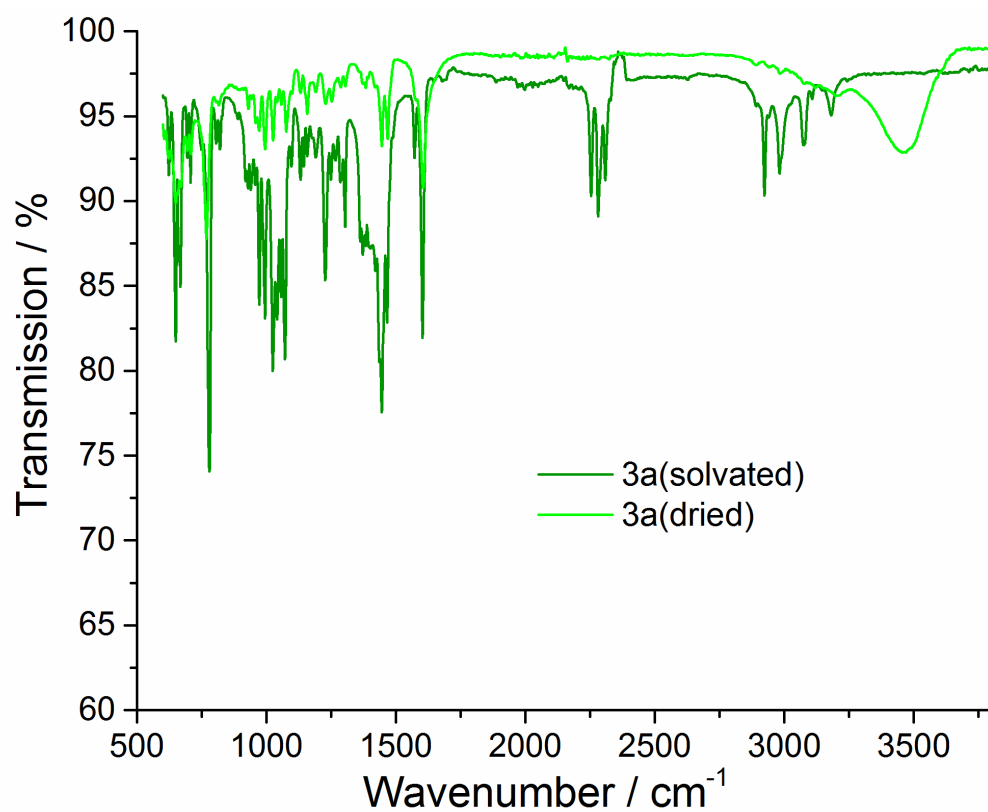


Figure S2. Infrared spectra of **3a(dried)** and **3a(solvated)**. In **3a(solvated)** the bands associated with both coordinated and solvated acetonitrile are clearly present (e.g. 2308, 2281 and 2253 cm⁻¹). For **3a(dried)** the bands associated with acetonitrile disappear and bands associated with water absorption around 3400 cm⁻¹ are observed.

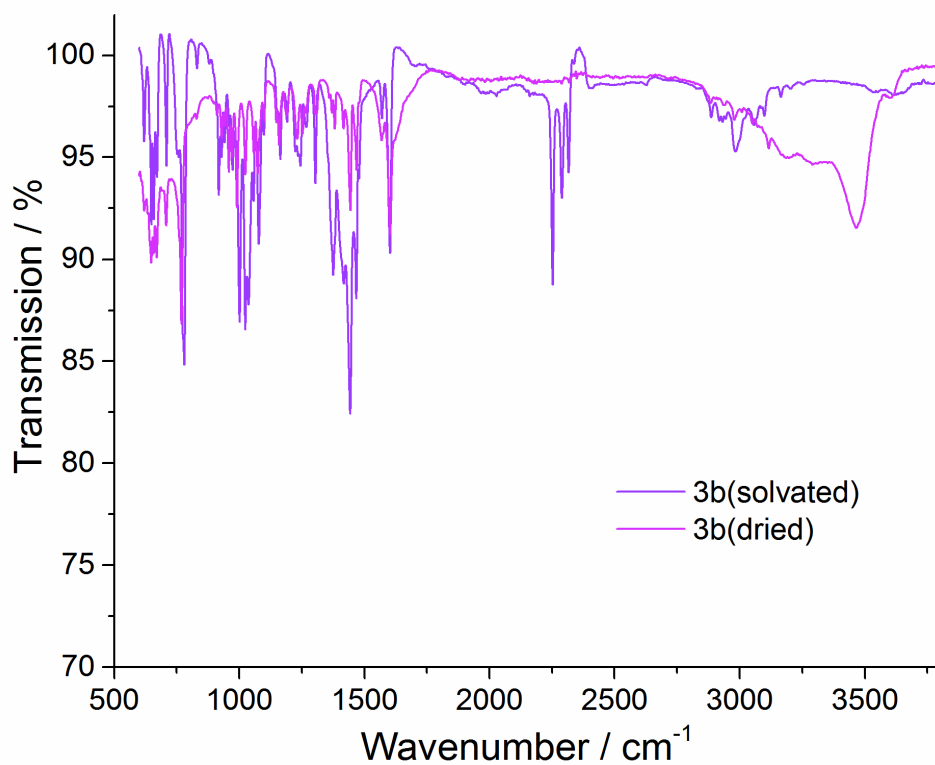


Figure S3. Infrared spectra of **3b(dried)** and **3b(solvated)**. In **3b(solvated)** the bands associated with both coordinated and solvated acetonitrile are clearly present (e.g. 2316, 2289 and 2253 cm⁻¹). For **3b(dried)** the bands associated with acetonitrile disappear and bands associated with water absorption around 3400 cm⁻¹ are observed.

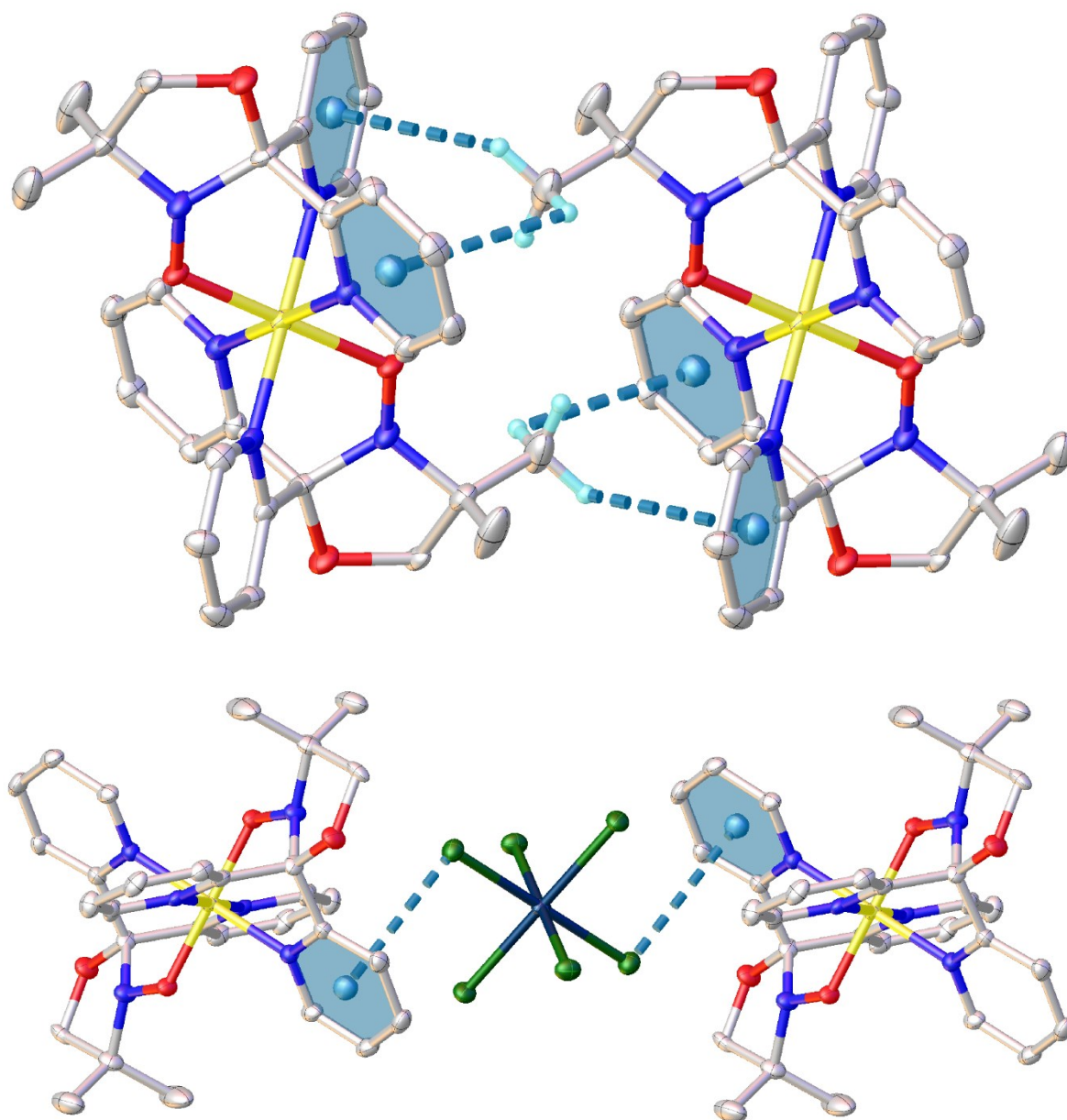


Figure S4. Intermolecular CH $\cdots\pi$ (top) and Cl $\cdots\pi$ (bottom) interactions for complex **1a**. Selected hydrogens and disordered second part of oxazolidine ring hidden for clarity. Colour code: Re, dark blue; Fe, yellow; Cl, dark green; N, blue; O, red; C, grey; H, cyan. Dashed lines represent the relevant intermolecular interaction.

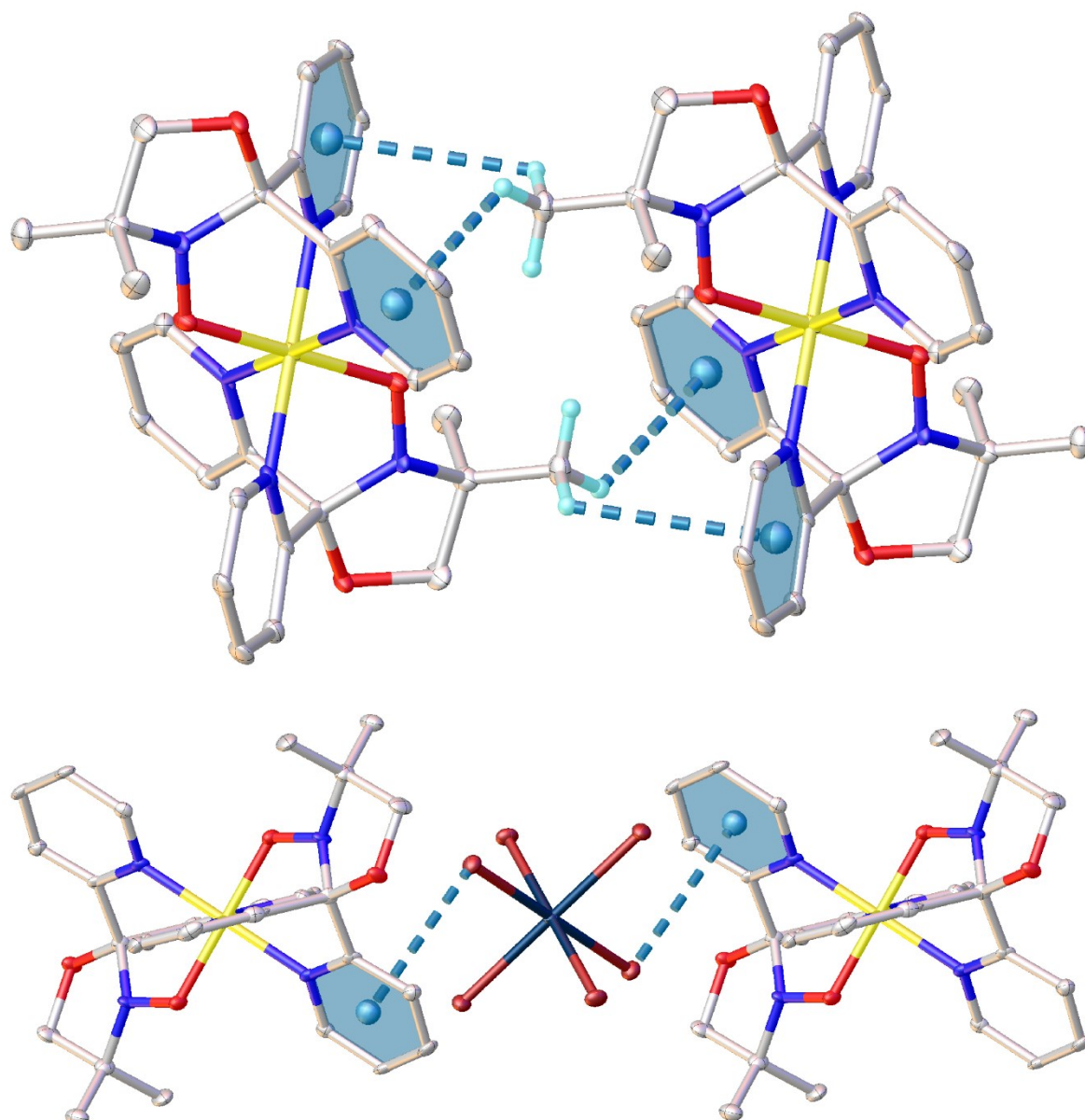


Figure S5. Intermolecular CH $\cdots\pi$ (top) and Br $\cdots\pi$ (bottom) interactions for complex **1b**. Selected hydrogens and disordered second part of oxazolidine ring hidden for clarity. Colour code: Re, dark blue; Fe, yellow; Br, dark red; N, blue; O, red; C, grey; H, cyan. Dashed lines represent the relevant intermolecular interaction.

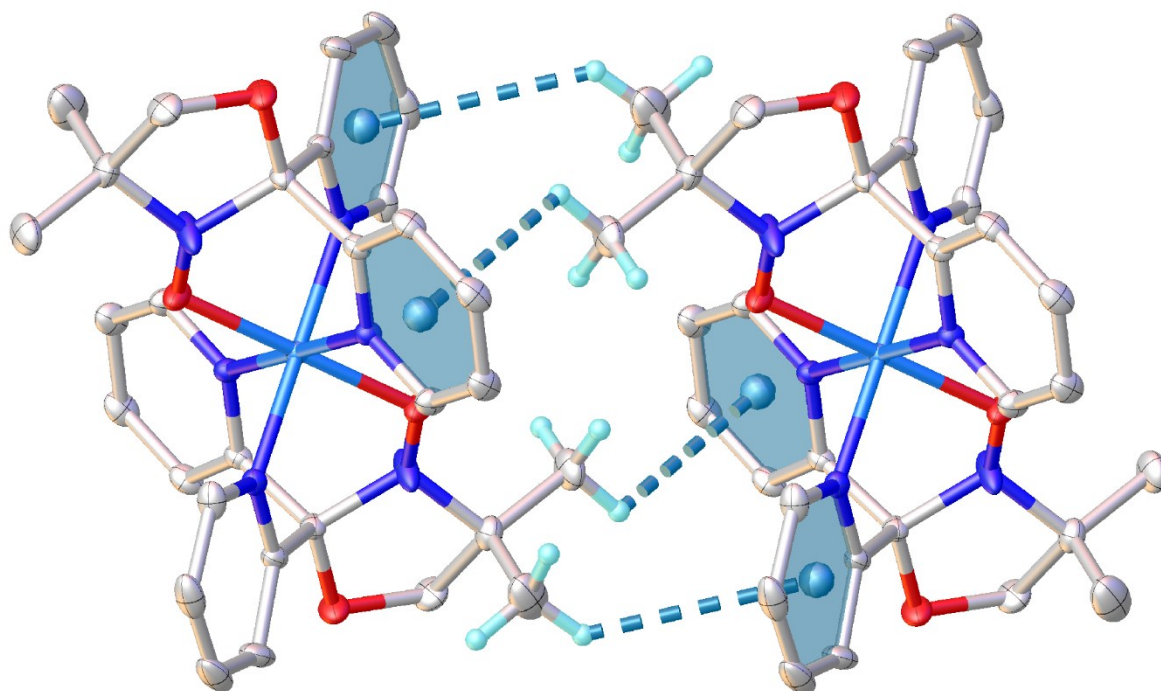


Figure S6. CH $\cdots\pi$ interactions for complex **2a**. Selected hydrogens and acetonitrile solvate molecule removed for clarity. Colour code: Co, light blue; N, blue; O, red; C, grey; H, cyan. Dashed lines represent the relevant intermolecular interaction.

Electronic Supporting Information (ESI)

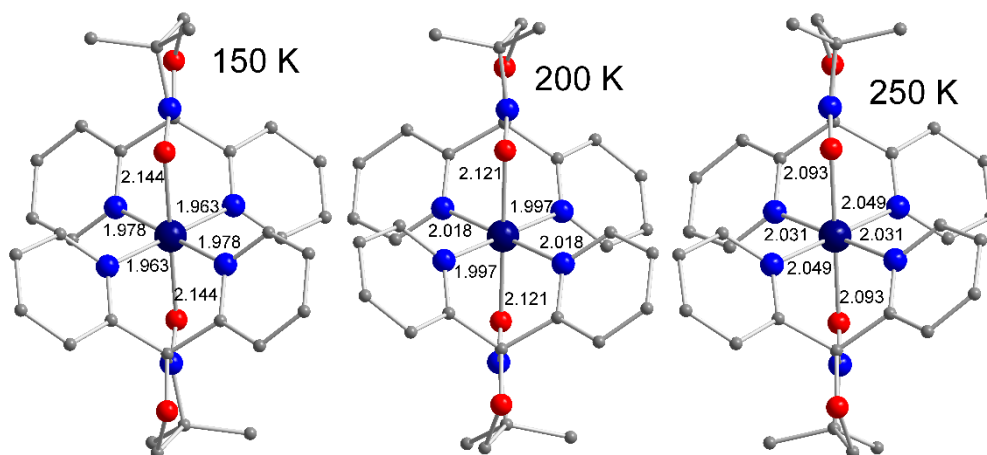


Figure S7. Crystal structure of the [Co^{II}(L*)₂]²⁺ cation at 150 (**2a**·150 K), 200 (**2a**·200 K) and 250 K (**2a**·250 K) with bond lengths (Å) indicated. Hydrogen atoms omitted for clarity. Colour code: Co, dark blue; N, blue; O, red; C, grey. Hydrogen atoms omitted for clarity.

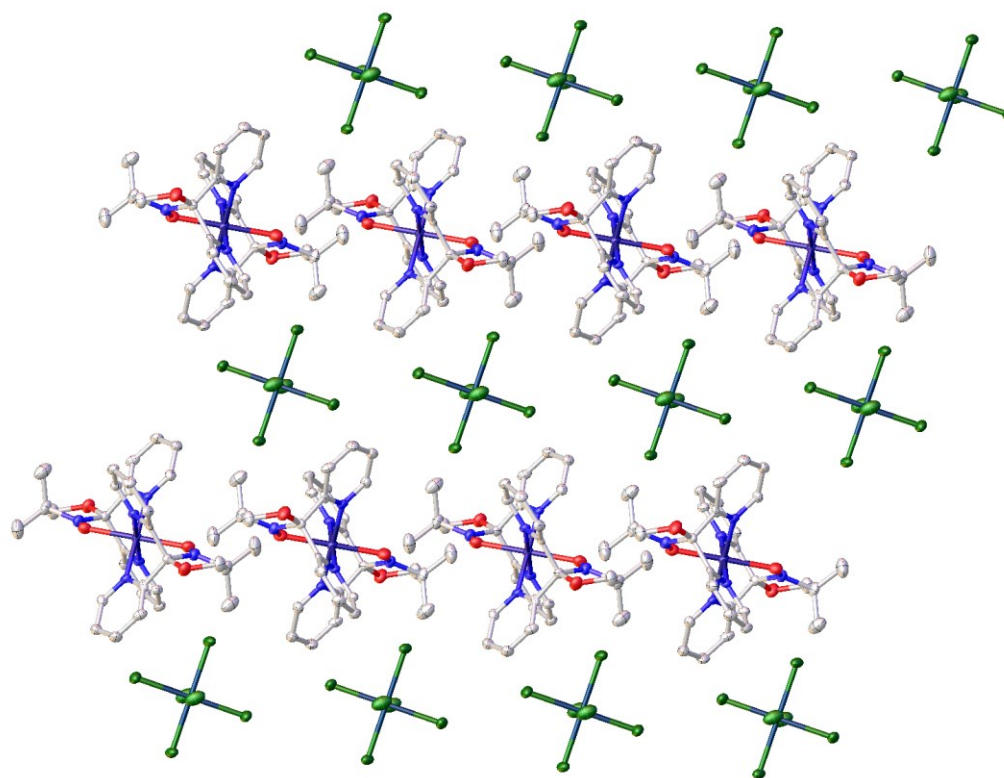


Figure S8. Crystal packing diagram of **2a**·150 K as viewed down the *b*-axis. This packing is representative of the packing present in **2a**·200 K and **2a**·250 K. Hydrogens atom and solvate acetonitrile molecules hidden for clarity. Colour code: Re, dark blue; Co, light blue; Cl, dark green; N, blue; O, red; C, grey.

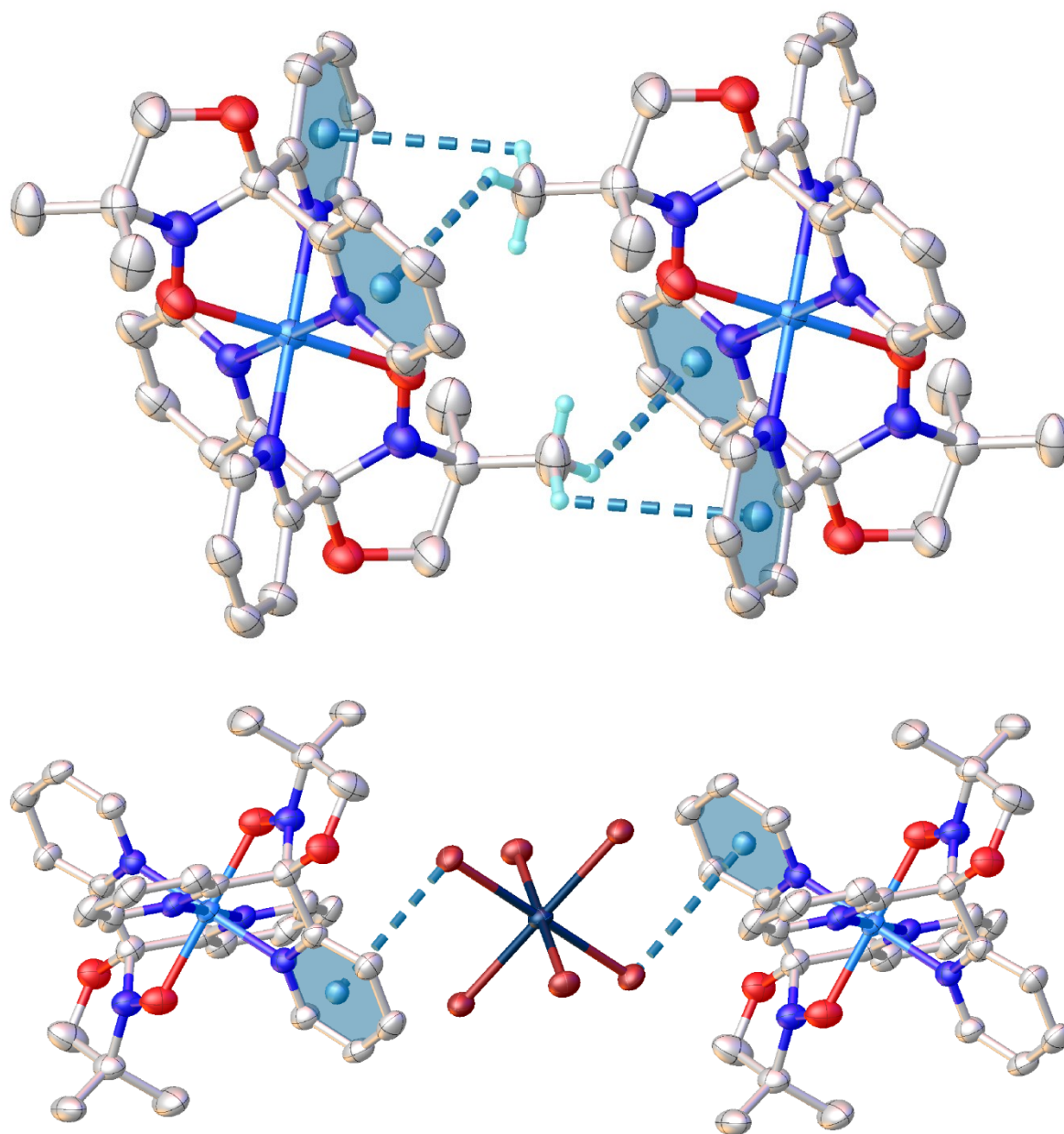


Figure S9. Intermolecular CH... π (top) and Br... π (bottom) interactions for complex **2b**. Selected hydrogens hidden for clarity. Colour code: Re, dark blue; Co, light blue; Br, dark red; N, blue; O, red; C, grey; H, cyan. Dashed lines represent the relevant intermolecular interaction.

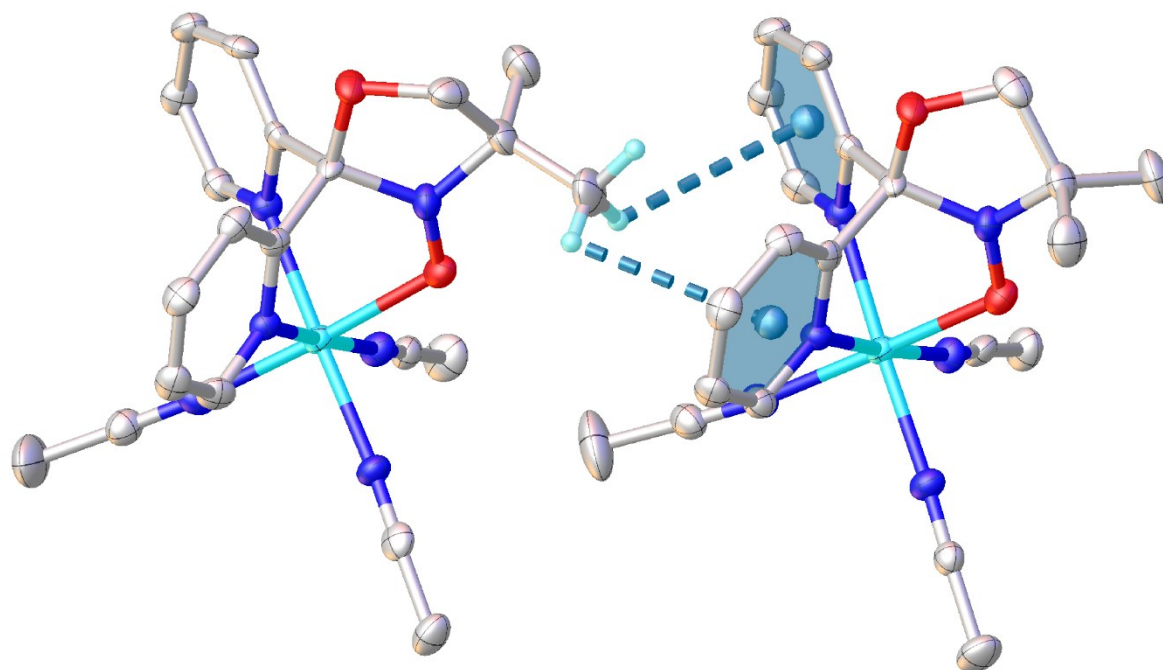


Figure S10. CH... π interactions for complex **3a**. Selected hydrogens and acetonitrile solvate molecule removed for clarity. Colour code: Ni, cyan; N, blue; O, red; C, grey; H, cyan. Dashed lines represent the relevant intermolecular interaction.

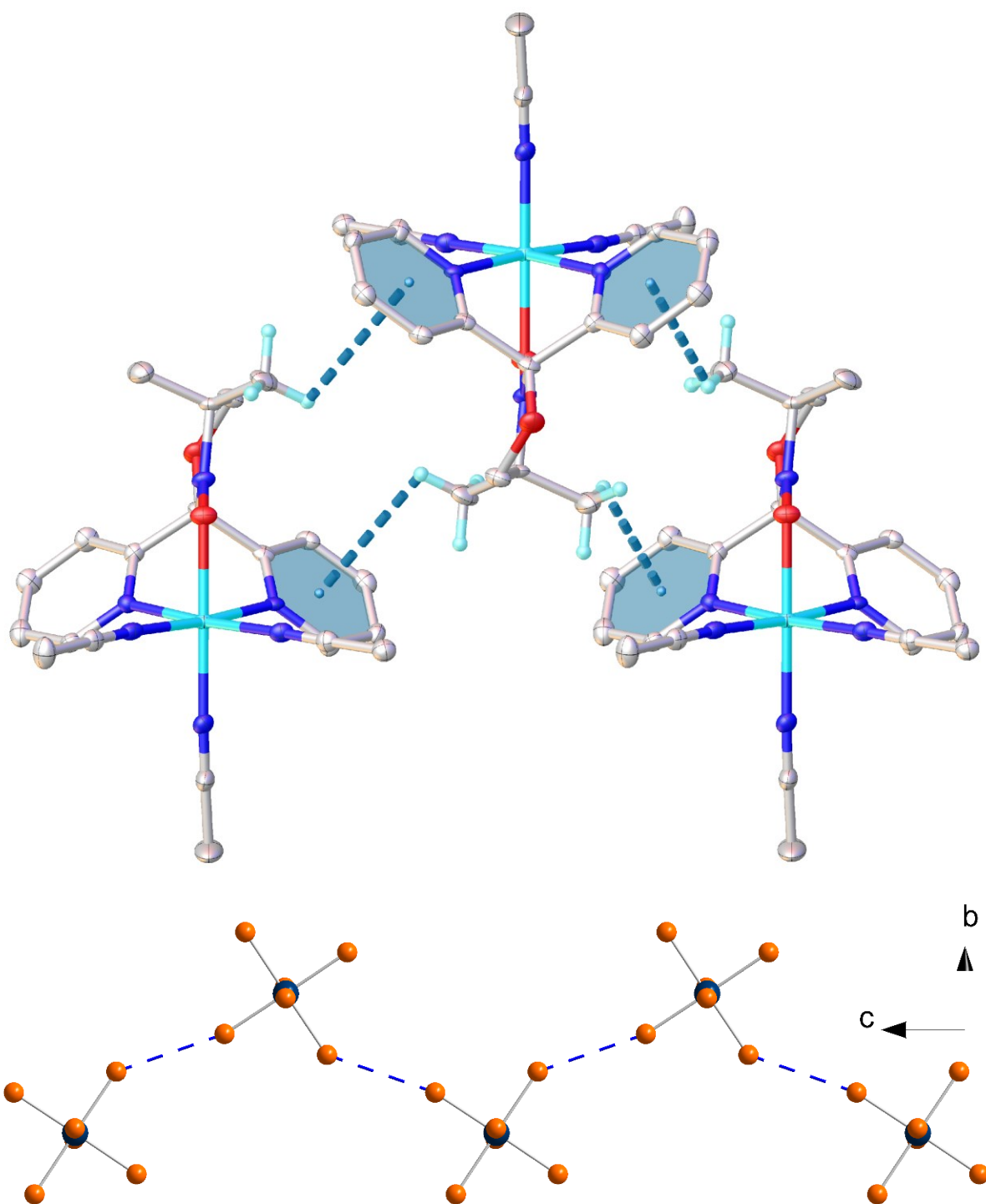


Figure S11. Intermolecular CH... π (top) and Br...Br interactions (bottom) for complex **3b**. Selected hydrogens hidden for clarity. Colour code: Ni, cyan; N, blue; O, red; C, grey; H, cyan. Dashed lines represent the relevant intermolecular interaction.

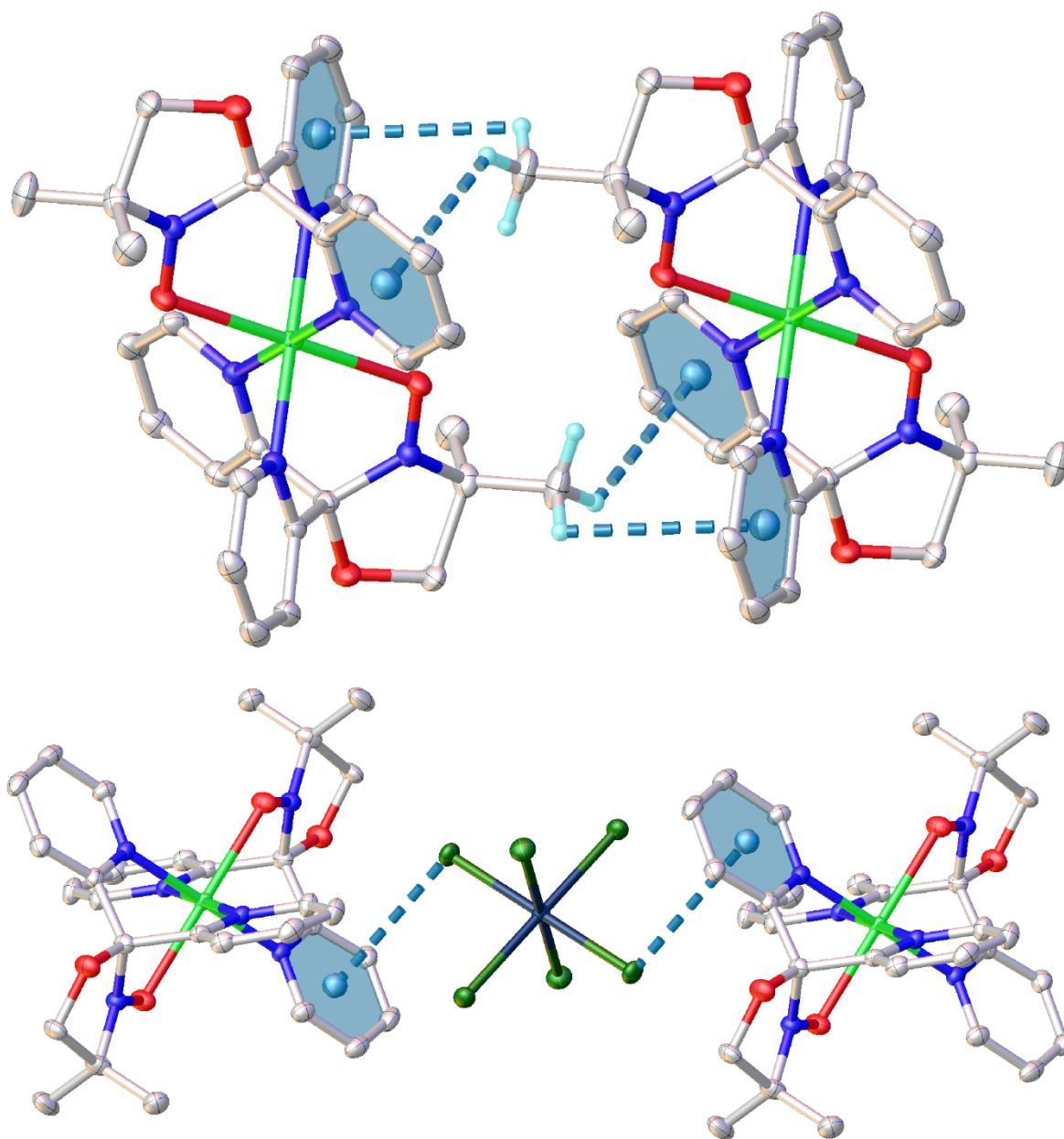


Figure S12. Intermolecular CH $\cdots\pi$ (top) and Cl $\cdots\pi$ (bottom) interactions for complex **4a**. Selected hydrogens and disordered second part of oxazolidine ring hidden for clarity. Colour code: Re, dark blue; Cu, green; Cl, dark green; N, blue; O, red; C, grey; H, cyan. Dashed lines represent the relevant intermolecular interaction.

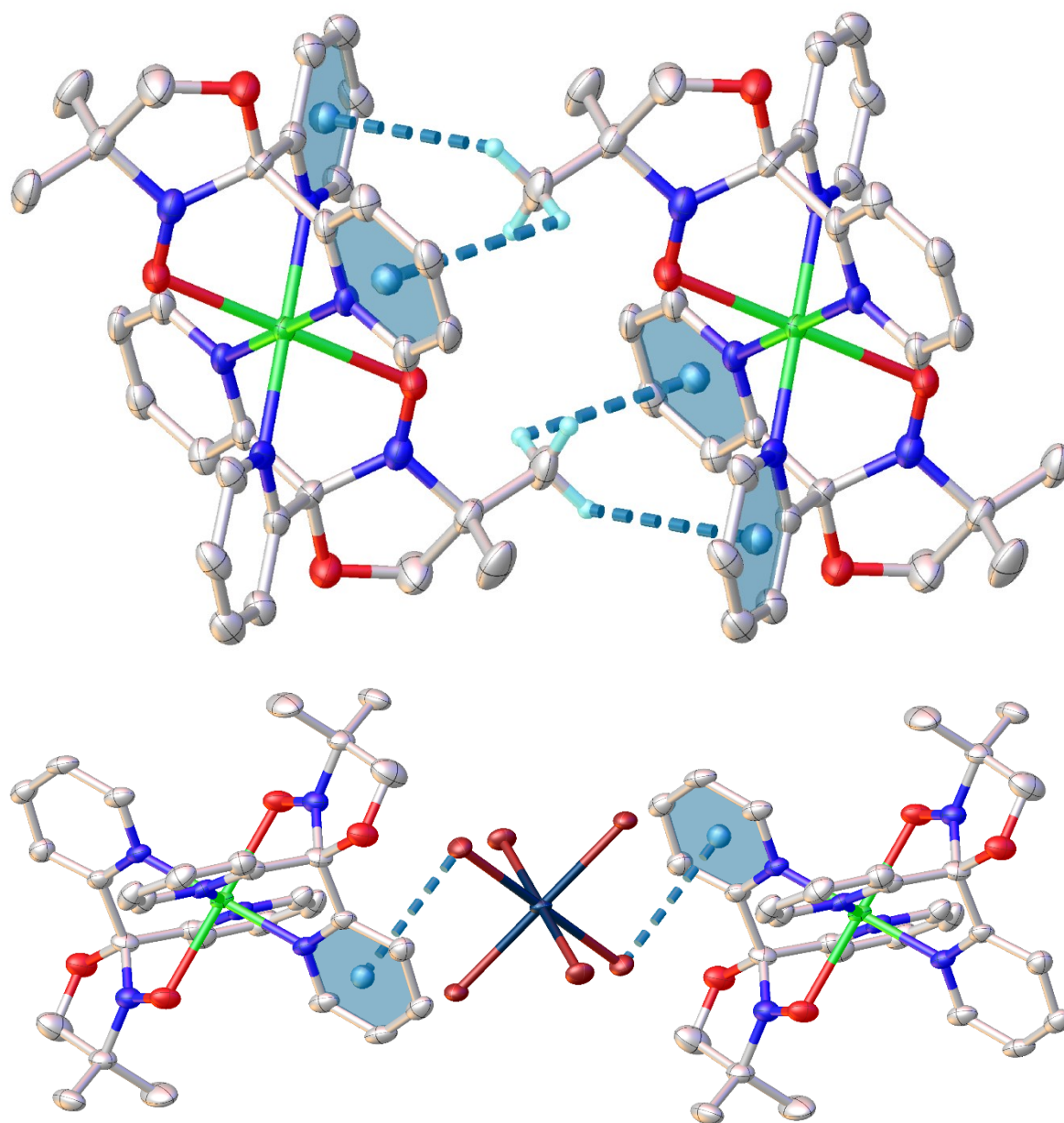


Figure S13. Intermolecular CH $\cdots\pi$ (top) and Br $\cdots\pi$ (bottom) interactions for complex **4b**. Selected hydrogens hidden for clarity. Colour code: Re, dark blue; Cu, green; Br, dark red; N, blue; O, red; C, grey; H, cyan. Dashed lines represent the relevant intermolecular interaction.

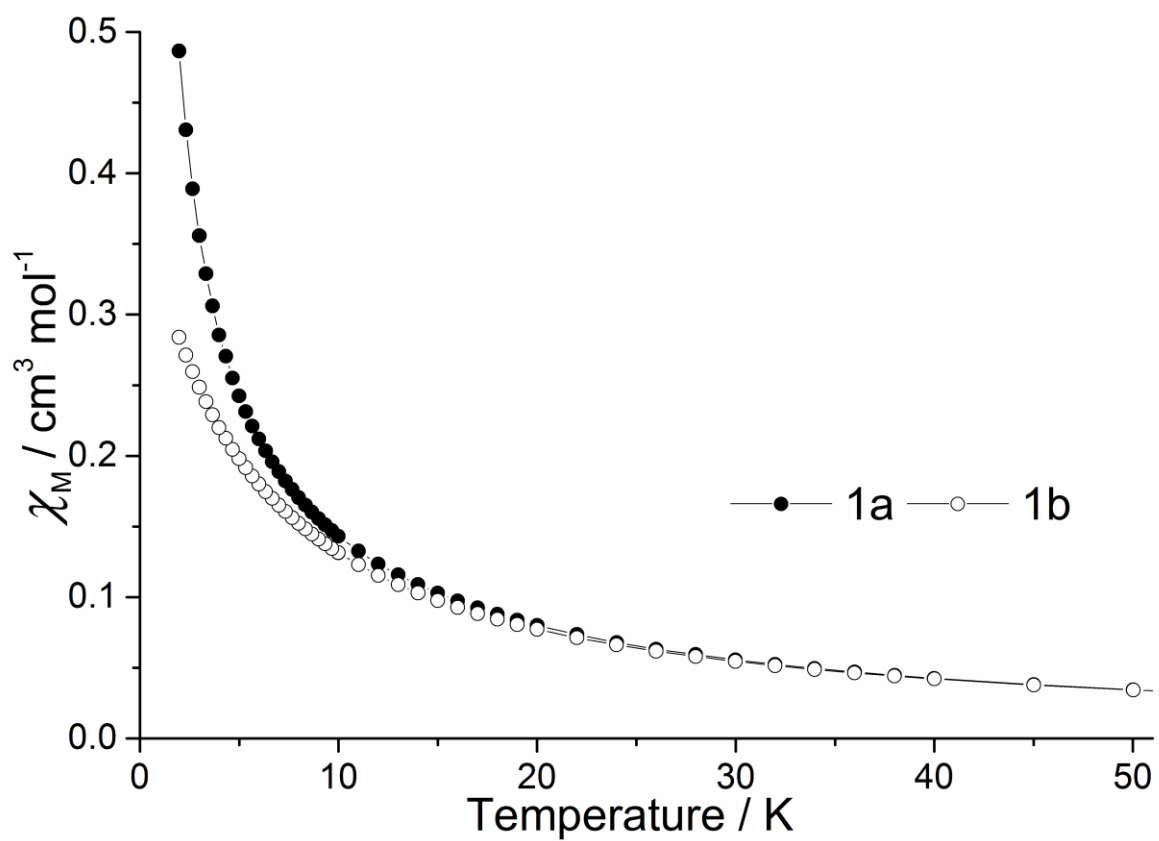


Figure S14. The χ_M vs T plot for complex **1a** and **1b**.

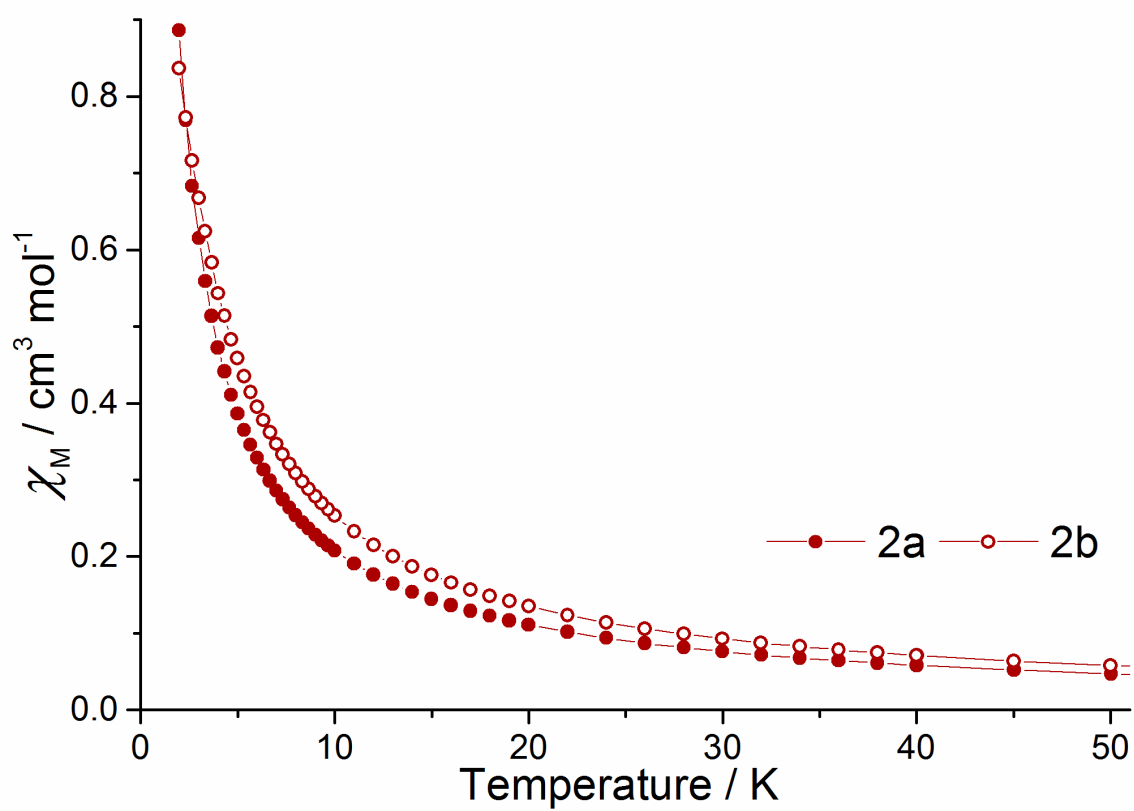


Figure S15. The χ_M vs T plot for complex **2a** and **2b**.

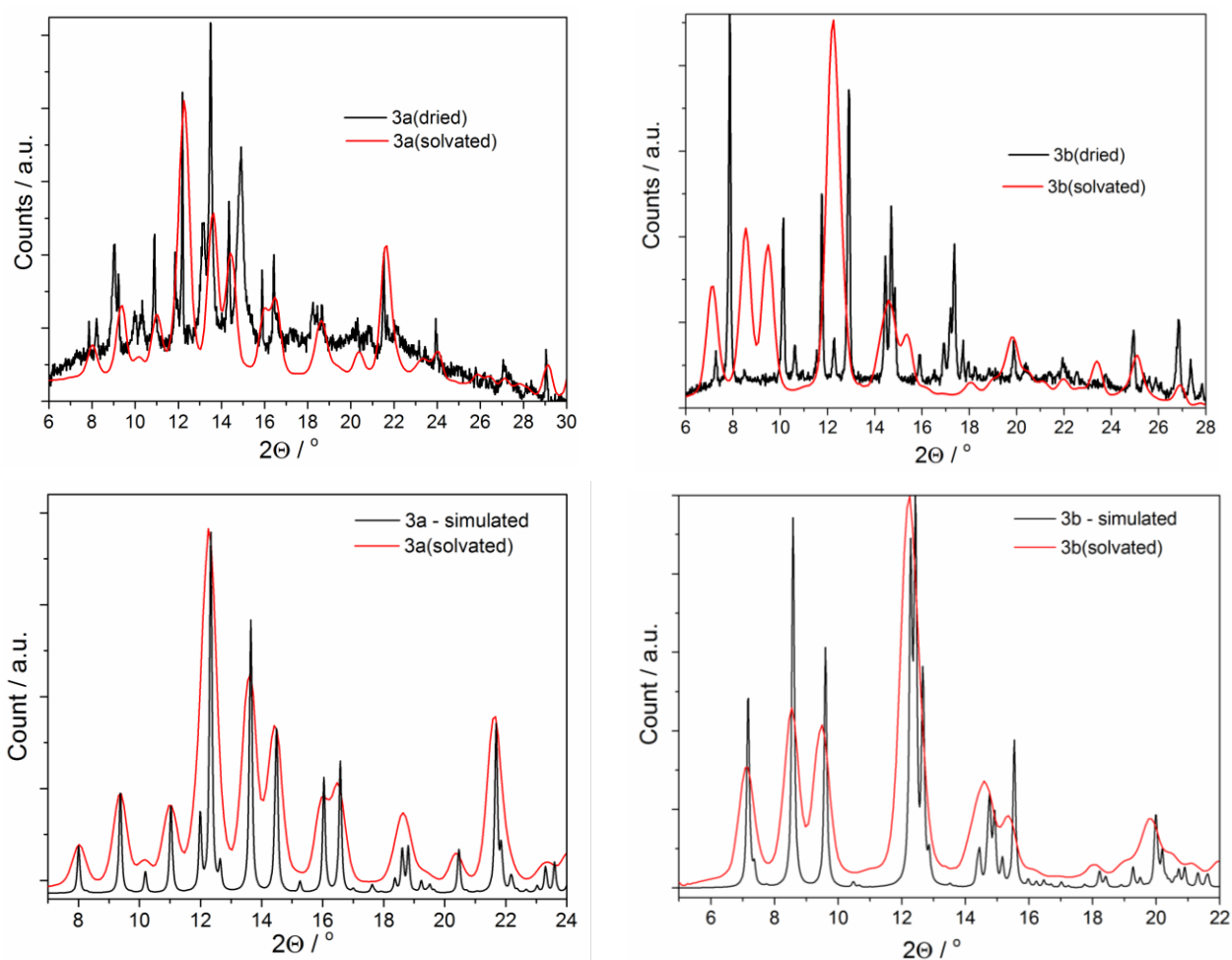


Figure S16. Powder X-ray diffraction (PXRD) experiments on **3a(dried)** (top left), **3b(dried)** (top right), **3a(solvated)** (bottom left) and **3b(solvated)** (bottom right) were performed on a Rigaku Oxford Diffraction SuperNova X-ray diffractometer at 298 K with a scan step size of 0.086° at a rate of 1° sec^{-1} . Calculated patterns from single crystal data were made using Mercury 3.7.

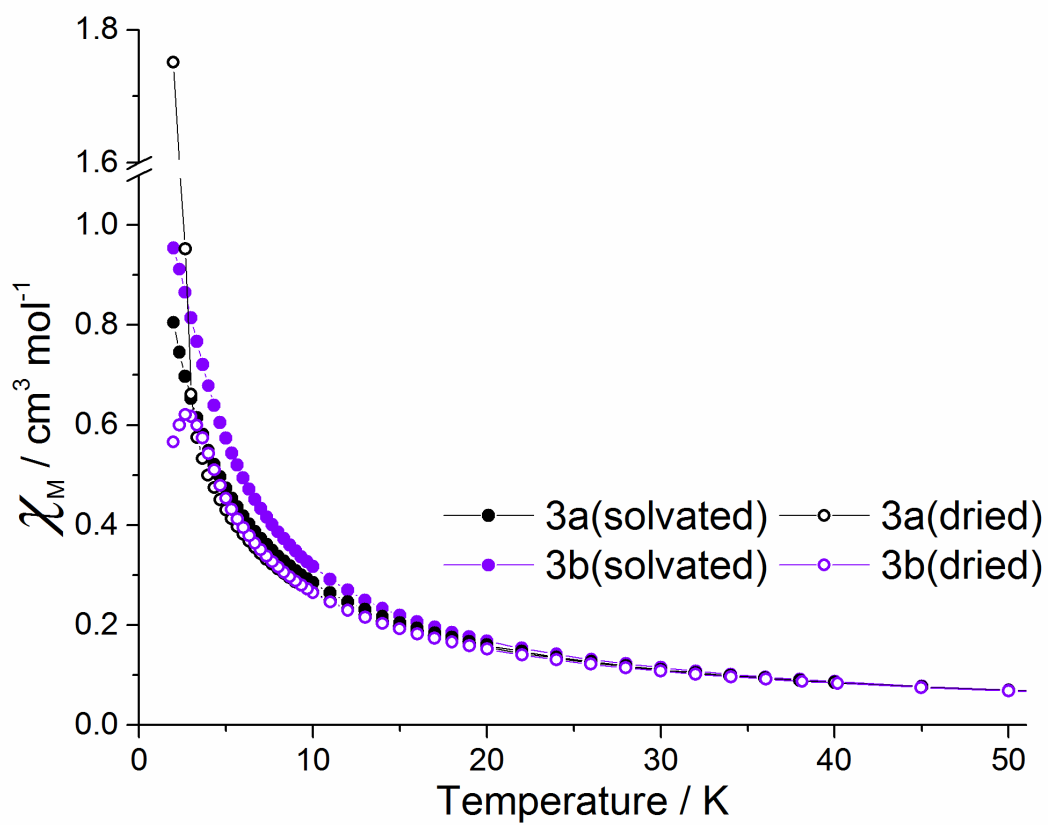


Figure S17. The χ_M vs T plot for complex **3a** and **3b**, dried and solvated.

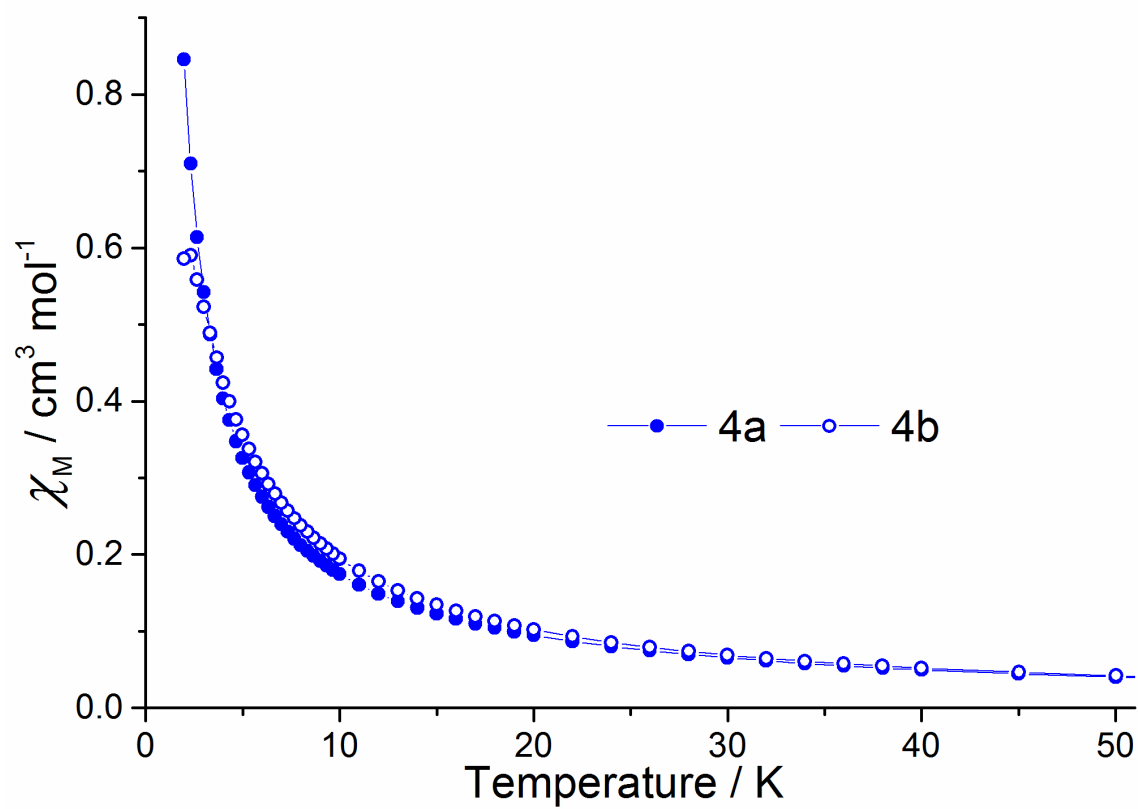


Figure S18. The χ_M vs T plot for complex 4a and 4b.

References

- 1 I. A. Gass, S. Tewary, A. Nafady, N. F. Chilton, C. J. Gartshore, M. Asadi, D. W. Lupton, B. Moubaraki, A. M. Bond, J. F. Boas, S. X. Guo, G. Rajaraman and K. S. Murray, *Inorg. Chem.*, 2013, **52**, 7557–7572.
- 2 I. A. Gass, S. Tewary, G. Rajaraman, M. Asadi, D. W. Lupton, B. Moubaraki, G. Chastanet, J.-F. Letard and K. S. Murray, *Inorg. Chem.*, 2014, **53**, 5055–5066.
- 3 T. Hamaguchi, M. D. Doud, J. Hilgar, J. D. Rinehart and C. P. Kubiak, *Dalt. Trans.*, 2016, **45**.
- 4 S.-G. Lee, K.-M. Park, Y. Habata and S. S. Lee, *Inorg. Chem.*, 2013, **52**, 8416–8426.
- 5 S. Liang, H. Wang, T. Deb, J. L. Petersen, G. T. Yee and M. P. Jensen, *Inorg. Chem.*, 2012, **51**, 12707–12719.
- 6 J. Cho, Y.-M. Lee, S. Y. Kim and W. Nam, *Polyhedron*, 2010, **29**, 446–450.
- 7 E. S. Wiedner, J. Y. Yang, W. G. Dougherty, W. S. Kassel, R. M. Bullock, M. R. Dubois and D. L. Dubois, *Organometallics*, 2010, **29**, 5390–5401.
- 8 Z. Zhang, Z.-R. Geng, X.-W. Kan, Q. Zhao, Y.-Z. Li and Z.-L. Wang, *Inorganica Chim. Acta*, 2010, **363**, 1805–1812.
- 9 W.-Z. Lee, H.-S. Tseng and T.-S. Kuo, *Dalt. Trans.*, 2007, 2563.
- 10 R. D. Köhn, M. Haufe and G. Kociok-Köhn, *J. Am. Chem. Soc.*, 2006, **128**, 10682–10683.
- 11 K. Uehara, S. Hikichi and M. Akita, *J. Chem. Soc. Dalt. Trans.*, 2002, **75**, 3529.