Nuclearity of Nickel and Mixed Sodium-Nickel Complexes: Dependence on the Spacer in Chelating Pyridine-Alcoholate Ligands

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Experimental

General Information: All reactions were carried out using standard Schlenk techniques under an inert atmosphere of nitrogen. THF, Et_2O, and pentane were distilled from sodium–benzophenone. Commercial NaH (60% dispersion in mineral oil), HL (pyridine-2-ylmethanol), HL_{Et} (pyridine-2-ylethanol) and $NiCl_2{\cdot}6H_2O$ were purchased from Aldrich and used as received. $NiCl_2{\cdot}2H_2O$ was prepared by heating $NiCl_2{\cdot}6H_2O$ at 100 °C for 12 h under vacuum. The residual water content was confirmed by measuring the weight loss. $NiCl_2{\cdot}2H_2O$ was used to prepare $[NiCl_2(DME)]$ (DME = 1,2-dimethoxyethane).[S-1] Due to the hygroscopicity of the latter, it was prepared in situ and its molarity was calculated on the basis of that of the starting $NiCl_2{\cdot}2H_2O$ reagent. Elemental analyses were performed by the microanalytical laboratory in house. The FTIR spectra reported below were collected on a Thermo-Nicolet 67000 spectrometer, equipped with a diamond crystal SMART ORBIT accessory. The spectra were compared with those recorded on single crystals, collected with a Thermo-Nicolet Centaurus microspectrometer in a microcompression cell with diamond windows.

Since no hydroxide ion was deliberately added during the synthesis of complexes **1** and **2**, we wondered about the origin of the OH groups present in their structure. A NaOH impurity may be contained in the commercial NaH reagent (a molar content of 5-7% would provide sufficient hydroxyde) or come from residual traces of water in THF that would react with NaH, although THF was distilled over sodium/benzophenone and collected when "deep blue". The water content in THF needed to reach the right stoichiometry, would be ca. 0.01% (v/v). It should be considered, moreover, that [$NiCl_2$(DME)] is a highly hygroscopic complex, itself prepared from the hydrated salt $NiCl_2·2H_2O$. Despite these uncertainties, the syntheses of **1** and **2** have been successfully repeated in two different laboratories starting from different and "fresh" batches of commercial NaH and showed great reproducibility.

Improved synthesis of [$Na_3Ni_4L_9(\mu_3$-OH)]Cl (1)

During the experiments performed in the course of this work, we improved the synthesis of **1**. A previous synthesis implied stirring the reaction mixture for 24 h (see below).[S-2] This rather long reaction time is actually not necessary, the formation of **1** in high yields being observed already after 1 h.

To a slurry of [$NiCl_2$(DME)] (0.66 g, 3.0 mmol, in 150 mL of THF) was added pyridine-2-ylmethanol (0.93 mL, 1.05 g, 9.6 mmol) and NaH (60% suspension in mineral oil, 0.42 g, 10.5 mmol) was rapidly added. Evolution of H_2 gas was observed, during which the reaction vessel was left open and a flow of inert gas (Ar or N_2) was maintained, resulting in a green suspension. After it was stirred for 1 h, the green solution was filtered and layered with a 50/50 mixture of THF/Et_2O (5 mL), then Et_2O (50 mL) and finally pentane (30 mL), affording green crystals of **2** (Yield: 0.69 g, 69%), showing a typical "roofed" prismatic shape.

Similar results were obtained using the same reagents quantities, by reacting pyridine-2-ylmethanol first with NaH in 100 mL. After evolution of gas has ceased, a suspension of [$NiCl_2$(DME)] in THF (50 mL) was added. After it was stirred for 1.5 h, the green solution was filtered and treated as reported above.

Synthesis of [$Na_8(NaL_2)(NiL_3)_6(\mu_4$-OH$)_2$] (2)

To a slurry of NaH (60% suspension in mineral oil, 0.72 g, 18 mmol) in THF (100 mL) was added pyridine-2-ylmethanol (1.45 mL, 1.64 g, 15 mmol). Evolution of H_2 gas was observed, during which the reaction vessel was left open and a flow of inert gas (Ar or N_2) was maintained. After 20 min, a suspension of [$NiCl_2$(DME)] in THF (50 mL) was added (0.66 g, 3.0 mmol), resulting in a green suspension. After it was stirred for 1 h, the green solution was filtered and layered with a

50/50 mixture of THF/Et_2O (5 mL), then Et_2O (50 mL) and finally pentane (30 mL), affording green crystals (blocks) of **3** (Yield: 0.82 g, 59%). Anal. Calcd for $C_{120}H_{122}N_{20}Na_{10}Ni_6O_{22}$ (%): C, 51.87; H, 4.43; N, 10.08. Found, after drying: C, 51.98; H, 4.84; N, 9.61.

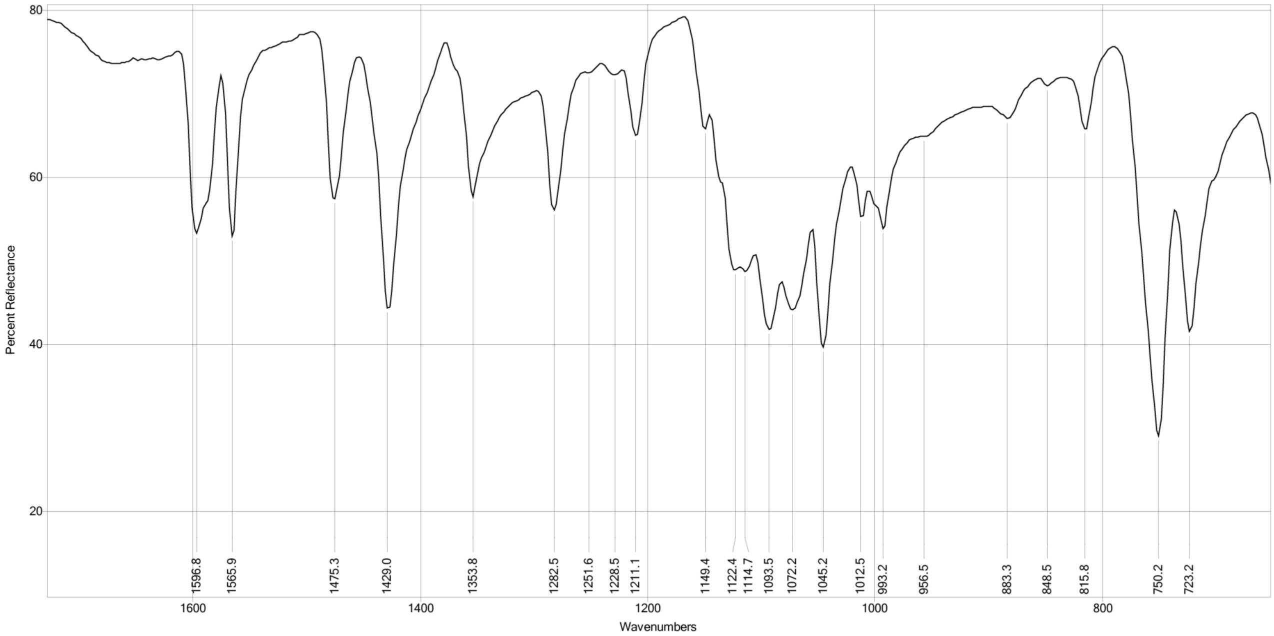

Figure S-1. FTIR spectrum of **2** (650-1700 cm^{-1} region). The diagnostic ν(CO) pattern is in the 970-1180 cm^{-1} region.

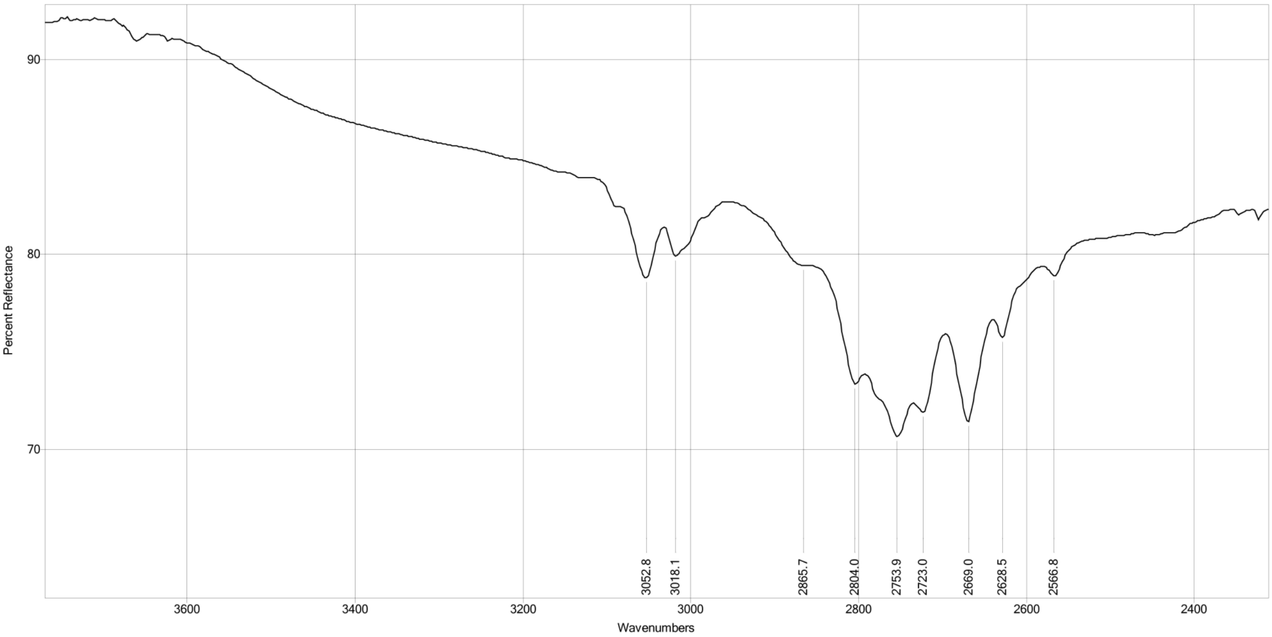

Figure S-2. FTIR spectrum of **2** (2350-3950 cm^{-1} region).

Synthesis of $[Ni_3(\mu\text{-}L_{Et})_2(\mu_3\text{-}L_{Et})_2(L_{Et})(HL_{Et})]Cl$ (**3**·Cl)

To a slurry of $[NiCl_2(DME)]$ in THF (0.66 g, 3.0 mmol, in 120 mL of THF), was added pyridine-2-ylethanol (1.01 mL, 1.10 g, 9 mmol). NaH (60% suspension in mineral oil, 0.60 g, 15 mmol) was rapidly added, resulting in a green suspension. Evolution of H_2 gas was observed, during which the reaction vessel was left open and a flow of inert gas (Ar or N_2) was maintained. After the mixture was further stirred for 12 h, the green solution was filtered and dried under vacuum. The resulting green solid was redissolved in CH_2Cl_2 (40 mL), resulting, after filtration, in a brilliant green solution, which was layered with pentane (50 mL). This afforded green crystals (plates) of **3**·Cl (Yield: 0.91 g, 76%). Anal. Calcd for $C_{42}H_{49}ClN_6Ni_3O_6\cdot 2CH_2Cl_2$ (%): C, 47.38; H, 4.79; N, 7.54. Found: C, 47.63; H, 4.97; N, 7.25 (see below for the residual solvent content).

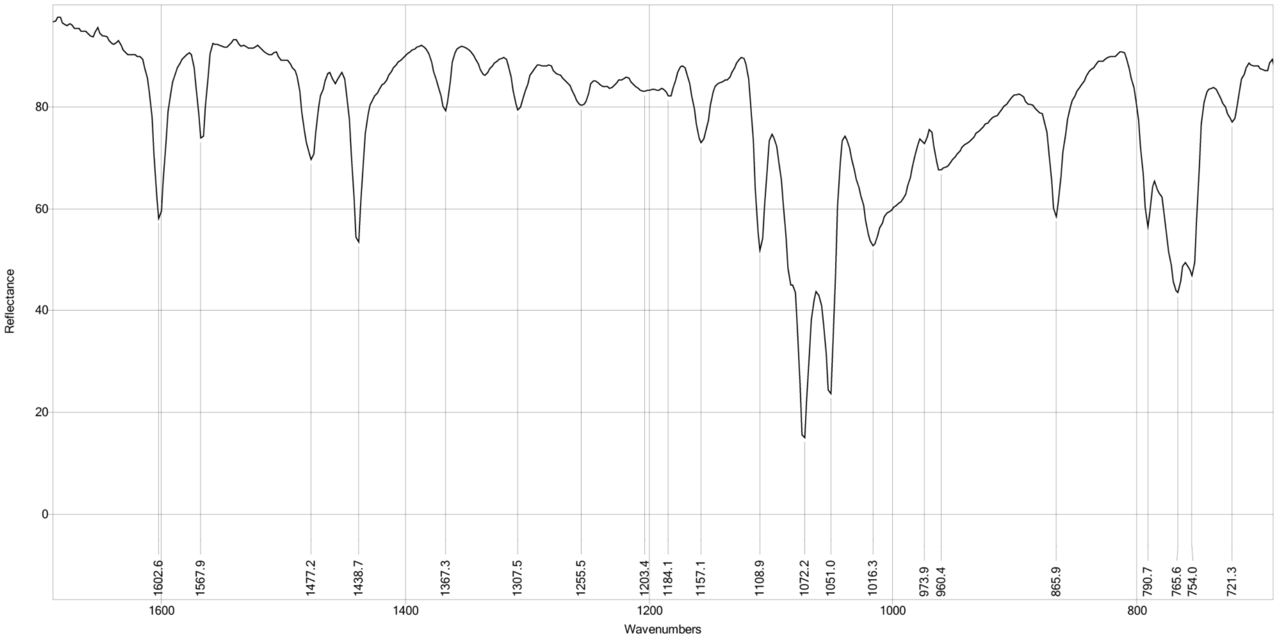

Figure S-3. FTIR spectrum of **3**·Cl (700-1650 cm^{-1} region). The diagnostic ν(CO) pattern is in the 900-1120 cm^{-1} region.

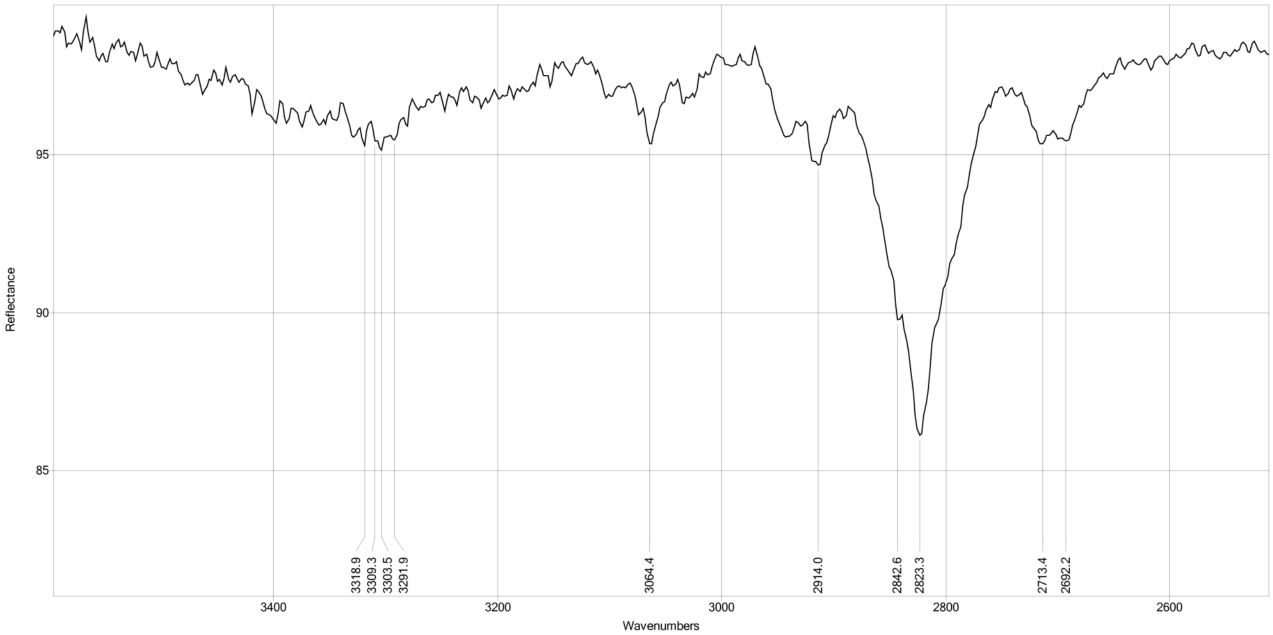

Figure S-4. FTIR spectrum of **3**·Cl (2550-3600 cm^{-1} region).

Crystallographic data

X-ray data collection, structure solution and refinement for $[Na_8(NaL)_2(NiL_3)_6(\mu_4\text{-}OH)_2]$ (2)

Suitable crystals for the X-ray analysis of **2** were obtained as described below. The intensity data were collected at 173(2) K on a Kappa CCD diffractometer[S-3] (graphite monochromated MoKα radiation, λ = 0.71073 Å). Crystallographic and experimental details for the structure are summarized in Table S1. The structure, defined by two independent halves of centrosymmetric molecules, was solved by direct methods (SHELXS-97) and refined by full-matrix least-squares procedures (based on F^2, SHELXL-97)[S-4] with anisotropic thermal parameters for all the non-hydrogen atoms. The hydrogen atoms were introduced into the geometrically calculated positions (SHELXS-97 procedures) and refined *riding* on the corresponding parent atoms, except those bound to the μ_5 oxygen. These were found in the F_o-F_c map and refined isotropically. A slice of this map is reported in Figure S-5. The O-H bond was constrained to 0.95 Å, in order to overcome the typical underestimation of O-H bonds lengths by X-ray diffraction. In the crystals of **2**, very large voids containing severely disordered solvent molecules were present. None of the atomic positions corresponded to more than a 2.5 e/Å^3 electron density. This disorder affected considerably the model quality and therefore we have chosen to apply a PLATON-SQUEEZE procedure [5] using the complete molecular model of compound **2**. The calculation estimated a residual electron density of 1868 e/unit cell, total void volume in the unit cell: 3375 Å.^{3} The modified reflection data were then used for the refinement of the molecular structure of **2**, resulting in improved refinement parameters. CCDC 776753 and 776754 contains the supplementary crystallographic data for this paper that can be obtained free of charge from the Cambridge Crystallographic Data Center via www.ccdc.cam.ac.uk/data_request/cif.

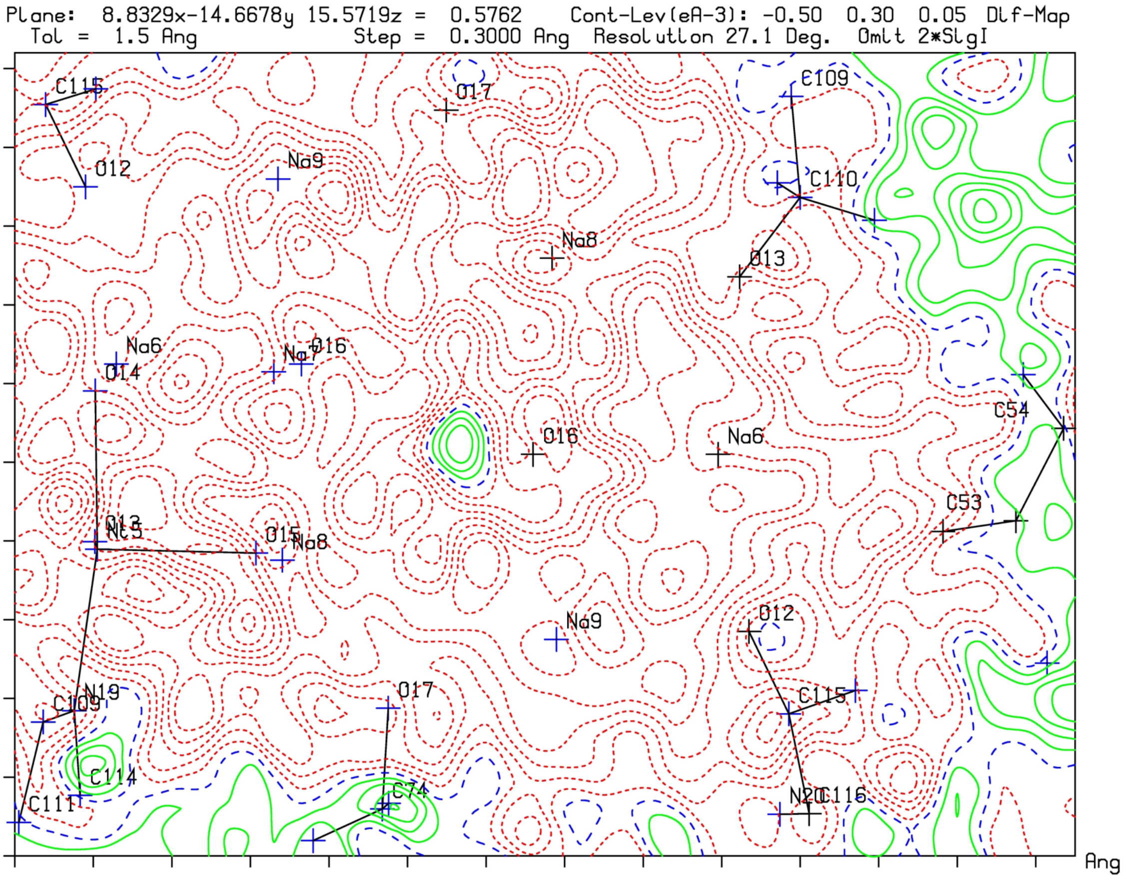

Figure S-5. Slice of the X-ray *F*o-*F*c map for one of the two independent molecules of **2** (plane O6-Na9-Na6, see Figure S-6) showing the missing electron density at *ca.* 1 Å from O16 [reflections with $I<2\sigma(I)$ omitted].

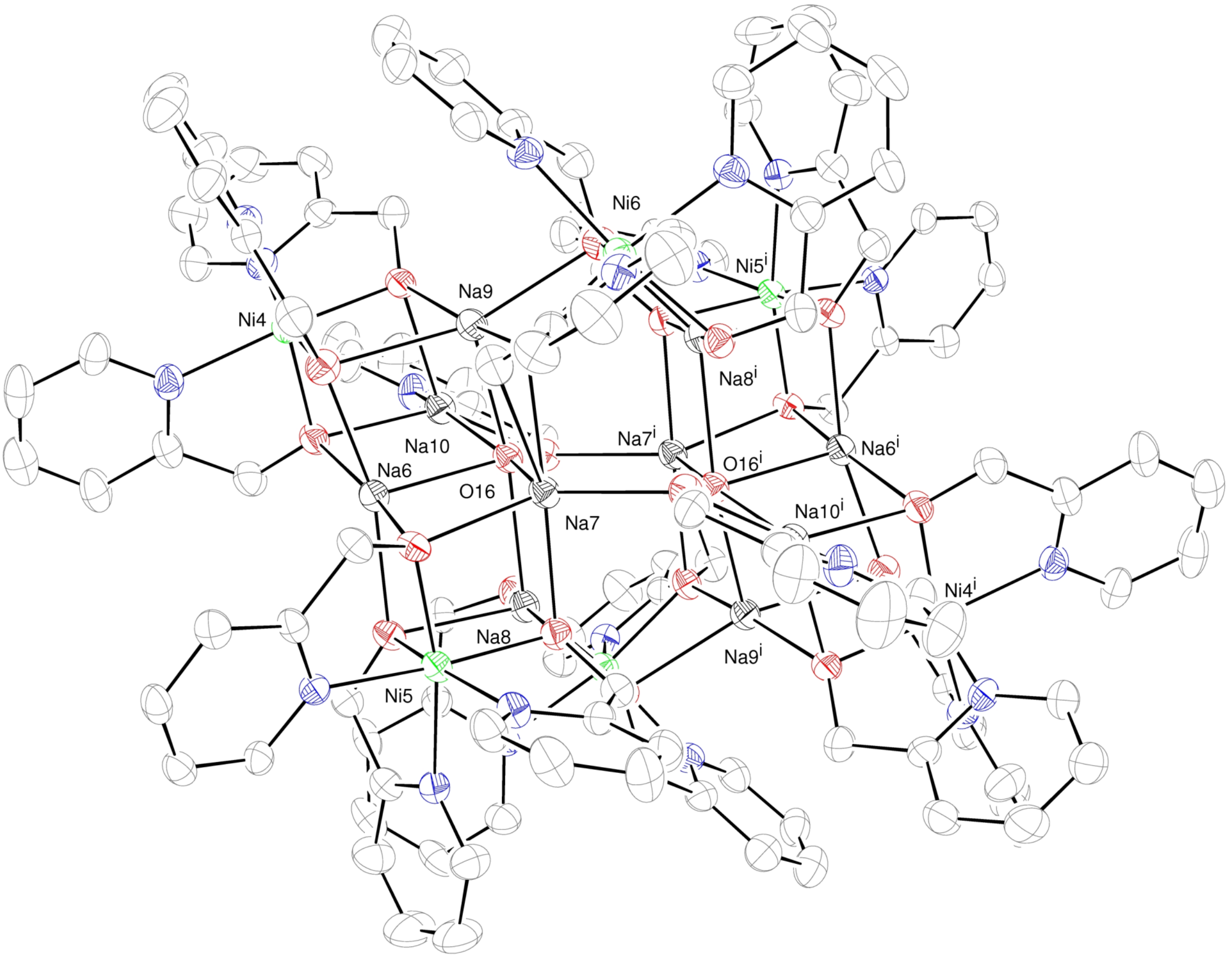

Figure S-6. ORTEP of the molecular structure of one of the two very similar, centrosymmetric, independent molecules of **2** (ellipsoids at 30% probability level). H atoms omitted. Symmetry operations generating equivalent atoms (^{i}): -x, -y, -z.

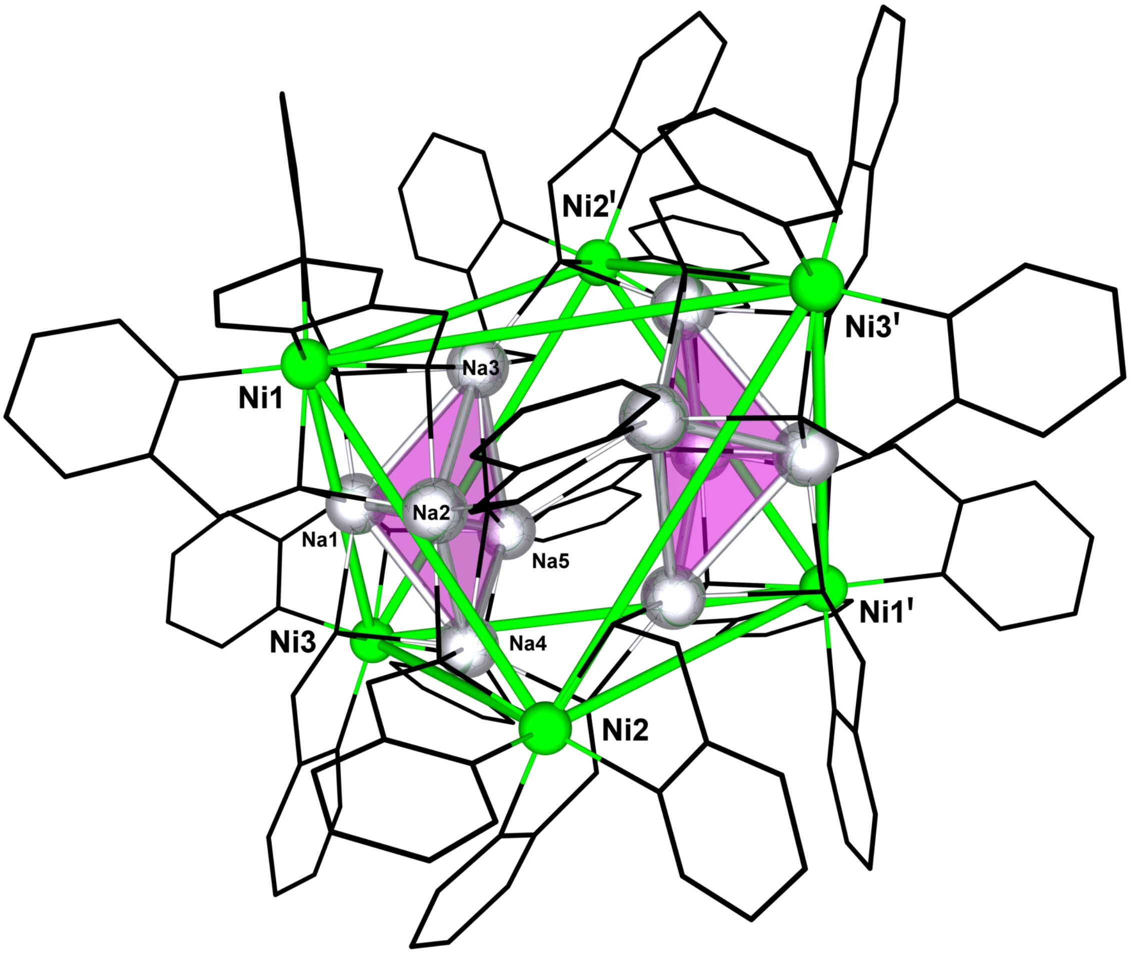

Figure S-7. Diagram of the molecular structure of one of the two independent molecules of **2**, highlighting the distorted octahedron formed by the Ni atoms and the two enclosed square based pyramids formed by the Na^+ cations. Metal···metal separations (Å): Ni1-Ni2′ 6.2018(8), Ni1-Ni3 6.5339(8), Ni2-Ni3 6.4695(9), Ni2-Ni3′ 8.0836(8), Ni2-Ni1 7.0830(8), Ni1-Ni3′ 8.4001(8); Na1-Na5 3.256(2), Na1-Na2 3.064(2), Na1-Na4 3.188(2), Na2-Na4 3.135(2), Na2-Na1 3.064(2), Na3-Na2 3.343(2), Na3-Na1 3.207(2), Na4-Na5 3.263(3), Na5-Na3 3.768(2), Na5-Na1 3.256(2). Symmetry operations generating equivalent atoms (′): -x, -y, -z.

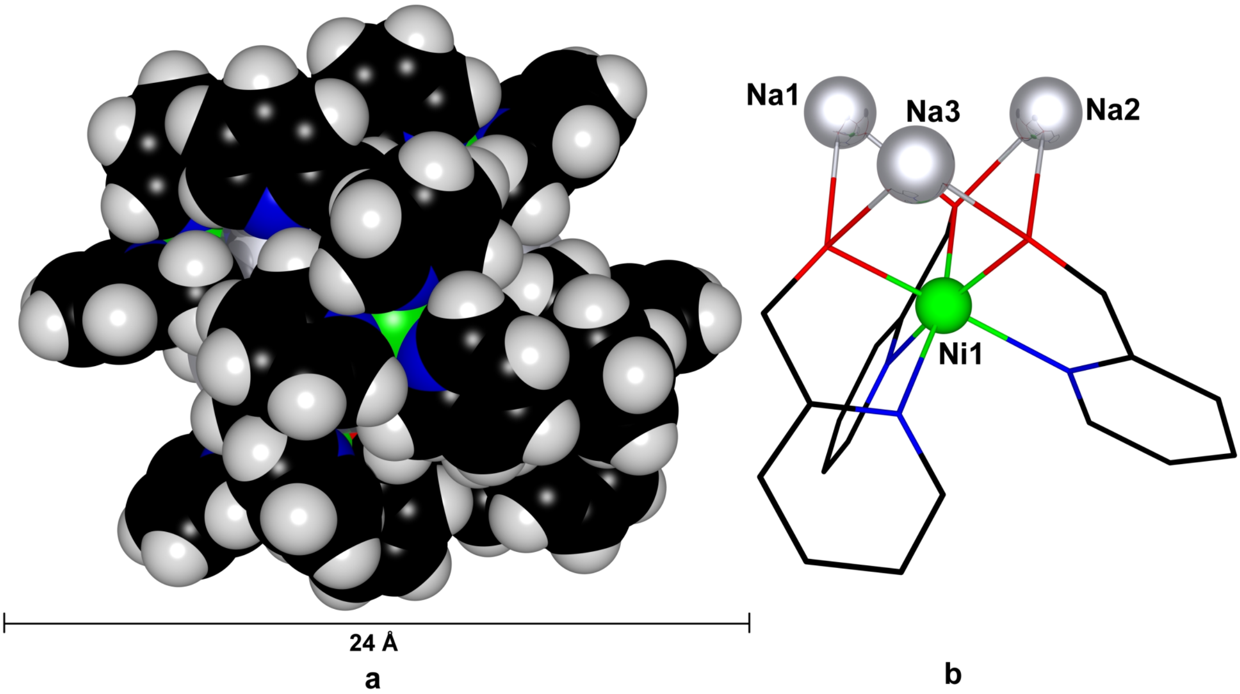

Figure S-8. a) Space filling diagram of the molecular structure of one of the two independent molecules of **2**. b) Diagram of one of the $[Na_3Ni(L)_3]^{2+}$ substructures in **2**, similar to that encountered in **1** (fragment b, Scheme 1).

X-ray data collection, structure solution and refinement for $[Ni_3(\mu\text{-}L_{Et})_2(\mu_3\text{-}L_{Et})_2(L_{Et})(HL_{Et})]Cl$ (3·Cl)

Suitable crystals for the X-ray analysis of **3**•Cl were obtained as described below. The intensity data were collected at 173(2) K on a Kappa CCD diffractometer[S-3] (graphite monochromated MoK$_\alpha$ radiation, λ = 0.71073 Å). Crystallographic and experimental details for the structure are summarized in Table S1. The structure was solved by direct methods (SHELXS-97) and refined by full-matrix least-squares procedures (based on F^2, SHELXL-97)[S-4] with anisotropic thermal parameters for all the non-hydrogen atoms. Two very similar crystallographically independent molecules were found in the asymmetric unit. The hydrogen atoms were introduced into the geometrically calculated positions (SHELXS-97 procedures) and refined *riding* on the corresponding parent atoms, except those bound to O atoms. These were found in the F_o-F_c map and refined isotropically. Several molecules of dichloromethane were found in the crystals of **3**•Cl. Two of these (one per molecule of **3**) were not disordered and were refined unconstrained. The remaining were badly disordered over multiple positions and this disorder considerably affected the model quality. A PLATON-SQUEEZE procedure [S-5] was run using the complete molecular model of compound **3**·Cl·CH_2Cl_2. The calculation estimated a residual electron density of 541 e/unit cell, indicating at least three missing dichloromethane molecules per asymmetric unit. The modified reflection data were then used for the refinement of the molecular structure of **3**·Cl, resulting in improved refinement parameters. CCDC 776753 and 776754 contain the supplementary crystallographic data for this paper that can be obtained free of charge from the Cambridge Crystallographic Data Center via www.ccdc.cam.ac.uk/data_request/cif.

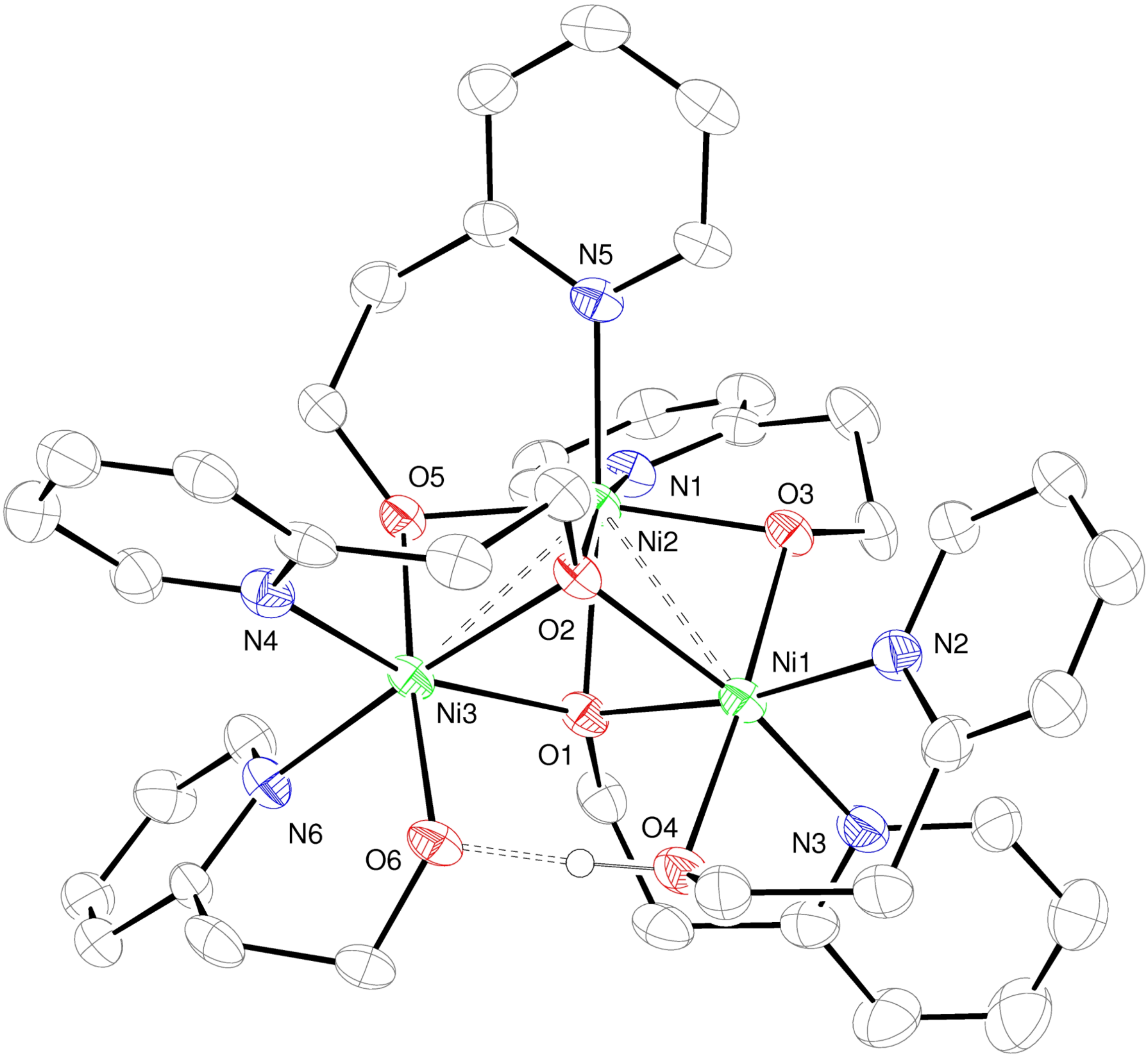

Figure S-9. ORTEP of the molecular structure of one of the two very similar independent molecules of **3** in **3**·Cl (ellipsoids at 40% probability level). H atoms omitted, except that bound to O(4).

Table S1: Data collection and refinement data for **2** and **3**·Cl·CH_2Cl_2

Compound reference	**2**	**3**·Cl·CH_2Cl_2
Chemical formula	$C_{120}H_{122}N_{20}Na_{10}Ni_6O_{22}$	$C_{42}H_{49}N_6Ni_3O_6$•CH_2Cl_2•Cl
Formula Mass	2778.54	1030.32
Crystal system	Triclinic	Triclinic
a/Å	16.6401(9)	15.2974(4)
b/Å	18.7399(9)	18.2533(5)
c/Å	28.9389(13)	21.4614(5)
α/°	98.239(3)	74.300(1)
β/°	91.523(3)	82.417(1)
γ/°	97.769(3)	65.885(1)
Unit cell volume/Å^3	8839.3(8)	5264.0(2)
Temperature/K	173(2)	173(2)
Space group	*P*-1	*P*-1
No. of formula units per unit cell, *Z*	2	4
Absorption coefficient, μ/mm^{-1}	0.705	1.260
No. of reflections measured	79012	51917
No. of independent reflections	32717	24052
R_{int}	0.0768	0.0462
Final R_1 values ($I > 2\sigma(I)$)	0.0579	0.0510
Final $wR(F^2)$ values ($I > 2\sigma(I)$)	0.1374	0.1376
Final R_1 values (all data)	0.1168	0.0828
Final $wR(F^2)$ values (all data)	0.1473	0.1492
Goodness of fit on F^2	0.971	0.974

References

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[S-4] Sheldrick., M; *SHELXL-97*, Program for crystal structure refinement; University of Göttingen: Germany, **1997**.

[S-5] A. L. Spek, *J. Appl. Cryst.*, 2003, **36**, 7-13