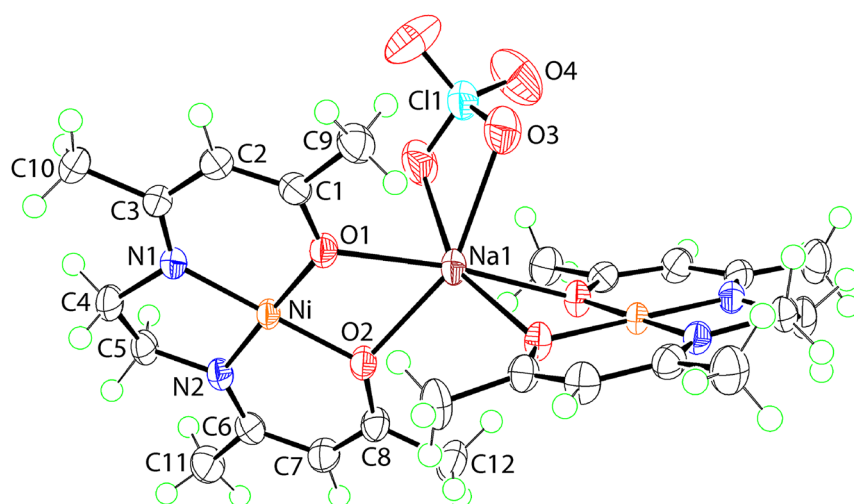


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Redetermination of the crystal structure of bis[*N,N'*-ethylenebis(acetylacetoniminato)nickel(II)] sodium perchlorate, $C_{24}H_{36}ClN_4NaNi_2O_8$



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Table 1: Data collection and handling.

Crystal:	Red block
Size:	0.20 × 0.20 × 0.20 mm
Wavelength:	Mo $K\alpha$ radiation (0.71073 Å)
μ :	1.48 mm ⁻¹
Diffractometer, scan mode:	Rigaku Saturn724, ω
θ_{\max} , completeness:	27.5°, >99%
$N(hkl)_{\text{measured}}$, $N(hkl)_{\text{unique}}$, R_{int} :	14,344, 3261, 0.033
Criterion for I_{obs} , $N(hkl)_{\text{gt}}$:	$I_{\text{obs}} > 2 \sigma(I_{\text{obs}})$, 3129
$N(\text{param})_{\text{refined}}$:	186
Programs:	REQAB [1], CrystalClear [2], SHELX [3, 4], WinGX/ORTEP [5]

Abstract

$C_{24}H_{36}ClN_4NaNi_2O_8$, monoclinic, $C2/c$ (no. 15), $a = 19.5909(11)$ Å, $b = 10.8023(6)$ Å, $c = 14.5722(8)$ Å, $\beta = 112.032(1)^\circ$, $V = 2858.7(3)$ Å³, $Z = 4$, $R_{\text{gt}}(F) = 0.0260$, $wR_{\text{ref}}(F^2) = 0.0701$, $T = 93(2)$ K.

CCDC no.: 2098373

The molecular structure is shown in the figure. Table 1 contains crystallographic data and Table 2 contains the list of the atoms including atomic coordinates and displacement parameters.

Table 2: Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (\AA^2).

Atom	x	y	z	U_{iso}^*/U_{eq}
Ni	0.67462 (2)	0.65612 (2)	0.82671 (2)	0.01590 (8)
O1	0.60788 (5)	0.72456 (9)	0.71032 (7)	0.0207 (2)
O2	0.58999 (5)	0.59640 (9)	0.83993 (7)	0.0207 (2)
N1	0.75757 (6)	0.71569 (10)	0.80915 (9)	0.0194 (2)
N2	0.73819 (6)	0.58926 (10)	0.94563 (8)	0.0184 (2)
C1	0.62408 (8)	0.79199 (13)	0.64739 (10)	0.0202 (3)
C2	0.69423 (8)	0.82287 (13)	0.65729 (11)	0.0239 (3)
H2	0.699881	0.874073	0.607606	0.029*
C3	0.75898 (8)	0.78446 (13)	0.73576 (11)	0.0219 (3)
C4	0.82698 (8)	0.66642 (14)	0.88110 (12)	0.0252 (3)
H4A	0.866150	0.729908	0.896655	0.030*
H4B	0.842624	0.593109	0.853181	0.030*
C5	0.81466 (7)	0.63091 (14)	0.97357 (11)	0.0215 (3)
H5A	0.848873	0.563636	1.008442	0.026*
H5B	0.824057	0.702938	1.018655	0.026*
C6	0.72007 (8)	0.52347 (13)	1.00862 (10)	0.0208 (3)
C7	0.64664 (8)	0.48441 (14)	0.98815 (11)	0.0238 (3)
H7	0.638224	0.430687	1.034448	0.029*
C8	0.58714 (8)	0.51861 (13)	0.90652 (10)	0.0212 (3)
C9	0.55915 (9)	0.83626 (14)	0.55946 (12)	0.0277 (3)
H9A	0.520992	0.772111	0.539704	0.042*
H9B	0.574860	0.853528	0.504330	0.042*
H9C	0.539327	0.911954	0.577096	0.042*
C10	0.83117 (9)	0.82580 (15)	0.73190 (14)	0.0325 (4)
H10A	0.855965	0.881642	0.787464	0.049*
H10B	0.822188	0.869280	0.669411	0.049*
H10C	0.862402	0.753415	0.736296	0.049*
C11	0.77744 (8)	0.48404 (15)	1.10601 (11)	0.0289 (3)
H11A	0.810566	0.423580	1.094259	0.043*
H11B	0.753314	0.446412	1.147139	0.043*
H11C	0.805829	0.556444	1.140091	0.043*
C12	0.51235 (8)	0.46434 (16)	0.88615 (12)	0.0301 (3)
H12A	0.475258	0.530180	0.865340	0.045*
H12B	0.511615	0.425025	0.946377	0.045*
H12C	0.501329	0.402391	0.833417	0.045*
Na1	0.500000	0.73770 (7)	0.750000	0.02234 (17)
Cl1	0.500000	1.02255 (5)	0.750000	0.02701 (12)
O3	0.54812 (6)	0.94232 (12)	0.82627 (9)	0.0382 (3)
O4	0.54217 (9)	1.09586 (15)	0.70970 (12)	0.0587 (4)

Source of material

Preparation of 5,7,12,14-tetramethyl-1,4,8,11-tetraaza-cyclotetradeca-4,6,11,13-tetraene (LH_2): Ethylenediamine (6.7 mL, 0.1 mmol) was added to acetylacetone (10.29 mL, 0.1 mmol) in methanol (50 mL) taken in a 100 mL volumetric flask. The solution was stirred on a magnetic stirrer while 70% perchloric acid (8.9 mL, 0.1 mmol) was added slowly from a dropping funnel. The temperature of the reaction mixture was maintained at 333–338 K, at which stage the solution turned yellow. The resulting mixture

was refluxed for 15 h. The reaction mixture was then allowed to stand for 2–3 days at room temperature, after which the solid product was filtered off, washed with methanol and finally with diethyl ether. The white crystalline product, LH_2 , was dried in vacuo.

Preparation of nickel(II) complex of L: Nickel acetate tetrahydrate (0.25 g, 1.0 mmol) and LH_2 (0.449 g, 1.0 mmol) were dissolved separately in 30 mL hot methanol and mixed. After heating on a water bath for a few minutes, the solution immediately turned brown. The solution was then heated for 30 min to reduce the volume to 20 mL. Sodium perchlorate (0.368 g, 3.0 mmol) was added to the cooled solution. After standing overnight, a deep-brown precipitate, anticipated to be $[NiL](ClO_4)_2$, was separated by filtration, washed with methanol followed by diethyl ether and stored in a vacuum desiccator.

Preparation of crystals: Crystals were grown by the slow crystallization from its acetonitrile/*n*-hexane (1:1, v/v) solution. X-ray crystallography proved to the formulation to be $[NiL]_2Na(ClO_4)_4$, a known species [6], so no further characterisation was performed. The melting point of the sample was not determined as perchlorates are explosive at elevated temperatures.

Experimental details

The C-bound H atoms were geometrically placed (C–H = 0.95–0.99 \AA) and refined as riding with $U_{iso}(H) = 1.2\text{--}1.5U_{eq}(C)$. Owing to poor agreement, one reflection, i.e. (–1 1 6), was omitted from the final cycles of refinement.

Comment

In continuation of recent and on-going studies of N_4 -donor macrocycles and their transition metal complexes [7, 8], an attempt was made to synthesise the nickel (II) complex derived from 5,7,12,14-tetramethyl-1,4,8,11-tetraazacyclotetradeca-4,6,11,13-tetraene, prepared from the 1:1 condensation reaction of ethylenediamine and acetylacetone. However, under the reaction conditions employed, cyclisation did not occur/persist and the title complex $[NiL]_2Na(ClO_4)_4$, hereafter (I), was obtained. While the crystal structure of (I) has been reported previously [6], the new data enables a more detailed discussion of geometric parameters and the absence of disorder facilitates the discussion of supramolecular association in the crystal.

The molecular structure of two-fold symmetric (I) is shown in the figure (70% probably displacement ellipsoids); the Na1 and Cl1 atoms lie on the two-fold axis of symmetry. The nickel(II) centre lies within a square-planar geometry defined by a N_2O_2 donor set with the r.m.s. deviation for the five atoms being 0.0175 Å; the maximum deviation from the least-squares plane being 0.0208(5) Å for atom O1. There is no pattern in the Ni–O and Ni–N bond lengths with Ni–N1 [1.8527(11) Å], Ni–N2 [1.8592(12) Å] and Ni–O2 [1.8552(9) Å] being equal within experimental error and shorter than Ni–O1 [1.8625(10) Å]. Greater ranges of Ni–O [1.8570(18) and 1.8663(18) Å] and Ni–N [1.8454(18) and 1.8553(18) Å] bond lengths are noted in the structure of NiL [9]. These observations suggest the interactions formed between the O1 and O2 atoms and the sodium cation [Na1⋯O1 = 2.3953(9) Å and Na1⋯O2 = 2.3285(11) Å] do not exert a significant influence upon the Ni–O bonds. In the N1–C3–C2–C1–O1 residue, the sequence of bond lengths, i.e. 1.3110(18), 1.414(2), 1.368(2) and 1.3003(16) Å, in particular the lengthening and shortening of the formal imine and alkoxy bonds, suggest considerable delocalisation of π -electron density; the equivalent values for the N2–C6–C7–C8–O2 residue are 1.3107(18), 1.419(2), 1.367(2) and 1.3006(17) Å, respectively.

The Na1 cation provides the link between the two NiL complexes and also interacts with symmetry equivalent perchlorate–O3 atoms [$2 \times 2.4948(15)$ Å]. This results in a disparity in the Cl–O bonds, with Cl1–O3 [1.4454(12) Å] being longer than Cl1–O4 [1.4208(14) Å], in keeping with expectation.

The structure of (I) is not the only example where a second residue links two NiL complexes. In another example, $Zn(NCS)_2$ mediates the formation of a three-molecule aggregate, with the zinc centre attaining a N_2O_4 donor set [10]. With each of $Cd(NCS)_2$ and $Cd(N_3)_2$, NiL₂ is an ancillary ligand in one-dimensional coordination polymers formulated as $\{Cd(NCS)_2NiL_2\}_n$ and $\{Cd(N_3)_2NiL_2\}_n$, respectively [11].

In the crystal, methylene–C–H⋯O(perchlorate) [C5–H5a⋯O3ⁱ: H5a⋯O3ⁱ = 2.50 Å, C5⋯O3ⁱ = 3.2369(19) Å with angle at H5a = 131° for symmetry operation (i): $3/2-x$, $3/2-y$, $2-z$] and methyl–C–H⋯O(perchlorate) [C10–H10c⋯O4ⁱⁱ: H10c⋯O4ⁱⁱ = 2.43 Å, C10⋯O4ⁱⁱ = 3.386(2) Å with angle at H10c = 165° for (ii): $3/2-x$, $-1/2+y$, $3/2-z$] interactions combine with methylene- and methyl–C–H⋯ π (chelate ring) interactions, well-known in coordination chemistry [12], within a three-dimensional architecture. While each ring participates in two C–H⋯ π (chelate ring) contacts, one to either side of the plane, only data for the shortest contact for each are given [C11–H11c⋯Cg(O1,N1,C1–C3)ⁱ: H11c⋯Cg(O1,N1,C1–C3)ⁱ = 2.78 Å with angle at H11c = 145°; C10–H10b⋯Cg(O2,N2,

C6–C8)ⁱⁱⁱ: H10b⋯Cg(O2,N2,C6–C8)ⁱⁱⁱ = 2.54 Å with angle at H10b = 149° for (iii): $3/2-x$, $1/2+y$, $3/2-z$].

An analysis of the calculated Hirshfeld surfaces and of the full and delineated two-dimensional fingerprint plots was also conducted, being calculated with Crystal Explorer 17 [13] employing literature methods [14]. The calculations show all surface contacts involve hydrogen and over half of these are H⋯H contacts, contributing 52.5%. The next most significant contributions to the Hirshfeld surface are O⋯H/H⋯O contacts at 23.2%. The remaining contributions to the surface are from C⋯H/H⋯C [14.2%], N⋯H/H⋯N [5.9%] and Ni⋯H/H⋯Ni [4.2%].

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