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A linear homotrinuclear nickel(II) complex with a reduced ONNO-type Schiff base

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Key indicators

Single-crystal X-ray study
T = 299 K
Mean σ(C–C) = 0.007 Å
R factor = 0.050
wR factor = 0.129
Data-to-parameter ratio = 18.3

For details of how these key indicators were automatically derived from the article, see http://journals.iucr.org/e.

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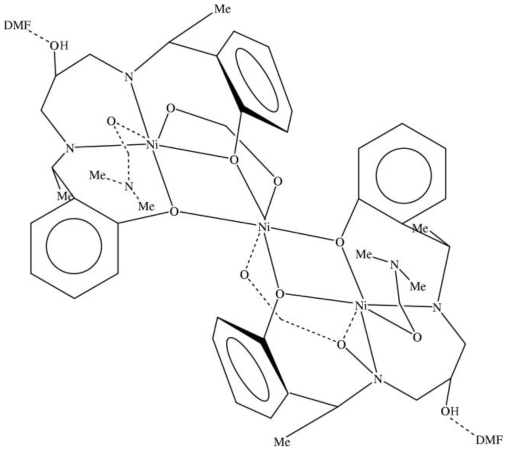
The structure of the title compound, bis{[μ-bis-*N*,*N*′[1-(2-oxyphenyl)ethyl]-2-hydroxy-1,3-propanediaminato](*N*,*N*-dimethylformamide)nickel(II)](μ-formato)}nickel(II)} *N*,*N*-dimethylformamide disolvate, $[Ni_3(CO_2H)_2(C_3H_7NO)_2(C_{19}H_{24}N_2O_3)_2]\cdot 2C_3H_7NO$, comprises a centrosymmetric linear homotrinuclear nickel(II) complex. The central and terminal nickel(II) atoms have distorted octahedral coordination geometries.

Comment

Trinuclear linear homo- or heteronuclear complexes based on Schiff base ligands are of interest because of their magnetic super-exchange interactions between bridged metal ions (Fukuhara *et al.*, 1990). In these complexes, various combinations of metal ions in the central and terminal locations, as well as the μ-bridges, such as acetate and nitrite anions, are observed (Atakol *et al.*, 1999; Yıldırım & Atakol, 2002). Schiff bases prepared from 2-amino-1,3-propanediamine are frequently reported in the literature in terms of their coordination chemistry (Averseng *et al.*, 2001; Mikuriya *et al.*, 1993; Guerrino *et al.*, 1989; Than *et al.*, 1999; Dominguez-Vera *et al.*, 2000; Golcaves *et al.*, 2002; Courtney *et al.*, 2002; Aneetha *et al.*, 1999 & Uhlenbrock *et al.*, 1996). An ONONO-type chelating agent is formed by the reaction between this amine and salicylaldehyde. Generally, multinuclear complexes are formed with these types of Schiff bases and in some cases the alcoholic OH group of this ligand is involved in coordination. In this study, the Schiff base derived from 2-hydroxyacetophenone and 2-hydroxy-1,3-propanediamine was reduced in MeOH medium with $NaBH_4$ and a homotrinuclear nickel(II) complex was subsequently prepared in DMF solution.



(I)

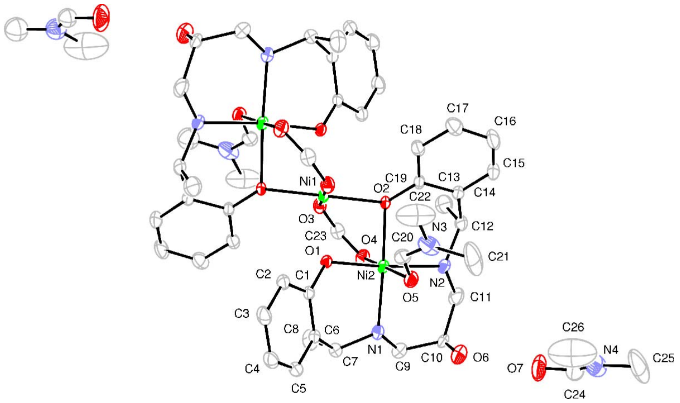


Figure 1
Atom-numbering scheme for (I). Displacement ellipsoids are drawn at the 30% probability level. Unlabelled atoms are related to labelled atoms by $1 - x$, $1 - y$, $1 - z$.

In $[Ni_3(CO_2H)_2(C_3H_7NO)_2(C_{19}H_{24}N_2O_3)_2]\cdot 2C_3H_7NO$, (I), the central Ni^{II} ion is located on an inversion centre. As shown in Fig. 1, the coordination around the central Ni atom is based on an O_6 donor set, and that around the two terminal Ni atoms is based on N_2O_4. The central Ni^{II} atom has an irregular octahedral environment, involving four bridging O atoms derived from the Schiff base ligands and two O atoms from the bidentate bridging formate ligands. The terminal Ni^{II} atom is coordinated by a tetradentate Schiff base ligand, *via* two O and two N atoms, as well as one O atom from the bridging formate ligand and one O atom from a coordinated DMF molecule. The Ni2/N1/C9/C10/C11/N2 ring adopts a distorted chair conformation and the C10—O6 bond is in an axial position; atom O6 does not participate in coordination. The coordination observed in (I) is similar to that reported for a linear homotrinuclear nickel complex containing nitrate bridges (Atakol *et al.*, 1999). Similar bond distances and angles were observed for both complexes (Table 1). The Ni1···Ni2 distances for these complexes are 3.1421 (6) [for (I)] and 3.0322 (7) Å.

There are both inter- and intramolecular hydrogen-bonding interactions in the structure, as summarized in Table 2. The O6/H group, in effect, links the complex, *via* N1/H, to a DMF solvent molecule, as shown in Fig. 2. The third interaction, involving N2—H and the coordinated O atom of DMF, adds stability to the trinuclear cluster.

Experimental

The ligand was prepared in two steps. In the first step, the Schiff base was synthesized from 2 hydroxyacetophenone (5.44 g, 40 mmol) and 2-hydroxy-1,3-propanediamine (1.80 g, 20 mmol) in MeOH solution (mole fraction 2/1). The mixture was left to stand in air. After 4–5 h, the yellow Schiff base crystallized. In the second step, the Schiff base (3.26 g, 10 mmol) was dissolved in cold MeOH (50 ml) and $NaBH_4$ was added slowly to this solution until it turned colourless. The reduced Schiff base precipitated after addition of excess water. The mixture was left to stand at 277 K for one day to obtain crystals and then was filtered. The crystals were allowed to dry in air. For the preparation of the title complex, the ligand (0.990 g, 3 mmol) was dissolved in hot DMF (60 ml), and solutions of $NiCl_2\cdot 6H_2O$ (1.067 g, 4.5 mmol) in hot MeOH (25 ml) and HCOONa (0.612 g, 9 mmol) in hot water (15 ml) were added. Crystals of the complex were obtained by filtration after one day. Analysis calculated for $C_{52}H_{78}N_8Ni_3O_{14}$: C 51.52, H 6.27, N 8.58, Ni 15.41%; found: C 51.09, H 5.97, N 8.34, Ni 14.88%. IR (cm^{-1}): ν(N—H) 3285, $\nu(C—H)_{Ar}$ 3053, $\nu(C—H)_{Aliph}$ 2934–2797, $\nu(C{=}O)_{DMF}$ 1645 $\nu(C{=}C)_{Ar}$ 1604, δ_{CH2} 1481, $\delta(C—H)_{Ar}$ 737, ν(O—H) 2720 cm^{-1}. Mass loss for DMF: calculated 19.19%; observed 20.36%.

Crystal data

$[Ni_3(CO_2H)_2(C_3H_7NO)_2(C_{19}H_{24}N_2O_3)_2]\cdot 2C_3H_7NO$
$M_r = 1215.29$
Triclinic, $P\overline{1}$
$a = 11.586$ (2) Å
$b = 11.8210$ (11) Å
$c = 12.652$ (2) Å
$\alpha = 96.50$ (1)°
$\beta = 107.03$ (1)°
$\gamma = 101.69$ (1)°
$V = 1594.5$ (4) Å^3
$Z = 1$
$D_x = 1.266$ Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 25 reflections
$\theta = 2.9$–28.8°
$\mu = 0.94$ mm^{-1}
$T = 299$ (2) K
Block, blue
0.45 × 0.20 × 0.16 mm

Data collection

Oxford Diffraction Xcalibur CCD diffractometer
ω scans
Absorption correction: none
9225 measured reflections
8345 independent reflections
2904 reflections with $I > 2\sigma(I)$
$R_{int} = 0.036$
$\theta_{max} = 28.8°$
$h = -14 \rightarrow 5$
$k = -13 \rightarrow 14$
$l = -15 \rightarrow 16$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.05$
$wR(F^2) = 0.129$
$S = 0.95$
6404 reflections
349 parameters
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0574P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max} = 0.41$ e Å^{-3}
$\Delta\rho_{min} = -0.60$ e Å^{-3}

Table 1
Selected geometric parameters (Å, °).

Ni1—Ni2	3.1421 (6)	Ni2—O2	2.165 (3)
Ni1—O1	2.148 (3)	Ni2—O4^i	2.105 (3)
Ni1—O2	2.047 (2)	Ni2—O5	2.218 (3)
Ni1—O3	2.213 (3)	Ni2—N1	2.196 (3)
Ni2—O1	2.024 (2)	Ni2—N2	2.093 (3)
Ni2—O1—Ni1	97.68 (10)	N2—Ni2—O2	91.93 (12)
Ni1—O2—Ni2	96.43 (10)	O4^i—Ni2—O2	96.91 (11)
O1—Ni1—O3	99.04 (10)	O1—Ni2—N1	93.56 (11)
O1^i—Ni1—O3	80.96 (10)	N2—Ni2—N1	92.56 (13)
O2^i—Ni1—O1	98.87 (9)	O4^i—Ni2—N1	88.80 (13)
O2—Ni1—O1	81.13 (9)	O2—Ni2—N1	172.48 (11)
O2^i—Ni1—O3	85.13 (10)	O1—Ni2—O5	91.01 (10)
O2—Ni1—O3	94.87 (10)	N2—Ni2—O5	81.80 (13)
O1—Ni2—N2	170.49 (13)	O4^i—Ni2—O5	175.14 (11)
O1—Ni2—O4^i	93.50 (10)	O2—Ni2—O5	85.55 (11)
N2—Ni2—O4^i	93.90 (13)	N1—Ni2—O5	89.13 (13)
O1—Ni2—O2	81.25 (10)		

Symmetry code: (i) $-x + 1, -y + 1, -z + 1$.

Table 2
Hydrogen-bond geometry (Å, °).

D—H···A	D—H	H···A	D···A	D—H···A
O6—H6···O7^{ii}	0.82	2.01	2.721 (6)	145
N1—H1···O6	0.91	2.35	2.773 (5)	108
N2—H2···O5	0.91	2.37	2.825 (5)	110

Symmetry code: (ii) $x, y, z + 1$.

m920 Arıcı et al. • $[Ni_3(CO_2H)_2(C_3H_7NO)_2(C_{19}H_{24}N_2O_3)_2]\cdot 2C_3H_7NO$ Acta Cryst. (2005). E61, m919–m921

All H atoms were placed geometrically (C—H = 0.93–0.98 Å, N—H = 0.91 Å and O—H = 0.82 Å) and refined in the riding-model approximation, with $U_{iso}(H) = 1.2U_{eq}(C)$ for CH, NH and CH_2, and $U_{iso}(H) = 1.5U_{eq}(C,O)$ for CH_3 and OH groups. It was noted that the DMF molecule has high thermal motion but multiple sites were not resolved.

Data collection: *CrysAlis CCD* (Oxford Diffraction, 2001); cell refinement: *CrysAlis RED* (Oxford Diffraction, 2001); data reduction: *CrysAlis RED*; structure solution: *SHELXS97* (Sheldrick, 1997); structure refinement: *SHELXL97* (Sheldrick, 1997); molecular graphics: *PLATON* (Spek, 2003); software used to prepare material for publication: *SHELXL97*.

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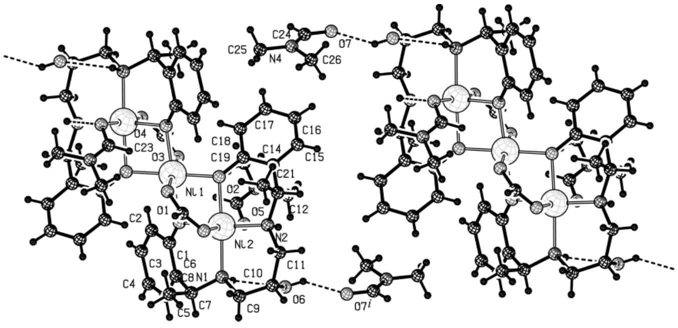

Figure 2
A view of the hydrogen bonding (dashed lines) in (I).

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