

Acta Cryst. (1997). **C53**, 1056–1057

Bis{(μ -acetato)[μ -bis(salicylidene)-1,3-propanediaminato](dimethyl sulfoxide)-nickel(II)}nickel(II)†

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(Received 6 December 1996; accepted 25 March 1997)

Abstract

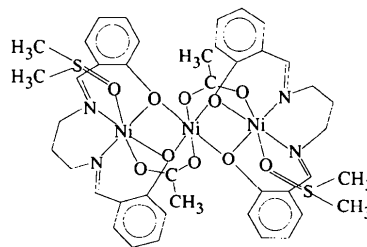
The coordination around the nickel ions in the title complex, [Ni₃(C₁₇H₁₆N₂O₂)₂(C₂H₃O₂)₂{(CH₃)₂SO}₂], is irregular octahedral. The central nickel ion occupying the inversion centre has four O atoms from two *N,N'*-bis(salicylidene)-1,3-propanediaminato (SALPD²⁻) ligands and one O atom from each bridging acetate group. The average Ni—O distance for the central Ni ion is 2.072 (2) Å. The coordination around the terminal Ni ions, related by an inversion centre, comprises two O atoms and two N atoms from a SALPD²⁻ ligand as well as one O_{acetate} and one O_{DMSO} atom. The DMSO and acetate ligands are *trans* about the terminal Ni atom. The average Ni—O and Ni—N distances for the terminal Ni ions are 2.087 (2) and 2.018 (3) Å, respectively. The Ni···Ni bridging distance is 3.043 (2) Å.

Comment

Oxygen-bridged polynuclear complexes of the first transition series are of interest because of their magnetic properties. These complexes may be homo- or heteronuclear as well as linear or non-linear. The ligand stereochemistry around the paramagnetic metal ions and the structure of the O-atom bridges influence the magnetic exchange interactions. Synthesis and magnetic studies of the trinuclear complexes of general formulae [MCu₂(CH₃CO₂)₂(SALPD)₂] (*M* = Mg²⁺, Mn²⁺, Co²⁺, Ni²⁺, Cu²⁺ or Zn²⁺) and [MNi₂(CH₃CO₂)₂(SALPD)₂] (*M* = Mg²⁺, Mn²⁺, Co²⁺ or Ni²⁺), where H₂SALPD is *N,N*-bis(salicylidene)-1,3-propanediamine, have been reported previously. In this series of compounds only the structure of [Zn{(CH₃CO₂)(SALPD)Cu}₂] has been determined by X-ray diffraction (Fukuhara, Tsuneyoshi, Matsumoto, Kida, Mikuriya & Mori, 1990). Simi-

lar complexes formulated as *M*{(CH₃CO₂)(SALPN)-[(CH₃)₂CNO]}₂, *M* = Co²⁺ or Fe²⁺, where SALPN is *N,N*-bis(salicylidene)-2,2-dimethylpropylenediamine (Gerli, Hagen & Marzilli, 1991) and Cd{(CH₃CO₂)(SALPD)[(CH₃)CNO]Ni}₂ (Ülkü, Tahir, Atakol & Nazir, 1997) have been also described.

We report here a new member in the family of linear trinuclear metal complexes. The triclinic unit cell of the title compound, (I), contains one centrosymmetric trimer complex, whose central Ni ion is located at the inversion centre on the origin. The coordination around the central metal ion, Ni2, is an irregular octahedron involving four bridging O atoms from two SALPD²⁻ ligands in the equatorial plane. The apical positions are occupied by an O atom from each of the two bridging acetate groups. The Ni2—O bond lengths range from 2.024 (3) to 2.098 (3) Å, the shortest bond being to the acetate O atom. The inversion-related terminal Ni ions also have an irregular octahedral coordination. The equatorial plane around Ni1 consists of two O and two N atoms from the SALPD²⁻ ligand. In the axial positions of this irregular octahedron, there is an O atom from the bridging acetate and another O atom from the dimethyl sulfoxide.



(I)

The Ni1—O bond lengths are in the range 2.010 (3)–2.254 (3) Å, the longest distance being to the DMSO O atom. The Ni1—N1 and Ni1—N2 bond lengths are 2.023 (4) and 2.014 (4) Å, respectively. The dihedral angle between the two equatorial planes (O1, O2, O1', O2' and O1, O2, N1, N2) of the neighbouring irregular octahedrons sharing atoms O1 and O2 is 21.9 (1)°. The terminal Ni1 atom is 0.0576 (5) Å out of the equatorial plane. The SALPD²⁻ ligand is not planar. The dihedral angles between the equatorial plane (O1, O2, N1, N2) and the two salicylidimine residues (N2, C11, C12–C17, O2 and N1, C7, C6–C1, O1) are 35.06 (7) and 33.1 (1)°, respectively. The Ni···Ni distance is 3.043 (2) Å. The six-membered chelate ring (Ni1, N1, C8, C9, C10, N2) has a chair conformation. The distances of the two *para*-positioned chair atoms, Ni1 and C9, from their respective planes are 0.5141 (5) and –0.715 (5) Å. Although the type of metal ions and some of the coordinating groups are different than the complexes mentioned above (Gerli *et al.*, 1991; Ülkü *et al.*, 1997), the coordination around the metal ions is very similar in these compounds.

† Alternative name: bis(μ -acetato)-1:2 κ^2 O:O';2:3 κ^2 O:O'-bis(dimethyl sulfoxide)-1 κ O,3 κ O-bis{ μ -2,2'-[1,3-propanediylbis(nitrilomethylidene)]diphenolato}-1 κ^4 N,N',O,O':2 κ^2 O,O';3 κ^4 N,N',O,O':2 κ^2 O,O'-trinickel(II).

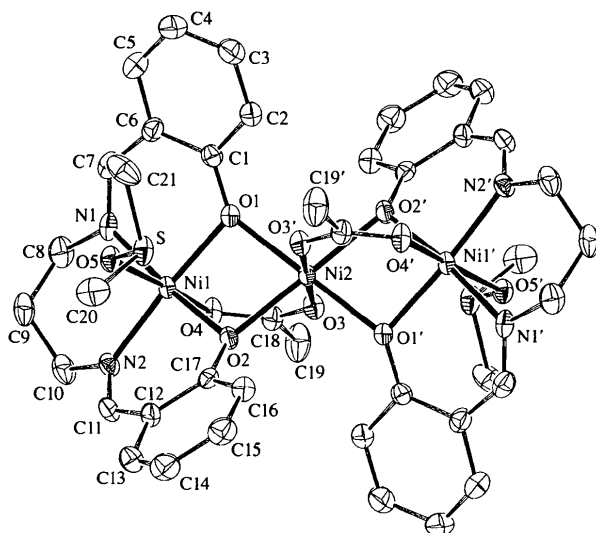
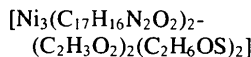


Fig. 1. PLATON (Spek, 1992) drawing of (I) with the atom-numbering scheme. The displacement ellipsoids are drawn at the 30% probability level. H atoms have been omitted for clarity.

Experimental

N,N'-Bis(salicylidene)-1,3-propanediamine (0.282 g, 1 mmol) was dissolved in 50 ml dimethyl sulfoxide at 403 K. To this solution, a solution of $[\text{Ni}(\text{CH}_3\text{COO})_2] \cdot 4\text{H}_2\text{O}$ (0.357 g, 1.5 mmol) in 30 ml hot methanol was added slowly. The mixture was set aside for five days and the green crystals which formed were filtered off and dried in air.

Crystal data



$M_r = 1011.15$

Triclinic

$P\bar{1}$

$a = 10.429(2) \text{ \AA}$

$b = 10.699(3) \text{ \AA}$

$c = 11.743(3) \text{ \AA}$

$\alpha = 114.41(2)^\circ$

$\beta = 107.43(3)^\circ$

$\gamma = 96.33(4)^\circ$

$V = 1096.3(6) \text{ \AA}^3$

$Z = 1$

$D_x = 1.53 \text{ Mg m}^{-3}$

D_m not measured

Mo $K\alpha$ radiation

$\lambda = 0.71073 \text{ \AA}$

Cell parameters from 25 reflections

$\theta = 10\text{--}18^\circ$

$\mu = 1.43 \text{ mm}^{-1}$

$T = 295 \text{ K}$

Prismatic

$0.30 \times 0.20 \times 0.12 \text{ mm}$

Green

Data collection

Enraf–Nonius CAD-4 diffractometer

$\omega/2\theta$ scans

Absorption correction: empirical via ψ scans (MolEN; Fair, 1990)

$T_{\min} = 0.739$, $T_{\max} = 0.841$

4703 measured reflections

4451 independent reflections

3006 reflections with

$I > \sigma(I)$

$R_{\text{int}} = 0.017$

$\theta_{\max} = 26.3^\circ$

$h = 0 \rightarrow 12$

$k = -13 \rightarrow 13$

$l = -14 \rightarrow 13$

3 standard reflections

frequency: 120 min

intensity decay: -2.7%

Refinement

Refinement on F

$R = 0.048$

$wR = 0.049$

$S = 0.96$

3006 reflections

277 parameters

H atoms: see below

$w = 1/[\sigma F^2 + (0.02F)^2 + 0.3]$

$(\Delta/\sigma)_{\max} = 0.002$

$\Delta\rho_{\max} = 0.839 \text{ e \AA}^{-3}$

$\Delta\rho_{\min} = -0.113 \text{ e \AA}^{-3}$

Extinction correction: none

Scattering factors from International Tables for X-ray Crystallography (Vol. IV)

Table 1. Selected geometric parameters (\AA , $^\circ$)

Ni1—O1	2.010 (3)	S—C20	1.788 (7)
Ni1—O2	2.024 (3)	S—C21	1.788 (5)
Ni1—O4	2.062 (3)	O1—C1	1.311 (4)
Ni1—O5	2.254 (3)	O2—C17	1.313 (7)
Ni1—N1	2.023 (4)	C5—C6	1.393 (6)
Ni1—N2	2.014 (4)	C6—C7	1.448 (7)
Ni2—O1	2.098 (3)	C8—C9	1.516 (9)
Ni2—O2	2.093 (3)	C9—C10	1.500 (6)
Ni2—O3	2.024 (3)	C11—C12	1.458 (8)
Ni1—Ni2	3.043 (2)	C12—C13	1.404 (9)
S—O5	1.509 (4)	C12—C17	1.422 (7)
O1—Ni1—O2	83.2 (1)	O5—Ni1—N2	87.4 (1)
O1—Ni1—O4	92.0 (1)	N1—Ni1—N2	96.2 (2)
O1—Ni1—O5	90.6 (1)	O1—Ni2—O2	79.4 (1)
O1—Ni1—N1	90.6 (2)	O1—Ni2—O3	88.8 (1)
O2—Ni1—O4	93.6 (1)	O2—Ni2—O3	87.1 (1)
O2—Ni1—O5	90.3 (1)	O5—S—C20	105.8 (3)
O2—Ni1—N2	89.8 (2)	O5—S—C21	105.3 (3)
O4—Ni1—N1	90.8 (1)	C20—S—C21	96.6 (3)
O4—Ni1—N2	90.5 (1)	Ni1—O1—Ni2	95.9 (1)
O5—Ni1—N1	85.6 (1)	Ni1—O2—Ni2	95.7 (1)

All non-H atoms were refined with anisotropic displacement parameters. The H atoms were placed geometrically 0.95 \AA from their parent C atoms with $U_{\text{iso}}(\text{H}) = 1.3U_{\text{eq}}(\text{C})$. After refining the H-atom coordinates for a few cycles, a riding model was used for all H atoms.

Data collection: CAD-4 EXPRESS (Enraf–Nonius, 1994). Data reduction: MolEN (Fair, 1990). Program(s) used to solve structure: SIMPEL in MolEN. Program(s) used to refine structure: LSFM in MolEN. Molecular graphics: PLATON (Spek, 1992). Software used to prepare material for publication: MolEN.

The authors wish to acknowledge the purchase of the CAD-4 diffractometer under Grant DPT/TBAG1 of the Scientific and Technical Research Council of Turkey.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: FR1035). Services for accessing these data are described at the back of the journal.

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