

- Siemens (1989). *P3 Diffractometer Program*. Version 3.13. Siemens Analytical X-ray Instruments Inc., Madison, Wisconsin, USA.
- Spivak, B. & Dori, Z. (1970). *J. Chem. Soc. Chem. Commun.* pp. 1716–1717.
- Spivak, B. & Dori, Z. (1973). *J. Chem. Soc. Dalton Trans.* pp. 1173–1177.

Acta Cryst. (1998). **C54**, 1268–1270

A Linear Trinuclear Ni^{II}–Mn^{II}–Ni^{II} Complex with a μ -Acetato Bridge: Bis{(μ -acetato)[μ -bis(salicylidene)-1,3-propanediaminato](*N,N*-dimethylformamide)nickel(II)}manganese(II)†

FILIZ ERCAN^a AND ORHAN ATAKOL^b

^aDepartment of Engineering Physics, Hacettepe University, Beytepe 06532, Ankara, Turkey, and ^bDepartment of Chemistry, Ankara University, Tandoğan 06100, Ankara, Turkey. E-mail: filiz@eti.cc.hun.edu.tr

(Received 4 December 1997; accepted 3 March 1998)

Abstract

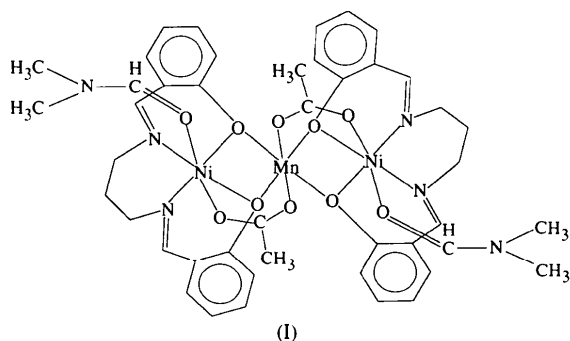
The structure of the title compound, [Mn{Ni(C₂H₃O₂)-(C₃H₇NO)(C₁₇H₁₆N₂O₂)}₂], consists of a linear hetero-trinuclear unit with a central Mn^{II} ion. Both the terminal Ni^{II} ions and the central Mn^{II} ion have irregular octahedral coordinations. The central Mn^{II} ion is located on the inversion centre. Each pair of metal ions is triply bridged *via* O atoms from the *N,N'*-bis(salicylidene)-1,3-propanediaminato (SALPD²⁻) ligands and from the acetate groups. The coordination around the Mn^{II} ion consists of four O atoms from two SALPD²⁻ ligands, and one O atom from each of two acetate ligands. The coordination of each terminal Ni^{II} ion is provided by the two O and two N atoms from a SALPD²⁻ ligand, and by one O atom each from a bridging acetate and a dimethylformamide (dmf) ligand. The dmf and acetate ligands are *trans* about the terminal Ni^{II} ion. The average Ni—O and Ni—N distances for the terminal ions are 2.071 (2) and 2.026 (2) Å, respectively. The Ni···Mn distance is 3.133 (2) Å.

Comment

Trinuclear metal complexes of the first transition series are of interest because of the magnetic super-exchange interactions between their bridged metal ions. The ligand stereochemistry around the paramagnetic

metal ions and the structure of the O-atom bridges influence these magnetic exchange interactions. The synthesis and magnetic properties of trinuclear complexes with the 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 represents *N,N'*-bis(salicylidene)-1,3-propanediamine, have been reported previously (Fukuhara *et al.*, 1990). In these groups of compounds, only the structure of [Zn{(CH₃CO₂)-(SALPD)Cu}₂] has been determined by X-ray diffraction (Fukuhara *et al.*, 1990). Structural studies of the complexes formulated as [M₃(SALPN)₂(CH₃CO₂)₂]-2dmf [*M* = Co²⁺ or Fe²⁺; SALPN = *N,N'*-bis(salicylidene)-2,2-dimethylpropylenediamine; dmf = dimethylformamide] have been reported by Gerli *et al.* (1991). [Ni₃{(CH₃CO₂)(SALPD)(dmsO)}₂] (dmsO = dimethyl sulfoxide) (Ülkü, Ercan *et al.*, 1997) and [Cd{Ni(CH₃CO₂)(SALPD)(dmf)}₂] (Ülkü, Tahir *et al.*, 1997) have also been studied in this laboratory.

We describe here the structure of a new linear heterometal trinuclear complex, [Mn{Ni(CH₃CO₂)-(SALPD)(dmf)}₂], (I). The structure consists of centrosymmetric trimers, with the central metal ion, Mn^{II}, occupying the inversion centre at the origin. The coordination around Mn is a distorted octahedron, involving four bridging O atoms from two SALPD²⁻ ligands in the equatorial plane and an O atom from each of the two bridging acetate groups in the axial positions. The Mn—O bond lengths range from 2.163 (1) to 2.194 (2) Å, the shortest bond being to the SALPD²⁻ O1 atom. The Ni—N1 and Ni—N2 bond lengths are 2.016 (2) and 2.036 (2) Å, respectively. The two inversion-related Ni^{II} ions also have a distorted octahedral environment. The four equatorial positions are occupied by the two N and the two O atoms from the SALPD²⁻ ligand. The axial positions of this distorted octahedron are completed by the O atom from the bridging acetate and another O atom from the dmf. The terminal Ni atom is 0.0632 (3) Å out of the equatorial plane defined by atoms N1, O1, N2 and O2.



The dihedral angle between the two equatorial planes (O1, O2, O1ⁱ, O2ⁱ and O1, O2, N1, N2) of the neighbouring polyhedra is 23.68 (8)° [symmetry code:

† Alternative name: bis(μ -acetato)-1:3 κ^2 O:O':2:3 κ^2 O:O'-bis(*N,N*-dimethylformamide)-1 κ O,2 κ O-bis{ μ -2,2'-[1,3-propanediylbis(nitrilomethylidyne)]diphenolato}-1 κ^4 N,N',O,O':3 κ^2 O,O':2 κ^4 N,N',O,O':-3 κ^2 O,O'-manganese(II)dinickel(II).

(i) $-x, -y, -z$]. A comparison of the dihedral angle between the two equatorial planes of the neighbouring polyhedra (φ), between the Ni—O—M(Ni, Cd, Mn)—O bridging plane and the coordination plane around the Ni atom (κ), along with the related distance ranges and bridging angles, are given in Table 1 for the three trimeric metal complexes recently studied in this laboratory. The bond lengths and angles within the ligands show no unusual values. The SALPD²⁻ ligand is not planar. The dihedral angles between the equatorial plane (O1, O2, N1, N2) and the two salicylidimine residues (N1, C11, C12–C17, O2 and N2, C7, C1–C6, O1) are 26.91 (7) and 32.36 (9)°, respectively. The Mn—O_{SALPD²⁻} bond lengths [2.163 (1)–2.166 (2) Å] are shorter than the Mn—O_{acetate} distances [2.194 (2) Å]. The Ni···Mn distance is 3.133 (2) Å. The six-membered chelate ring (Ni, N2, C8, C9, C10, N1) has a flattened chair conformation. The distances of the two *para*-positioned chair atoms, Ni and C9, from the plane of N1, N2, C8 and C10, are 0.0428 (1) and -0.344 (3) Å, respectively. The magnetic behaviour of this compound is currently under investigation.

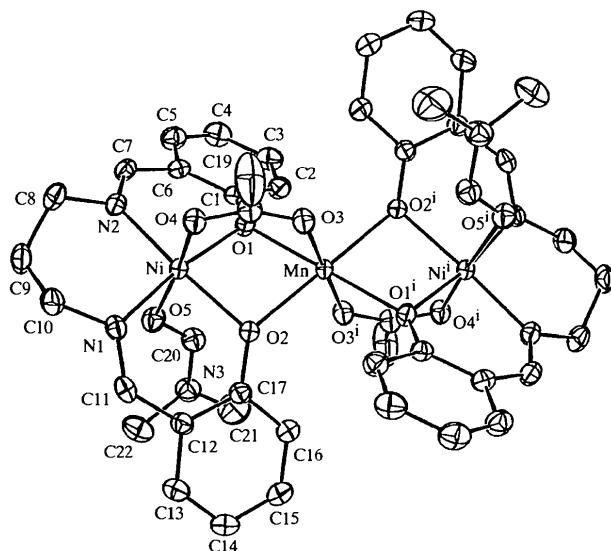


Fig. 1. The molecular structure of the title compound, with the atom-numbering scheme. Displacement ellipsoids are drawn at the 30% probability level. H atoms have been omitted for clarity. [Symmetry code (i) $-x, -y, -z$].

Experimental

To a solution of bis-*N,N'*-salicylidene-1,3-propanediamine (0.565 g, 2 mmol) in hot ethanol (50 ml), ammonia solution (20%, 10 ml) was added and the mixture heated to boiling point. Then, a solution of NiCl₂·6H₂O (4.75 g, 2 mmol) in hot water (30 ml) was added, and the resulting mixture was set aside. After 2 h, the light-green Ni complex was filtered, and dried at 423–433 K for 4 h. This complex (0.338 g, 1 mmol) was dissolved in hot DMF (50 ml) and the temperature of the solution was increased to boiling point (383 K). Manganese acetate solution (0.173 g, 1 mmol, in 20 ml hot methanol) was added dropwise to the final mixture. Green crystals formed after 24 h.

Crystal data

[MnNi₂(C₂H₃O₂)₂·
(C₃H₇NO)₂·
(C₁₇H₁₆N₂O₂)₂]

M_r = 997.30

Triclinic

P $\bar{1}$

a = 9.614 (4) Å

b = 10.664 (4) Å

c = 12.260 (3) Å

α = 112.37 (3)°

β = 100.77 (3)°

γ = 90.20 (3)°

V = 1137.9 (4) Å³

Z = 1

D_s = 1.46 Mg m⁻³

D_m not measured

Mo K α radiation

λ = 0.71073 Å

Cell parameters from 25
reflections

θ = 10–18°

μ = 1.15 mm⁻¹

T = 295 K

Prismatic

0.32 × 0.20 × 0.16 mm

Green

Data collection

Enraf–Nonius CAD-4
diffractometer

$\omega/2\theta$ scans

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

T_{min} = 0.776, *T_{max}* = 0.831

4862 measured reflections

4604 independent reflections

3569 reflections with
I > $\sigma(I)$

R_{int} = 0.011

θ_{\max} = 26.3°

h = $-11 \rightarrow 11$

k = $-13 \rightarrow 0$

l = $-14 \rightarrow 15$

3 standard reflections
frequency: 120 min
intensity decay: 1.4%

Refinement

Refinement on *F*

R = 0.031

wR = 0.040

(Δ/σ)_{max} = 0.002

$\Delta\rho_{\max}$ = 0.37 e Å⁻³

$\Delta\rho_{\min}$ = -0.09 e Å⁻³

Table 1. Structural data, bridging angles and dihedral angles (φ and κ) for three homo- or hetero-trinuclear complexes

Complex	Ni—O (Å)	M—O (Å)	Ni—M (Å)	O—M—O (°)	O—Ni—N (°)	φ (°)	κ (°)
[Ni ₃ (CH ₃ CO ₂) ₂ (SALPD) ₂ (dmsO) ₂] [†]	2.010 (3)–2.254 (3)	2.024 (3)–2.098 (3)	3.043 (2)	79.4 (1)	89.8 (2)–90.6 (2)	21.9 (1)	33.1 (1)–35.06 (7)
[CdNi ₂ (CH ₃ CO ₂) ₂ (SALPD) ₂ (dmf) ₂] [‡]	2.012 (1)–2.190 (2)	2.260 (1)–2.293 (2)	3.227 (5)	73.66 (5)	88.09 (7)–89.76 (6)	23.10 (7)	26.38 (6)–32.80 (7)
[MnNi ₂ (CH ₃ CO ₂) ₂ (SALPD) ₂ (dmf) ₂] [§]	2.017 (2)–2.184 (2)	2.163 (1)–2.194 (2)	3.133 (2)	76.66 (6)	88.93 (8)–90.38 (7)	23.68 (8)	26.91 (7)–32.36 (9)

[†] Ülkü, Ercan *et al.* (1997). [‡] Ülkü, Tahir *et al.* (1997). [§] The title compound.

S = 1.10
3569 reflections
286 parameters
H atoms: see below
 $w = 1/[\sigma F^2 + (0.02F)^2 + 0.10]$

Extinction correction: none
Scattering factors from *International Tables for X-ray Crystallography* (Vol. IV)

Ülkü, D., Ercan, F., Atakol, O. & Dinçer, F. N. (1997). *Acta Cryst.* C53, 1056–1057.

Ülkü, D., Tahir, M. N., Atakol, O. & Nazır, H. (1997). *Acta Cryst.* C53, 872–874.

Table 2. Selected geometric parameters (Å, °)

Ni···Mn	3.133 (2)	O1—C1	1.309 (2)
Ni—O1	2.035 (2)	O2—C17	1.320 (3)
Ni—O2	2.017 (2)	O3—C18	1.251 (3)
Ni—O4	2.046 (2)	O4—C18	1.247 (4)
Ni—O5	2.184 (2)	O5—C20	1.226 (3)
Ni—N1	2.016 (2)	N1—C10	1.465 (3)
Ni—N2	2.036 (2)	C9—C10	1.514 (3)
Mn—O1	2.163 (1)	C11—C12	1.452 (4)
Mn—O2	2.166 (2)	C18—C19	1.510 (5)
Mn—O3	2.194 (2)		
O1—Ni—O2	82.98 (7)	O5—Ni—N2	84.79 (8)
O1—Ni—O4	93.66 (8)	N1—Ni—N2	97.49 (9)
O1—Ni—O5	88.22 (8)	O1—Mn—O2	76.66 (6)
O1—Ni—N1	172.58 (8)	O1—Mn—O3	85.95 (6)
O2—Ni—O4	95.10 (7)	O2—Mn—O3	87.74 (7)
O2—Ni—O5	91.55 (7)	Ni—O1—Mn	96.49 (6)
O2—Ni—N2	171.23 (8)	Ni—O1—C1	123.4 (2)
O4—Ni—N1	90.23 (8)	Mn—O1—C1	135.9 (2)
O4—Ni—N2	88.77 (8)	Ni—O2—Mn	96.95 (7)
O5—Ni—N1	88.64 (8)	Mn—O3—C18	130.5 (2)

All non-H atoms were refined with anisotropic displacement parameters. The H-atom positions were taken from difference maps. A riding model was used for all H atoms, with $U_{iso}(H) = 1.3U_{eq}(C)$ of the parent atom.

Data collection: *CAD-4 EXPRESS* (Enraf–Nonius, 1993). 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: *ORTEPII* (Johnson, 1976) in *MolEN*. 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: FR1111). Services for accessing these data are described at the back of the journal.

References

- Enraf–Nonius (1993). *CAD-4 EXPRESS*. Version 1.1. Enraf–Nonius, Delft, The Netherlands.
- Fair, C. K. (1990). *MolEN. An Interactive Intelligent System for Crystal Structure Analysis*. Enraf–Nonius, Delft, The Netherlands.
- Fukuhara, C., Tsuneyoshi, K., Matsumoto, N., Kida, S., Mikuriya, M. & Mori, M. (1990). *J. Chem. Soc. Dalton Trans.* pp. 3473–3479.
- Gerli, A., Hagen, K. S. & Marzilli, L. (1991). *Inorg. Chem.* 30, 4673–4676.
- Johnson, C. K. (1976). *ORTEPII*. Report ORNL-5138. Oak Ridge National Laboratory, Tennessee, USA.

Acta Cryst. (1998). C54, 1270–1272

Triaqua(pyridine-2,6-dipicolinato-*O,N,O'*)-iron(III) Bis(pyridine-2,6-dipicolinato-*O,N,O'*)iron(III) Hexahydrate: an Unusual Ion-Pair Compound

KHALIL A. ABBOUD, CHENG XU AND RUSSELL S. DRAGO

Department of Chemistry, University of Florida, PO Box 117200, Gainesville, Florida 32611-7200, USA. E-mail: abboud@chem.ufl.edu

(Received 24 November 1997; accepted 6 January 1998)

Abstract

The reaction of dipicolinic acid (2,6-pyridinedicarboxylic acid) with FeCl₃ results in the unusual title ion-pair compound, [Fe(C₇H₃NO₄)(H₂O)₃][Fe(C₇H₃NO₄)₂].6H₂O. Each Fe atom has an octahedral geometry. The dipicolinate ligands are nearly planar, with the two in the anion being perpendicular to each other and displaying a dihedral angle of 93.74 (6)°. The Fe—O(carboxylate) bond distances are comparable and range from 2.008 (2) to 2.028 (2) Å, while the Fe—N distances are 2.059 (2), 2.054 (2) and 2.054 (2) Å. The Fe—O(water) distances are 1.971 (2), 1.987 (2) and 2.004 (2) Å. The cation, anion and water molecules are involved in an extensive three-dimensional hydrogen-bonding network, with O···O distances ranging from 2.36 (2) to 2.953 (3) Å and angles ranging from 129 to 177°.

Comment

The reaction of iron with dipicolinic acid (2,6-pyridinedicarboxylic acid, dipicH₂) is more complicated than expected, particularly in the solid state. Several crystal structures of iron(III) and iron(II) complexes with dipicH₂ and its derivatives have been reported in which mononuclear, binuclear and polynuclear structures are formed. The ligand-to-iron ratio can be one and two, and six- and seven-coordinate iron complexes have been reported (Laine *et al.*, 1995, 1995*a,b,c*; Hseu *et al.*, 1991; Marsh, 1993; Cousson *et al.*, 1992; Thich *et al.*, 1976). Interest in this area stems from the biological