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Acta Cryst. (1998). C**54**, 468–470

Bis[μ-*N*,*N*′-bis(salicylidene)-1,3-propanediaminato]bis(dimethylformamide)di(μ-nitrito)copper(II)dinickel(II)–Dimethylformamide (1/2)†

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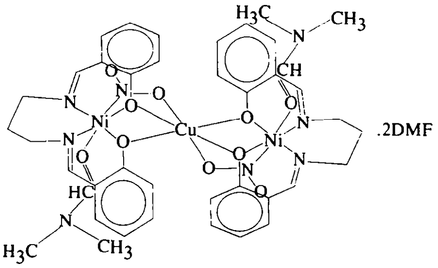
(*Received 22 July 1997; accepted 7 October 1997*)

Abstract

The unit cell of the title compound, $[CuNi_2(NO_2)_2(C_{17}H_{16}N_2O_2)_2(C_3H_7NO)_2].2C_3H_7NO$, contains two molecules of the linear heterotrinuclear complex and four solvent molecules. The central Cu^{II} ion and the terminal Ni^{II} ions have distorted octahedral coordination spheres. The Cu–Ni pairs are each triply bridged, by the O atoms of an *N*,*N*′-bis(salicylidene)-1,3-propanediaminato ($salpd^{2-}$) ligand, and by an O and an N atom of a nitrite group. The central Cu^{II} ion, located on an inversion centre, has a total of six O atoms in its coordination sphere: two from each $salpd^{2-}$ ligand and one from each bridging nitrite group. The Ni^{II} ions are related by the inversion centre and each is coordinated by the two O and two N atoms of a $salpd^{2-}$ ligand and one N atom from a nitrite and an O atom from a dimethylformamide (dmf) ligand. The dmf and nitrite groups are mutually *trans* about the Ni^{II} ion. The Cu—Ni distance is 2.9967 (4) Å.

Comment

Binuclear and trinuclear metal complexes based on Schiff base ligands have been the subject of considerable interest in our laboratories, *e.g.* $[Cu_2(C_{11}H_{10}ClNO_2)_2]$ (Tahir *et al.*, 1996), $[Cu_2(C_{14}H_{11}NO_2)_2]$ (Ülkü, Ercan, Atakol, Ercan & Gencer, 1997), $[Cd(C_2H_3O_2)_2\{Ni(C_3H_7NO)(C_{17}H_{16}N_2O_2)\}_2]$ (Ülkü, Tahir *et al.*, 1997) and $[Ni_3(C_{17}H_{16}N_2O_2)_2(CH_3CO_2)_2].2[(CH_3)_2SO]$ (Ülkü, Ercan, Atakol & Dinçer, 1997). The magnetic super-exchange interactions of the paramagnetic ions over the bridges made up of diamagnetic atoms make these polynuclear complexes interesting. The structure and magnetic properties of the trinuclear complex $[Zn\{(CH_3CO_2)(salpd)Cu\}_2]$ (Fukuhara *et al.*, 1990) have been reported previously. Structural details are available for similar complexes formulated as $[M_3(salpn)_2(CH_3CO_2)_2].2dmf$ [*M* = Co, Fe; salpn is *N*,*N*′-bis(salicylidene)-2,2-dimethylpropylenediaminate and dmf is dimethylformamide] (Gerli *et al.*, 1991). We report here a new heterometallic trinuclear complex, (I), which, in addition to the two O-atom bridges between a pair of metal ions, has a third bridge provided by an NO_2 group. In previously studied complexes, the third bridge is usually an acetate group.



(I)

The unit cell of the title complex contains two centrosymmetric trinuclear $[Cu\{(NO_2)(salpd)Ni(dmf)\}_2]$ molecules, with the central Cu^{II} ion located on an inversion centre. Two additional dmf solvent molecules per trinuclear complex bridge the trimers *via* hydrogen bonds C21—H21···O4(*x*, *y*, *z*) and C19—H191···O6($x-\frac{1}{2}$, $-y+\frac{1}{2}$, $z+\frac{1}{2}$). The coordination around the central Cu^{II} ion is distorted octahedral, consisting of four bridging O atoms from two $salpd^{2-}$ ligands in the equatorial plane [O1, O2, O1^{i} and O2^{i}; symmetry code: (i) $-x$, $-y$, $-z$] and two O atoms from two bridging NO_2 groups (Fig. 1). The Cu—O bond lengths range from 2.048 (2) to 2.103 (2) Å, the longest bond belonging to a nitrite O atom. Due to the centre of symmetry, the Cu^{II} ion is in the equatorial plane. The two terminal Ni^{II} ions, related by the inversion centre, also have distorted octahedral coordination environments, each involving two N and two O atoms from a $salpd^{2-}$ ligand, with the apical positions of the octahedron occupied by the O and N atoms from a dmf ligand and a nitrite group, respectively. The Ni—O and Ni—N bond-length ranges are 2.003 (2)–2.152 (2) and 2.014 (3)–2.131 (3) Å, respectively. The Ni^{II} ion lies only 0.0377 (4) Å out of the equatorial plane defined by atoms O1, O2, N1 and N2. The equatorial plane

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† Alternative name: bis(dimethylformamide)-1κ*O*,2κ*O*-di-μ-nitrito-1:3κ^2*N*:*O*;2:3κ^2*N*:*O*-bis{μ-2,2′-[1,3-propanediylbis(nitrilomethylidyne)diphenolato}-1κ^4*N*,*N*′,*O*,*O*′:3κ^2*O*,*O*′;2κ^4*N*,*N*′,*O*,*O*′:3κ^2*O*,*O*′-copper(II)dinickel(II) bis(dimethylformamide) solvate.

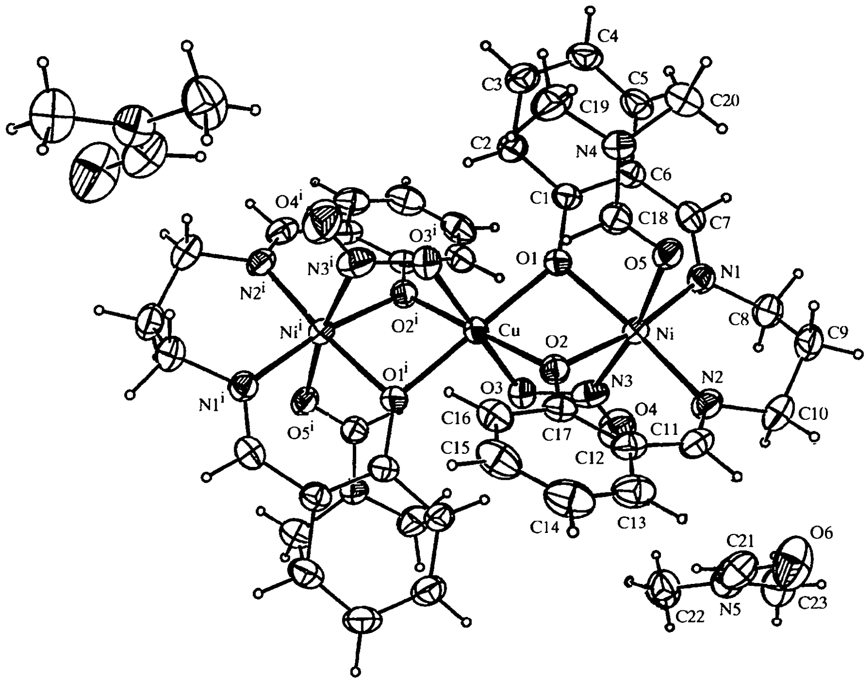

Fig. 1. The molecular structure of the title compound with the atomic numbering scheme. The displacement ellipsoids are drawn at the 30% probability level. H atoms are shown as small circles of arbitrary radii. [Symmetry code: (i) $-x$, $-y$, $-z$.]

formed by atoms O1, O2, O1^{i} and O2^{i}, and that formed by atoms O1, O2, N1 and N2, of the two octahedra sharing O1 and O2, have a dihedral angle of 30.8 (1)°. The dihedral angles between the equatorial plane defined by atoms O1, O2, N1 and N2 around the Ni^{II} centre and the least-squares planes of the two salicylaldimine residues, O1, C1–C6, C7, N1 and N2, C11, C12–C17, O2, are 28.4 (1) and 20.3 (1)°, respectively. The salpd^{2-} ligand has a flat-shell conformation. The Cu···Ni distance is 2.9967 (4) Å, which is too long to have a direct exchange. The chelate ring formed by atoms Ni, N1, C8, C9, C10 and N2 has a chair conformation. The mutually-*para* Ni and C9 atoms are located 0.299 (4) and −0.746 (4) Å, respectively, from the best plane through atoms N1, C8, C10 and N2. The coordination in the title compound resembles the structures of the known trinuclear complexes mentioned above. The most noticeable difference in the title compound is the presence of two additional dmf molecules, cross-linking the complexes *via* intermolecular hydrogen bonds, as detailed in Table 2.

Experimental

To a solution of N,N'-bis(salicylidene)-1,3-propanediamine (0.282 g, 1.00 mmol) in hot ethanol (50 ml), 20% ammonia solution (10 ml) was added and the mixture was heated to boiling point. Then a solution of $NiCl_2.6H_2O$ (0.238 g, 1.00 mmol) in hot water (30 ml) was added and the resulting mixture was set aside. After 2 h, the light-green nickel complex was filtered and dried at 423 K for 3 h. The complex (0.339 g, 1.00 mmol) was then dissolved in hot dimethylformamide (50 ml) and the temperature of the solution was increased to 383 K. A solution of $CuCl_2.2H_2O$ (0.085 g, 0.5 mmol) in hot MeOH (10 ml) and a solution of $NaNO_2$ (0.069 g, 1 mmol) in hot water (5 ml) were added slowly to the solution. The resulting mixture was set aside for 24 h. Brown prismatic air-sensitive crystals were sealed in capillary tubes for X-ray measurements.

Crystal data

$[CuNi_2(NO_2)_2(C_{17}H_{16}N_2O_2)_2(C_3H_7NO)_2].2C_3H_7NO$
$M_r = 1126.011$
Monoclinic
$P2_1/n$
$a = 11.0474\,(11)$ Å
$b = 15.6902\,(12)$ Å
$c = 15.0930\,(11)$ Å
$\beta = 104.974\,(2)°$
$V = 2527.4\,(4)$ Å^3
$Z = 2$
$D_x = 1.4796$ Mg m^{-3}
D_m not measured

Mo $K\alpha$ radiation
$\lambda = 0.71073$ Å
Cell parameters from 25 reflections
$\theta = 11.46–20.84°$
$\mu = 1.226$ mm^{-1}
$T = 295$ K
Parallelepiped
0.35 × 0.20 × 0.15 mm
Brown

Data collection

Enraf–Nonius CAD-4 diffractometer

3312 reflections with $I > 3\sigma(I)$

$\omega/2\theta$ scans
Absorption correction: empirical *via* ψ scans (Fair, 1990)
$T_{min} = 0.671$, $T_{max} = 0.832$
5092 measured reflections
4836 independent reflections

$R_{int} = 0.016$
$\theta_{max} = 25.46°$
$h = -13 \rightarrow 0$
$k = -18 \rightarrow 0$
$l = -17 \rightarrow 17$
3 standard reflections
frequency: 120 min
intensity decay: none

Refinement

Refinement on F
$R = 0.033$
$wR = 0.040$
$S = 0.93$
3312 reflections
322 parameters
H atoms riding (see below)
$w = 1/[\sigma(F^2) + (0.02F)^2 + 0.5]$; $w = 0$ if $F^2 < 3\sigma(F^2)$

$(\Delta/\sigma)_{max} = 0.00014$
$\Delta\rho_{max} = 0.510$ e Å^{-3}
$\Delta\rho_{min} = -0.121$ e Å^{-3}
Extinction correction: none
Scattering factors from *International Tables for X-ray Crystallography* (Vol. IV)

Table 1. *Selected geometric parameters (Å, °)*

Cu—Ni	2.9967 (4)	Ni—O5	2.152 (2)
Cu—O1	2.048 (2)	Ni—N1	2.019 (3)
Cu—O2	2.063 (2)	Ni—N2	2.014 (3)
Cu—O3	2.103 (2)	Ni—N3	2.131 (3)
Ni—O1	2.016 (2)	O3—N3	1.319 (4)
Ni—O2	2.003 (2)	O4—N3	1.183 (4)
O1—Cu—O2	78.70 (8)	O5—Ni—N1	87.3 (1)
O1—Cu—O3	85.16 (9)	O5—Ni—N2	89.0 (1)
O2—Cu—O3	85.86 (9)	O5—Ni—N3	171.0 (1)
O1—Ni—O2	80.88 (8)	N1—Ni—N2	98.5 (1)
O1—Ni—O5	88.83 (9)	N1—Ni—N3	97.3 (1)
O1—Ni—N1	89.4 (1)	N2—Ni—N3	97.9 (1)
O1—Ni—N2	171.7 (1)	Cu—O1—Ni	95.02 (8)
O1—Ni—N3	83.4 (1)	Cu—O2—Ni	94.94 (8)
O2—Ni—O5	90.87 (9)	Cu—O3—N3	110.4 (2)
O2—Ni—N1	170.2 (1)	Ni—N3—O3	116.3 (2)
O2—Ni—N2	91.1 (1)	Ni—N3—O4	129.8 (3)
O2—Ni—N3	83.3 (1)	O3—N3—O4	114.0 (3)

Table 2. *Hydrogen-bonding geometry (Å, °)*

D—H···A	D—H	H···A	D···A	D—H···A
C19—H191···O6^{i}	1.01	2.41	3.332 (6)	152
C21—H21···O4	0.98	2.47	3.387 (5)	154

Symmetry code: (i) $x - \frac{3}{2}, \frac{1}{2} - y, \frac{1}{2} + z$.

All non-H atoms were refined with anisotropic displacement parameters. H atoms were placed geometrically, 0.95 Å from their parent C atoms, except for the H atoms of the dmf and propanediamine ligands, which were refined for a few cycles. A riding model was subsequently used for all H atoms, with $U_{eq}(H) = 1.3U_{eq}(C)$.

Data collection and cell refinement were performed using *CAD*-4 *EXPRESS* (Enraf–Nonius, 1993). *MolEN* (Fair, 1990) was used for data reduction, structure solution and refinement, molecular graphics and the preparation of material for publication. Other programs used include *PLATON* (Spek, 1990).

The authors wish to acknowledge the Scientific and Technical Research Council of Turkey (grant DPT/TBAG1) for the purchase of the CAD-4 diffractometer.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: BM1190). Services for accessing these data are described at the back of the journal.

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Acta Cryst. (1998). C**54**, 470–473

Bis(tetra-*n*-butylammonium) Bis[(4-cyanophenyl)dithiocarbimato(2–)-*S*,*S*′]nickel(II)[†]

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(*Received 27 May 1997; accepted 17 November 1997*)

Abstract

The title compound, $[N(C_4H_9)_4]^+_2.[Ni(C_8H_4N_2S_2)_2]^{2-}$, crystallizes with the Ni atom on a crystallographic inversion center. The phenyl rings of the ligands make an angle of 50.50 (5)° with the plane spanned by the central nickel–sulfur fragment. The bond lengths do not indicate that the formal negative charge on the dithiocarbimato moiety is delocalized into the phenyl ring.

[†] Alternative name: bis(tetra-*n*-butylammonium) bis[(4-cyanophenylimino)dithiocarboxylato(2−)-*S*,*S*′]nickel(II).

Acta Crystallographica Section C
ISSN 0108-2701 © 1998