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Lists of structure factors, anisotropic displacement parameters and H-atom coordinates have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 71716 (35 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England. [CIF reference: HU1048]

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trans-Bis(2-hydroxyiminopropionato-*N*,*O*)-dimethanolnickel(II) Dimethanol Solvate, $[Ni\{CH_3C(NOH)COO\}_2(CH_3OH)_2].2CH_3OH$

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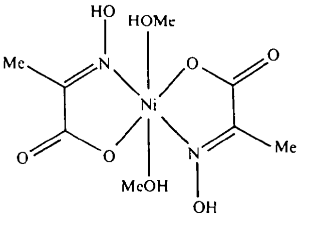
Abstract

$[Ni(C_3H_4NO_3)_2(CH_3OH)_2].2CH_3OH$ contains Ni in a six-coordinated state and decomposes rapidly in air by loss of methanol. The Ni coordination environment is a slightly distorted octahedron. The anions of the 2-hydroxyiminopropionic acids lie in a plane in a *trans* position to each other. Octahedral coordination is completed by two CH_3OH molecules.

Comment

trans-Bis(2-hydroxyiminopropionato-*N*,*O*)dimethanolnickel(II) dimethanol solvate, $[Ni\{CH_3C(NOH)COO\}_2(CH_3OH)_2].2CH_3OH$, was prepared during our work on the synthesis and systematic study of complexes of 2-oximinocarboxylic acids with divalent metal ions (Lampeka, Skopenko, Sliva & Hennig, 1988; Skopenko, Lampeka, Sliva & Stakhov, 1990). Some anionic complexes have been analysed by X-ray diffraction (Simonov, Sliva, Mazus, Dvorkin & Lampeka, 1989; Dvorkin, Simonov, Sliva, Lampeka, Mazus & Skopenko, 1989). In these compounds the oximino groups are mutually *cis* and form the usual intramolecular hydrogen bond. The mutal arrangement of the oximino groups in neutral complexes is of interest. The present paper reports the structure of one example from this family of compounds. The geometry and atom numbering of the complex (I) are illustrated in Fig. 1.



(I)

The complex unit has an inversion centre at the Ni atom. Ni displays slightly distorted octahedral coordination. Each of the two bidentate 2-oximinopropionic anions is bound to Ni through the oxime N atom and carboxylic O atom. Both anions lie in the same plane with the oxime groups on opposite sides of the Ni ion. This renders formation of an intramolecular hydrogen bond impossible. Two methanol molecules are bonded to the metal atom above and below the equatorial $Ni[CH_3C(NOH)COO]_2$ plane, thus completing the octahedral coordination at the Ni atom.

Bond distances for the 2-oximinopropionate ions are close to those reported in the literature (Simonov, Sliva, Mazus, Dvorkin & Lampeka, 1989;

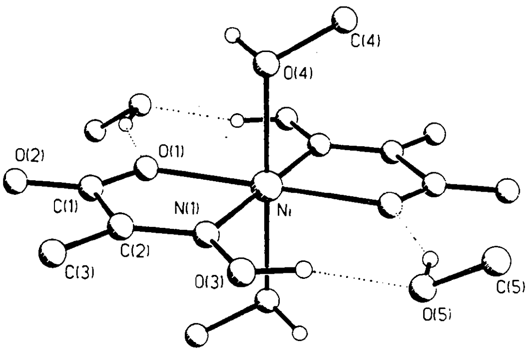


Fig. 1. The geometry and atom-numbering scheme of the complex molecule (dashed lines show the hydrogen bonds).

Dvorkin, Simonov, Sliva, Lampeka, Mazus & Skopenko, 1989; Skopenko, Sliva, Simonov, Dvorkin, Mazus & Lampeka, 1990). The absence of an intramolecular hydrogen bond implies an increase of the Ni—N(1)—O(3) angle and a decrease of the C(2)—N(1)—O(3) angle, by about 6° each, in comparison to those in complexes where an O···H···O bond is present. The uncoordinated methanol closes a sort of intramolecular cycle. Thus, the methanol O atom accepts one hydrogen bridge from the oximino group and the methanol H(O) atom forms related bonds with the O(1) atom of the other anion of the same complex unit.

The structure is held together by a network of intermolecular hydrogen bridges. Each coordinated methanol molecule forms a hydrogen bridge extending to the O(2) atom of the carboxyl group of the neighbouring Ni complex.

Experimental

Crystals were grown from methanol. Previous experiments have shown that the crystals decompose on drying. The crystal for the X-ray study was picked from the mother liquor, cemented to a glass capillary and cooled to 118 K.

Crystal data

$[Ni(C_3H_4NO_3)_2(CH_4O)_2].2CH_4O$
$M_r = 391.0$
Triclinic
$P\bar{1}$
$a = 6.436\ (3)$ Å
$b = 7.681\ (3)$ Å
$c = 9.637\ (3)$ Å
$\alpha = 107.25\ (3)°$
$\beta = 98.85\ (3)°$
$\gamma = 104.59\ (3)°$
$V = 427\ (1)$ Å^3

$Z = 1$
$D_x = 1.52$ Mg m^{-3}
Cu $K\alpha$ radiation
$\lambda = 1.5418$ Å
Cell parameters from 20 reflections
$\theta = 30$-$50°$
$\mu = 1.19$ mm^{-1}
$T = 118$ K
Stick
0.2 × 0.15 × 0.1 mm
Light blue

Data collection

Enraf-Nonius CAD-4 diffractometer
ω scans
Absorption correction: none
1399 measured reflections
1268 independent reflections
1192 observed reflections $[I > 3\sigma(I)]$

$\theta_{max} = 60°$
$h = 0 \rightarrow 7$
$k = -8 \rightarrow 8$
$l = -10 \rightarrow 10$
3 standard reflections monitored every 100 reflections intensity variation: 0.984-1.038

Refinement

Refinement on F
$R = 0.034$
$wR = 0.060$
1192 reflections
118 parameters
$w = 4F_o^2/\sigma^2(F_o^2)$
$(\Delta/\sigma)_{max} = 0.23$

$\Delta\rho_{max} = 0.65$ e Å^{-3}
$\Delta\rho_{min} = -0.43$ e Å^{-3}
Extinction correction: none
Atomic scattering factors from *International Tables for X-ray Crystallography* (1974, Vol. IV)

Table 1. *Fractional atomic coordinates and equivalent isotropic displacement parameters* (Å^2)

$$B_{eq} = (4/3)\Sigma_i\Sigma_j\beta_{ij}\mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	B_{eq}
Ni(1)	0	0	0	1.285 (7)
O(1)	−0.3295 (2)	−0.1393 (1)	−0.0517 (1)	1.56 (2)
O(2)	−0.5932 (2)	−0.3017 (2)	0.0281 (1)	1.94 (2)
O(3)	0.1263 (2)	−0.0754 (2)	0.3058 (1)	2.05 (2)
O(4)	−0.0681 (2)	0.2418 (1)	0.1199 (1)	1.62 (2)
O(5)	0.4728 (2)	−0.1034 (2)	−0.2960 (1)	2.39 (3)
N(1)	−0.0294 (2)	−0.0996 (2)	0.1802 (1)	1.52 (3)
C(1)	−0.3991 (3)	−0.2124 (2)	0.0415 (2)	1.49 (3)
C(2)	−0.2281 (2)	−0.1887 (2)	0.1776 (2)	1.53 (3)
C(3)	−0.2970 (3)	−0.2638 (2)	0.2936 (2)	2.23 (4)
C(4)	0.0988 (3)	0.4264 (2)	0.1904 (2)	2.55 (4)
C(5)	0.3160 (3)	−0.2584 (3)	−0.4167 (2)	2.95 (4)

Table 2. *Selected geometric parameters* (Å, °)

Ni(1)—O(1)	2.0266 (8)	O(3)—N(1)	1.379 (1)
Ni(1)—O(4)	2.0661 (7)	O(4)—C(4)	1.437 (1)
Ni(1)—N(1)	2.111 (1)	O(5)—C(5)	1.415 (1)
O(1)—C(1)	1.271 (2)	C(1)—C(2)	1.510 (2)
N(1)—C(2)	1.282 (2)	O(1)···O(5′)	2.690 (2)
C(2)—C(3)	1.478 (2)	O(3)···O(5′)	2.640 (1)
O(2)—C(1)	1.231 (2)	O(2)···O(4′)	2.630 (1)
O(1)—Ni(1)—O(4)	86.91 (3)	O(3)—N(1)—C(2)	113.96 (9)
O(1)—Ni(1)—N(1)	78.04 (3)	O(1)—C(1)—O(2)	125.1 (1)
O(4)—Ni(1)—N(1)	88.28 (3)	O(1)—C(1)—C(2)	116.84 (9)
Ni(1)—O(1)—C(1)	116.36 (7)	O(2)—C(1)—C(2)	118.0 (2)
Ni(1)—O(4)—C(4)	122.53 (6)	N(1)—C(2)—C(1)	114.0 (1)
Ni(1)—N(1)—O(3)	131.23 (7)	N(1)—C(2)—C(3)	126.0 (2)
Ni(1)—N(1)—C(2)	114.68 (8)	C(1)—C(2)—C(3)	120.1 (1)

O(4)—Ni(1)—O(1)—C(1)	−87.19 (0.11)
O(1)—Ni(1)—O(4)—C(4)	−175.40 (0.12)
O(1)—Ni(1)—N(1)—O(3)	−177.93 (0.14)
O(4)—Ni(1)—N(1)—O(3)	−90.72 (0.13)
Ni(1)—O(1)—C(1)—O(2)	−179.96 (0.15)
Ni(1)—N(1)—C(2)—C(1)	2.80 (0.17)
O(3)—N(1)—C(2)—C(1)	179.02 (0.12)
O(1)—C(1)—C(2)—N(1)	−1.43 (0.21)
O(2)—C(1)—C(2)—N(1)	177.80 (0.15)
N(1)—Ni(1)—O(1)—C(1)	1.70 (0.11)
N(1)—Ni(1)—O(4)—C(4)	106.49 (0.12)
O(1)—Ni(1)—N(1)—C(2)	−2.52 (0.11)
O(4)—Ni(1)—N(1)—C(2)	84.69 (0.12)
Ni(1)—O(1)—C(1)—C(2)	−0.78 (0.18)
Ni(1)—N(1)—C(2)—C(3)	−176.48 (0.13)
O(3)—N(1)—C(2)—C(3)	−0.26 (0.23)
O(1)—C(1)—C(2)—C(3)	177.90 (0.15)
O(2)—C(1)—C(2)—C(3)	−2.87 (0.23)

Data were corrected for Lorentz-polarization effects. The structure was solved by the Patterson method and refined by full-matrix least-squares techniques. All H atoms were located in the difference Fourier maps. H(O3), H(O4) and H(O5) were refined isotropically; all other H atoms were included with fixed positional and displacement parameters. Structural calculations were carried out with a PDP − 11/23+ computer using the *SDP* program package (Frenz, 1978).

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A Binuclear Copper(II) Complex of the Deprotonated Anion of *N*,*N'*-Diglycylethylenediamine

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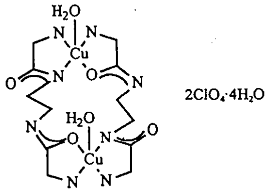
Abstract

The title compound, diaquabis[μ-N,N'-diglycylethylenediaminato(1 −)]-1κ^2N,N'':2$\kappa N',\kappa O'$;1$\kappa N'$,$\kappa O'$:2κ^2N,N''-dicopper(II) diperchlorate tetrahydrate, $[Cu_2(C_6H_{13}N_4O_2)_2(H_2O)_2]2ClO_4.4H_2O$, in which only one of the two amide protons of each *N*,*N'*-diglycylethylenediamine is released in solution, exists as a binuclear complex with inversion symmetry in the solid state. Each Cu^{II} ion is five-coordinate with a distorted square-pyramidal geometry. Two donar N atoms of one tetradentate ligand and one N atom and one O atom of the other ligand form a slightly distorted plane and a water O atom occupies the axial position. Hydrogen bonds help stabilize the crystal structure.

Comment

It has been shown by potentiometric and spectrophotometric methods (Bai & Martell, 1969; Smith & Martell, 1972; Muir & Rechani, 1974; Armani, Marchelli, Dossena, Casasti & Dallavalle, 1986) that in solution the Cu^{II} ion reacts with deprotonated diaminodiamide, $H_{-1}L$, to form the binuclear chelate $[Cu_2(H_{-1}L)_2]^{2+}$. Previously, we have studied the binuclear complex formed by Cu with a diaminodiamide ligand containing terminal propyl groups (Tahirov, Lu, Shu & Chung, 1994). In order to study the steric effects governing the differences between the two crystal structures, we prepared the title binuclear complex (I), the structure of which has been predicted by Smith & Martell (1972).



(I)

The ligand, *N*,*N'*-diglycylethylenediamine, was prepared as described by Goto, Okubo, Sawai & Yoshikawa (1970). A solution of $Cu(ClO_4)_2.6H_2O$ (0.01 mol in 100 ml water) was added dropwise to an aqueous solution of the ligand (0.01 mol in 100 ml water). The solution changed gradually from purple to blue and was stirred continuously for another 10 min. After adding sodium hydroxide (0.02 mol in 50 ml water), the solution changed from blue to dark red and was then filtered. The dark red filtrate was evaporated to dryness and recrystallized from an aqueous methanol solution.

The coordination geometry about each of the two Cu^{II} ions is a distorted square pyramid with a water O atom in the axial position, and two amine N atoms, one deprotonated amide N atom and an amide O atom in equatorial positions. The Cu^{II} ion deviates by 0.14 Å from the equatorial best plane towards the axial water O atom. Cu–water O-atom distances are in good agreement with the usual Cu–axial O-atom distances in Cu^{II} complexes with macrocyclic ligands. An analysis of the Cu—O distances in 166 Cu^{II} complexes using the Cambridge Structural Database (Allen, Kennard & Taylor, 1983) shows that these distances are within the wide range 1.9–2.8 Å, with one sharp peak at *ca* 1.9–2.0 Å for equatorial bonds and one wide peak with a maximum at 2.4 Å for axial bonds.