

Fig. 3. Projection of the structure along c . Open circles denote molecules with centers of gravity at $z = 0$, filled circles those with centers of gravity at $z = \frac{1}{2}$. The numbers indicate the positions of the midpoints of the molecules.

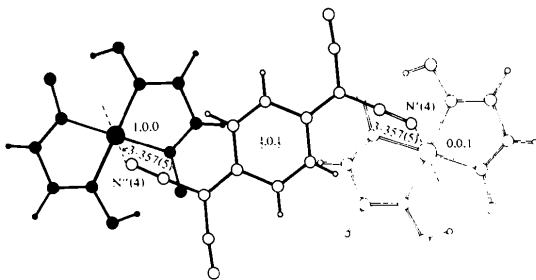


Fig. 4. Projection of two $Ni(gh)_2$ units and a TCNQ molecule onto the plane of the complex molecules showing the short contact between Ni and one of the nitrile N atoms of TCNQ (Å). The midpoints of the molecules are at the indicated positions, so that the molecules lie along $|101|$.

that of the benzoquinone dioximato compounds mentioned above (Keller *et al.*, 1977), despite the lower lattice symmetry ($P1$) of the latter systems.

The closest intermolecular interaction between $Ni(gh)_2$ and TCNQ occurs in direction $|\bar{1}01|$ along the diagonal of the xz plane. This is indicated in Fig. 4, which shows a projection of $Ni(gh)_2$ molecules at 1,0,0 and 0,0,1, and TCNQ at $\frac{1}{2}, 0, \frac{1}{2}$ onto the plane of the complex molecules. There is a short contact, 3.357 (5) Å, between Ni and one of the two terminal nitrile N atoms at each end of TCNQ. The angles, δ ,

between oxime N atoms, Ni, and the TCNQ N atom are 76.2 [N(1)—Ni—N'(4)] and 79.1° [N(2)—Ni—N'(4)], and their symmetry-related counterparts $180^\circ - \delta$. Due to the different surroundings of the two $C\equiv N$ groups at each end of TCNQ, a splitting of the $C\equiv N$ stretching frequencies at about 2215 cm^{-1} should be expected. Such a splitting amounting to ten wave numbers is observed in the benzoquinone dioximato compounds; in the present compound it is only about four wave numbers.

It has been stated (Flandrois & Chasseau, 1977) that the amount of charge transfer in TCNQ compounds can be estimated from the bond lengths. As in $Ni(gh)_2$ -TCNQ the quinoid character of TCNQ is at least as pronounced as in neutral TCNQ (Long, Sparks & Trueblood, 1965); zero charge transfer may be assumed, so that the compound is best considered to consist of neutral $Ni(gh)_2$ and neutral TCNQ. The black color of the crystals, however, may indicate an electronic interaction probably involving the Ni atoms and the terminal $C\equiv N$ groups of TCNQ along the path shown in Fig. 4.

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Structure of Bis[tris(hydroxymethyl)aminomethane]nickel(II) Diperchlorate*†

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Abstract. $Ni[H_2NC(CH_2OH)_3]_2(ClO_4)_2 \cdot C_8H_{22}N_2NiO_6^{2+} \cdot 2ClO_4^-$, $M_r = 499.93$, monoclinic. $P2_1/a$, $a =$

11.7249 (5), $b = 12.2353$ (5), $c = 6.3352$ (2) Å, $\beta = 92.857$ (3)°, $Z = 2$, $V = 907.70$ Å³, $D_x = 1.829$, $D_m = 1.83$ (1) Mg m⁻³, $\mu(Mo K\alpha) = 1.44$ mm⁻¹. The intensities were measured on a four-circle diffractometer. Least-squares refinement of 1405 unique reflexions gave an R value of 0.044. The structure consists of

* Metal Complexes with Mixed Ligands. 23.

† IUPAC name: bis(2-amino-2-hydroxymethyl-1,3-propanediol)-nickel(II) diperchlorate.

Table 1. Fractional atomic coordinates ($\times 10^4$) and equivalent isotropic thermal parameters, with *e.s.d.*'s in parentheses

$$B_{\text{eq}} = \frac{1}{3}(a^2\beta_{11} + b^2\beta_{22} + c^2\beta_{33} + 2ac\beta_{13}\cos\beta).$$

	x	y	z	B_{eq} (\AA^2)
Ni	0	0	0	1.92 (2)
N	3919 (3)	6269 (3)	620 (6)	2.4 (1)
C(1)	3261 (4)	4975 (4)	3179 (7)	3.2 (1)
C(2)	1909 (4)	6411 (4)	1862 (8)	2.4 (1)
C(3)	2527 (4)	4943 (4)	-656 (7)	2.8 (1)
C(4)	2885 (4)	5661 (3)	1242 (7)	3.4 (1)
O(1)	4335 (3)	4493 (3)	2784 (5)	3.7 (1)
O(2)	1695 (3)	7248 (3)	339 (6)	3.6 (1)
O(3)	3500 (3)	4369 (2)	-1417 (5)	2.6 (1)
O(4)	5057 (7)	1378 (4)	2566 (9)	9.5 (3)
O(5)	5888 (4)	1159 (4)	5887 (6)	7.0 (2)
O(6)	4835 (5)	2694 (4)	5130 (8)	10.8 (2)
O(7)	6503 (4)	2472 (4)	3536 (7)	8.1 (2)
Cl	5545 (1)	1889 (1)	4269 (2)	3.31 (4)

Table 2. Distances (\AA) and angles ($^\circ$) within the complex cation, with *e.s.d.*'s in parentheses

Corresponding values from tris in square brackets (Rudman *et al.*, 1978) have been included for comparison.

Ni—O(1)	2.059 (3)	O(3)—C(3)	1.442 (6) [1.431 (2)]
Ni—O(3)	2.082 (3)	N—C(4)	1.492 (6) [1.472 (2)]
Ni—N	2.055 (4)	C(1)—C(4)	1.533 (6) [1.522 (2)]
		C(2)—C(4)	1.534 (6) [1.531 (2)]
		C(3)—C(4)	1.531 (6) [1.522 (2)]
O(1)—C(1)	1.424 (6) [1.412 (2)]		
O(2)—C(2)	1.420 (6) [1.426 (2)]		
O(1)—Ni—O(3)	84.8 (1)	C(1)—C(4)—C(3)	111.8 (4)
O(1)—Ni—N	78.5 (1)	C(1)—C(4)—N	106.2 (3)
O(3)—Ni—N	81.2 (1)	C(1)—C(4)—C(3)	111.5 (4)
		C(2)—C(4)—N	113.3 (4)
Ni—O(1)—C(1)	113.7 (3)	C(3)—C(4)—N	105.9 (3)
Ni—O(3)—C(3)	109.9 (3)	C(4)—C(2)—O(2)	111.5 (4)
Ni—N—C(4)	101.0 (2)	C(4)—C(3)—O(3)	110.6 (4)
C(1)—C(4)—C(2)	108.1 (4)	C(4)—C(1)—O(1)	107.9 (4)

Table 3. Distances (\AA) and angles ($^\circ$) for the perchlorate group and the hydrogen-bond contacts in the structure, with *e.s.d.*'s in parentheses

Cl—O(4)	1.349 (6)	Cl—O(6)	1.416 (5)
Cl—O(5)	1.403 (4)	Cl—O(7)	1.427 (5)
O(4)—Cl—O(5)	112.5 (3)	O(5)—Cl—O(6)	108.2 (3)
O(1)—Cl—O(6)	113.3 (4)	O(5)—Cl—O(7)	110.7 (3)
O(4)—Cl—O(7)	106.3 (3)	O(6)—Cl—O(7)	105.4 (3)
O(2)···O(3)	2.697 (4)	N···O(6)	3.256 (6)
O(1)···O(6)	2.704 (5)	N···O(7)	3.069 (5)
O(2)···O(4)	2.891 (6)		
O(3)—H(O3)···O(2)	172 (7)	H(N1)···O(6)	161 (6)
O(1)—H(O1)···O(6)	171 (7)	H(N2)···O(7)	167 (6)
O(2)—H(O2)···O(4)	156 (5)		

complex in Table 2 and distances and angles for the perchlorate group and the hydrogen-bond contacts in Table 3.*

Discussion. The title compound is built up from mononuclear $[\text{Ni}\{\text{H}_2\text{NC}(\text{CH}_2\text{OH})_3\}_2]^{2+}$ complex cations (Fig. 2) and ClO_4^- anions, packed in every second layer perpendicular to the z axis. The closest anion–cation approach involves the hydroxymethyl O(1) and the perchlorate O(6) which are linked by means of a hydrogen bond. Hydrogen bonds also occur between adjacent cations, involving the Ni-bonded O(3) in one complex unit and the terminal O(2) in the other (Fig. 3, Table 3).

The $[\text{Ni}\{\text{H}_2\text{NC}(\text{CH}_2\text{OH})_3\}_2]^{2+}$ complex cation. The Ni atom is at a centre of symmetry, surrounded by two symmetry-related tridentate tris ligands. These are

* Lists of structure factors, anisotropic thermal parameters and coordinates and distances of H atoms have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 36707 (11 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

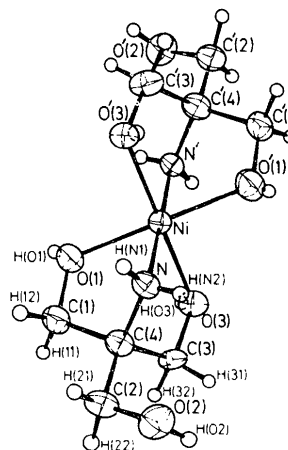


Fig. 2. The $[\text{Ni}\{\text{H}_2\text{NC}(\text{CH}_2\text{OH})_3\}_2]^{2+}$ cation (ORTEP, Johnson, 1965).

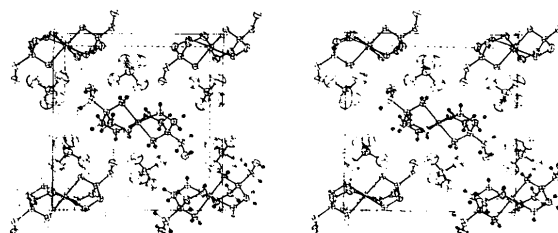


Fig. 3. A stereoscopic representation, viewed along the z axis, showing the hydrogen-bond interactions between adjacent complex cations. The contacts are indicated by dashed lines. Thermal ellipsoids are scaled to include 50% probability.

bonded *via* two hydroxymethyl groups, Ni–O = 2.082 and 2.059 Å, and one amino group, Ni–N = 2.055 Å, making a distorted octahedral arrangement. As the Ni²⁺ ion has a spherically symmetrical *d*⁸ electron configuration the distortion may reflect the chelation effects as well as non-equivalent ligand atoms. The longest bond distance is to the hydroxyl group, which is, as mentioned above, in hydrogen-bond contact with an adjacent cation complex. The other two Ni-bonded atoms are in hydrogen-bond contact with the anion (Fig. 3). The same situation is found in Ni[HN-(CH₂CONH₂)₃]₂(ClO₄)₂ (Sekizaki, 1976) where there are four Ni–O distances and two Ni–N distances in the range 2.01–2.11 Å with the angles in the range 81–108°.

With the exception of the N–C(4) bond the interatomic distances within the ligand molecule differ by less than 2σ (σ = e.s.d.'s in the present work) from the values found in free tris (Rudman, Eilerman & LaPlaca, 1978; Eilerman & Rudman, 1980, Table 2). The smallest differences are found when O(2) or C(2) is involved. The bonding situations for these atoms in the two structures are similar, *i.e.* they are within hydrogen-bond distance with the surrounding groups. The influence of the metal atom on the interatomic distances in the ligand is thus small except for the N–C(4) interaction where a lengthening of the bond greater than 3σ is shown.

The C–H, N–H and O–H distances vary between 0.60 (6) and 1.00 (6) Å. These are normal distances according to earlier reported values determined from X-ray data.

The perchlorate group. All perchlorate O atoms with the exception of O(5) are in hydrogen-bond contact with the metal complex. The Cl–O(4) bond is much shorter than the other three, Table 3. This bond length is subject to error due to the presence of high thermal motions. When this is considered the following distances are found: Cl–O(4) = 1.458, Cl–O(5) = 1.446, Cl–O(6) = 1.477, Cl–O(7) = 1.473 Å (*International Tables for X-ray Crystallography*, 1974).

These distances correspond much better with expected values according to interactions with surrounding atoms, *i.e.* an increase in bond length with increased interactions.

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