

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 $(P\bar{1})$ of the latter systems.

The closest intermolecular interaction between Ni(gh)₂ and TCNQ occurs in direction |101| 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.

References

- ENDRES, H. (1982). In *Extended Linear Chain Systems*, edited by J. S. MILLER. New York: Plenum. In the press.
- FLANDROIS, S. & CHASSEAU, D. (1977). Acta Cryst. B33, 2744–2750.
- International Tables for X-ray Crystallography (1974). Vol. IV. Birmingham: Kynoch Press.
- KELLER, H. J., LEICHERT, I., MÉGNAMISI-BÉLOMBÉ, M., NÖTHE, D. & WEISS, J. (1977). Z. Anorg. Allg. Chem. 429, 231–236.
- LONG, R. E., SPARKS, R. A. & TRUEBLOOD, K. N. (1965). Acta Cryst. 18, 932–939.
- SHELDRICK, G. M. (1979). SHELXTL. An integrated system for solving, refining and displaying crystal structures from diffraction data. Univ. of Göttingen, Federal Republic of Germany.

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

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Abstract. Ni $[H_2NC(CH_2OH)_3]_2(CIO_4)_2$, $C_8H_{22}N_2Ni-O_6^{2+}.2CIO_4^{-}$, $M_r = 499.93$, monoclinic. $P2_1/a$, a =

† IUPAC name: bis(2-amino-2-hydroxymethyl-1,3-propanediol)nickel(II) diperchlorate. 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, μ (Mo K α) = 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

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^{*} Metal Complexes with Mixed Ligands. 23.

discrete $[Ni{H_2NC(CH_2OH)_3}_2]^{2+}$ cations and $ClO_4^$ anions. The Ni atom is surrounded by two symmetryrelated tridentate tris(hydroxymethyl)aminomethane ligands in a distorted octahedral arrangement with Ni-O = 2.059 (3), 2.082 (3) and Ni-N = 2.055 (4) Å.

Introduction. Tris(hydroxymethyl)aminomethane, H₂-NC(CH₂OH)₃, tris, is a widely used buffering agent for studies in biochemical systems and sea water in the pH range 7 to 9 (Bates & Robinson, 1973; Ramette, Culberson & Bates, 1977). An increasing awareness of the role of metal ions in biochemical reactions makes it important to clarify the metal interaction with the buffering agent. Although several determinations of equilibria of metal-tris complexes in aqueous solutions have been reported (Durovič & Kupčik, 1959; Kemula, Brachaczek & Hulanicki, 1962; Bai & Martell, 1969; Dotson, 1972; Brignac & Mo, 1975; Fischer, Häring, Tribolet & Sigel, 1979) and possible metal-tris coordination figures have been suggested, no X-ray crystal-structure investigation has so far been published.

At this institute aqueous equilibria of the form

$$pH^{+} + qMe^{n+} + rH_{3}NC(CH_{2}OH)_{3}^{+}$$

$$\Rightarrow (H)_{\rho}Me_{q}[H_{3}NC(CH_{2}OH)_{3}]_{r}^{(\rho+qn+r)+}$$

are studied by means of e.m.f. titrations (298 K, $3 \cdot 0 M$ NaClO₄ medium). The M^{n+} species examined so far are Ag⁺, Cd²⁺ (Granberg, 1982) and Ni²⁺ (Forsling, 1978). Parallel with these investigations, crystallization experiments are performed and the crystals are then subjected to X-ray structure determinations.

In the system Ni-tris at least three different solid phases were found according to X-ray powder photographs. With the exception of the title compound they



Fig. 1. Predominance area diagram for the system Ni^2 -tris at pH = 7.500 in 3 *M* NaClO₄ medium; HL = H₂N(CH₂OH)₃ (Forsling, 1978).

are microcrystalline. According to results obtained from the aqueous equilibria investigations (Fig. 1, Forsling, 1978), the solid phases are built up from triand tetranuclear complexes. Attempts to obtain crystals of these (large enough for X-ray structure analyses) will continue. Structure investigations of Cu-tris and Cd-tris are in progress.

Experimental. Blue single crystals were obtained by evaporation at room temperature of an aqueous solution with the composition 1 M Ni(ClO₄)₂ and 2 M $H_2NC(CH_2OH)_3$ in 60% NaClO₄ solution. Weissenberg photographs showed monoclinic symmetry and systematic extinctions were found for h0l, h = 2n + 1and 0k0, k = 2n + 1, consistent with space group $P2_1/a$. The preliminary unit-cell parameters determined from these photographs were refined from a Guinier-Hägg powder photograph, taken with Cu Ka radiation $(\lambda = 1.54051 \text{ Å})$ with Si (a = 5.43059 Å) as internal standard at room temperature. The density was measured with the flotation method using bromoform and xylol. The dimensions of the crystal chosen for the intensity measurements were $0.10 \times 0.08 \times 0.16$ mm. 1701 reflexions were recorded with an Enraf-Nonius four-circle diffractometer, using graphite-monochromatized Mo $K\alpha$ radiation and the ω -2 θ scan technique. The scan width, aperture width and height used were $(0.5 + 0.35 \tan \theta)^{\circ}$, $(2 + 1.28 \tan \theta)$ mm, and 4.6 mm respectively, and $2\theta_{max} = 50^{\circ}$. Three reference reflexions were monitored at an interval of 50 reflexions to check for intensity fluctuations and crystal orientation. Net intensities with $I < 3\sigma(I)$ were omitted leaving a data set of 1405 independent reflexions. Corrections for Lorentz, polarization and absorption $[\mu(Mo K\alpha) = 1.44 \text{ mm}^{-1}]$ effects were performed (numerical method). The transmission factor varied between 0.862 and 0.897.

The positions of the Ni and Cl atoms were located from a Patterson map and remaining non-H atoms by Fourier methods. The refinement using full-matrix least-squares techniques, with anisotropic temperature factors, gave $R = \sum ||F_o| - |F_c|| / \sum |F_o| = 0.054$. The function minimized was $\sum w(\Delta F)^2$, where $w = 1/\sigma_{mod}^2$ with $\sigma_{mod}^2 = [4\sigma(F_o)]^2 + (0.06F_o)^2$.

The positional parameters for the H atoms, located from a difference synthesis, with an overall temperature factor B of 3.5 Å^2 included in the refinement, resulted in a final R = 0.044, $R_w = 0.048$. All shift/error values were ≤ 0.1 in the last refinement cycle.

Scattering factors used were taken from International Tables for X-ray Crystallography (1974).

Calculations of the net intensities (I) and $\sigma(I)$ as well as the Lp and absorption corrections were made by the program *CADAK* at the University of Uppsala. The other programs used have been listed by Antti (1976).

Final atomic positional parameters are given in Table 1, distances and angles within the cation

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

 $B_{\rm eq} = \frac{4}{3} \left(a^2 \beta_{11} + b^2 \beta_{22} + c^2 \beta_{33} + 2 \, ac \, \beta_{13} \cos \beta \right).$

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

	X	ŗ	Ζ	$B_{\rm cq}$ (Å ²)
Ni	0	0	0	1.92 (2)
Ν	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 (Å) and angles (°) 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) Ni-O(3) Ni-N	2.059 (3) 2.082 (3) 2.055 (4)		O(3) - C(3) N-C(4) C(1) - C(4) C(2) - C(4)	1+442 1+492 1+533 1+534	$\begin{array}{c} (6) & 1 \cdot 431 & (2) \\ (6) & 1 \cdot 472 & (2) \\ (6) & 1 \cdot 522 & (2) \\ (6) & 1 \cdot 531 & (2) \end{array}$
O(1)C(1) O(2)C(2)	1·424 (6) 1·420 (6)	1-412 (2) 1-426 (2)	C(3)–C(4)	1.531	(6) 1.522 (2)
O(1)-Ni-O(O(1)-Ni-N O(3)-Ni-N	(3)	84-8 (1) 78-5 (1) 81-2 (1)	C(1)-C(4)-C(4)-C(1)-C(4)-C(1)-C(4)-C(4)-C(4)-C(4)-C(4)-C(4)-C(4)-C(4	C(3) N C(3) N	$111 \cdot 8 (4) 106 \cdot 2 (3) 111 \cdot 5 (4) 113 \cdot 3 (4)$
Ni-O(1)-C(Ni-O(3)-C(Ni-N-C(4) C(1)-C(4)-	(1) (3) C(2)	13.7 (3) 09.9 (3) 01.0 (2) 08.1 (4)	C(3)C(4) C(4)C(2) C(4) C(3) C(4) C(1)-	N O(2) O(3) O(1)	105.9 (3) 111.5 (4) 110.6 (4) 107.9 (4)

Discussion. The title compound is built up from mononuclear $\{Ni\{H_2NC(CH_2OH)_3\}_2\}^{2+}$ 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 $[Ni{H_2NC(CH_2OH)_3}_2]^{2-}$ 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 $|Ni{H_2NC(CH_2OH_3|_2)^2}$ cation (*ORTEP*, Johnson, 1965).

Table 3. Distances (Å) and angles (°) for theperchlorate group and the hydrogen-bond contacts inthe structure, with e.s.d.'s in parentheses

Cl-O(4) Cl-O(5)	1·349 (6) 1·403 (4)	Cl-O(6) Cl-O(7)	1·416 (5) 1·427 (5)
O(4)-Cl-O(5) O(1)-Cl-O(6) O(4)-Cl-O(7)	112.5 (3) 113.3 (4) 106.3 (3)	O(5)ClO(6) O(5)ClO(7) O(6)ClO(7)	108+2 (3) 110+7 (3) 105+4 (3)
$\begin{array}{c} O(2) \cdots O(3) \\ O(1) \cdots O(6) \end{array}$	2·697 (4) 2·704 (5)	O(6) N:	3.256 (6)
$O(2) \cdots O(4)$	2.891(6)	•O(7)	3.069 (5)
$O(3) = H(O3) \cdots$ $O(1) = H(O1) \cdots$ $O(2) = H(O2) \cdots$	O(2) 172 (7) O(6) 171 (7) O(4) 156 (5)	$N \xrightarrow{H(N1)\dots 0} H(N2)\dots 0$	$(6) 161(6) \\ (7) 167(6)$



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°_0} probability.

bonded *via* two hydroxymethyl groups, Ni–O = 2.082and 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 $81-108^{\circ}$.

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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References

- ANTTI, B.-M. (1976). Acta Chem. Scand. Ser. A, 30, 24-30.
- BAI, K. S. & MARTELL, A. E. (1969). J. Inorg. Nucl. Chem. 31, 1697–1707.
- BATES, R. G. & ROBINSON, R. A. (1973). Anal. Chem. 45(2), 420.
- BRIGNAC, R. J. JR & MO, C. (1975). Anal. Chem. 47, 1465–1466.
- DOTSON, R. L. (1972). J. Inorg. Nucl. Chem. 34, 3131-3138.
- Ďurovič & Kupčik, V. (1959). Chem. Zvesti, 13, 565–571.
- EILERMAN, D. & RUDMAN, R. (1980). J. Chem. Phys. 72, 5656–5666.
- FISCHER, B. E., HÄRING, U. K., TRIBOLET, R. & SIGEL, H. (1979). Eur. J. Biochem. 94, 523–530.
- ForsLing, W. (1978). Acta Chem. Scand. Ser. A, 32, 857–865.
- GRANBERG, I. (1982). To be published.
- *International Tables for X-ray Crystallography* (1974). Vol. IV, pp. 72–79, 149, 323. Birmingham: Kynoch Press.
- JOHNSON, C. K. (1965). ORTEP. Report ORNL-3794. Oak Ridge National Laboratory, Tennessee.
- KEMULA, W., BRACHACZEK, W. & HULANICKI, A. (1962). Rocz. Chem. 36, 1727–1735.
- RAMETTE, R. W., CULBERSON, C. H. & BATES, R. G. (1977). Anal. Chem. 49, 867–870.
- RUDMAN, R., EILERMAN, D. & LAPLACA, S. J. (1978). Science, 200, 531–533.
- SEKIZAKI, M. (1976). Acta Cryst. B32, 1568-1570.