$$C_{16}H_{36}Cl_2Co_2O_8^{2+} \cdot 2SbCl_6^-$$

However, Mn also forms another (monomeric) complex with the same ligand, from which no crystals could be obtained (van Gils *et al.*, 1981).

All calculations were carried out on the Leiden University computers (IBM 370/158 and Amdahl V7B). The authors would like to thank N. van Gils for permission to use his results before publication. The authors are also indebted to Dr A. J. de Kok and Drs J. C. Lapidaire for their interest and valuable discussions.

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1:1 Adduct of Bis(ethanedial dioximato)nickel(II) with 7,7,8,8-Tetracyano-*p*-quinodimethane* (TCNQ)

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Abstract. $C_{16}H_{10}N_8NiO_4$, $C_4H_6N_4NiO_4 \cdot C_{12}H_4N_4$, $M_r = 437 \cdot 02$, monoclinic, $P2_1/a$, $a = 7 \cdot 221$ (2), $b = 15 \cdot 496$ (5), $c = 8 \cdot 160$ (2) Å, $\beta = 102 \cdot 54$ (2)°, $V = 891 \cdot 3$ Å^3, $Z = 2$, $d_c = 1 \cdot 63$ Mg m^{-3}. Final $R = 0 \cdot 041$ for 862 observed diffractometer data. The compound is obtained as black crystals on reacting equimolar amounts of bis(ethanedial dioximato)nickel(II), $Ni(gh)_2$, and TCNQ. The structure is best described as interpenetrating stacks of $Ni(gh)_2$ and TCNQ along the diagonal of the *xz* plane in [101] direction.

Introduction. Adducts or salts of TCNQ (an important component in 'organic metals') and square-planar transition-metal complexes represent one of the systems of interest in current investigations of low-dimensional physical properties (Endres, 1982). We have been working on adducts of TCNQ with transition-metal complexes whereby the complex components are α,β-dione dioximato complexes of the metals of the Ni

triad and we earlier described the synthesis and crystal structure of bis(1,2-benzenedione dioximato)-nickel(II)–TCNQ and its Pd^{II} counterpart (Keller, Leichert, Mégnamisi-Bélombé, Nöthe & Weiss, 1977). In the following we describe the preparation and structure of the analogous 1:1 adduct bis(ethanedial dioximato)nickel(II)–TCNQ, $Ni(gh)_2$–TCNQ.

For the preparation of the compound analytical-grade reagents were used. 116 mg (0·5 mmol) $Ni(gh)_2$ were dissolved in a warm mixture of 70 ml CHCl$_3$ and 30 ml CH$_3$CN, and the red solution was filtered. 102 mg (0·5 mmol) TCNQ (as purchased from Aldrich, 98 %) were dissolved likewise in a warm mixture of 60 ml CHCl$_3$ and 25 ml CH$_3$CN, and the yellow solution was filtered. The two solutions were mixed together and heated to boiling, while stirring, for 15 min. The red-yellowish mixture was evaporated almost to dryness, the residue was treated with 150 ml hot CHCl$_3$, and the light-red solution was filtered. On evaporating the filtrate slowly at room temperature, long black crystals formed within a few days.

Lattice parameters were derived from the setting angles of 25 reflections centered on a Syntex R3 diffractometer operating with Mo *K*α radiation. Data

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collection by ω scans, background-peak-background, 2θ ≤ 60°, yielded 862 independent observed |I > 2·0σ(I)| reflections. They were corrected empirically (ψ scans) for absorption effects.

The positions of Ni and one of the oxime N atoms were derived from a Patterson synthesis, and the other non-H atoms were located from Fourier maps. Refinement with anisotropic temperature factors gave weighted (unweighted) $R = 0.052$ (0·058). All the H atoms showed up in a difference Fourier map. They were inserted with individual isotropic temperature factors, and final refinement by 'cascade-matrix' least squares converged with weighted (unweighted) $R = 0.041$ (0·049).* The weighting scheme was $w = 1/\sigma^2(F)$.

Calculations were carried out on a NOVA 3 computer, plots were drawn on a Tektronix plotter. The program package was *SHELXTL* (Sheldrick, 1979), which uses atomic scattering factors from *International Tables for X-ray Crystallography* (1974) and takes anomalous dispersion into account.

Discussion. Atomic coordinates are listed in Table 1. The centers of gravity of the Ni(gh)₂ molecule as well

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* Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 36720 (8 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.
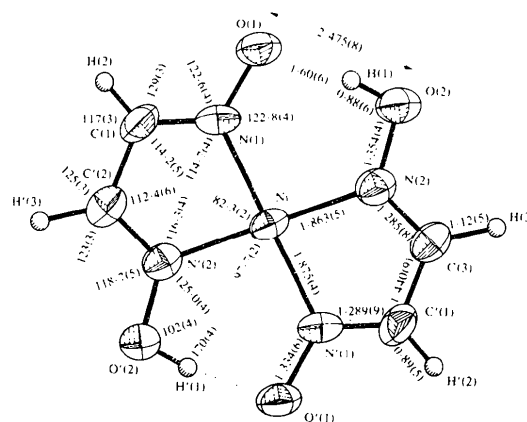

Fig. 1. The bis(ethanedial dioximato)nickel(II) complex molecule with bond distances (Å) and angles (°).
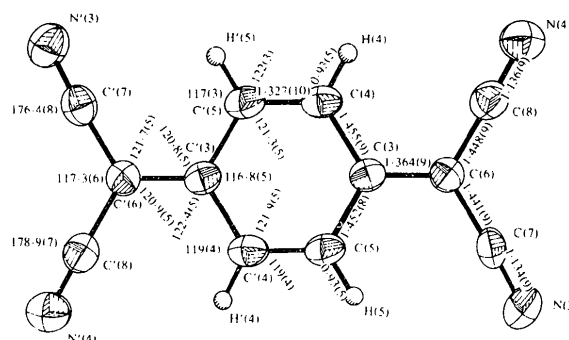
Fig. 2. The 7,7,8,8-tetracyano-p-quinodimethane molecule with bond distances (Å) and angles (°).

Table 1. *Atomic coordinates* $(\times 10^4, for \ H \times 10^3)$ *and isotropic temperature factors* $(\times 10^3)$ *equivalent to the refined anisotropic values*

U_{eq} is defined as $U_{eq} = \frac{1}{3}$ trace $\tilde{U}$. $\tilde{U}$ signifying the diagonalized U matrix.

	x	y	z	U_{eq} (Å²)
Ni	0	0	0	36·9 (4)
N(1)	−112 (6)	−43 (4)	2273 (5)	43 (2)
N(2)	1155 (7)	1077 (3)	31 (6)	44 (2)
C(1)	−821 (9)	−745 (4)	2723 (7)	46 (3)
C(2)	1445 (10)	1351 (5)	−1379 (7)	49 (3)
O(1)	499 (6)	600 (3)	3341 (4)	50 (2)
O(2)	1694 (7)	1579 (3)	1409 (5)	61 (2)
C(3)	706 (8)	4301 (4)	4180 (7)	34 (2)
C(4)	−84 (8)	5071 (6)	3273 (7)	38 (2)
C(5)	757 (9)	4280 (4)	5969 (7)	37 (2)
C(6)	1407 (9)	3631 (4)	3416 (7)	37 (2)
C(7)	2280 (10)	2893 (5)	4349 (8)	45 (3)
C(8)	1391 (10)	3656 (4)	1639 (8)	48 (3)
N(3)	2943 (9)	2330 (4)	5158 (7)	61 (3)
N(4)	1368 (9)	3690 (4)	244 (7)	67 (3)
H(1)	136 (8)	126 (4)	219 (7)	73 (20)*
H(2)	−102 (7)	−89 (3)	372 (6)	40 (15)*
H(3)	207 (8)	200 (3)	−153 (6)	53 (18)*
H(4)	−20 (7)	509 (4)	211 (6)	56 (17)*
H(5)	124 (7)	378 (3)	654 (6)	32 (16)*

* Isotropic.

as those of the TCNQ moiety coincide with crystallographic inversion centers, Ni at 0,0,0 and TCNQ around $0,\frac{1}{2},\frac{1}{2}$. The numbering scheme, bond distances and angles in the two species are shown in Figs. 1 and 2. The complex molecule is essentially planar, the mean (maximum) deviation of a non-H atom from the least-squares plane through these atoms is 0·017 Å |0·035 Å for O(1)|. As usual the TCNQ molecule is slightly bent at C(6); least-squares planes through the quinoid part of the molecule and through the terminal C(CN)₂ group form an angle of 3·4°. Mean (maximum) deviations of atoms of the two planes are 0·003 Å |0·007 Å for C(3)| in the quinoid parts, and 0·0007 Å |0·0015 Å for C(8)| in the terminal C(CN)₂ group.

Fig. 3 shows a projection of the structure along c. It is evident that molecules with their centers of gravity at the same value of y are practically parallel and are arranged in a herring-bone fashion relative to those with centers of gravity at $y = +\frac{1}{2}$. Due to the different values of the z coordinate for the midpoints of the molecules with the same y coordinate, it is clear that no mixed stacks of the metal complex and of TCNQ are formed. In this aspect the structure closely resembles
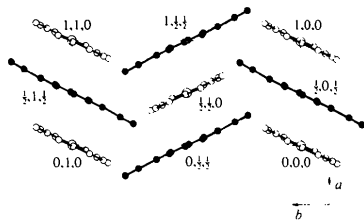
Fig. 3. Projection of the structure along c. Open circles denote molecules with centers of gravity at $z = 0$, filled circles those with centers of gravity at $z = \frac{1}{2}$. The numbers indicate the positions of the midpoints of the molecules.
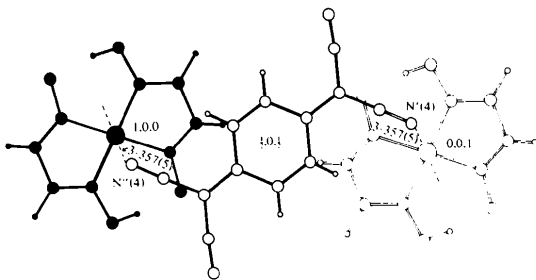

Fig. 4. Projection of two Ni(gh)$_2$ units and a TCNQ molecule onto the plane of the complex molecules showing the short contact between Ni and one of the nitrile N atoms of TCNQ (Å). The midpoints of the molecules are at the indicated positions, so that the molecules lie along |101|.

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 |$\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 $180° - \delta$. Due to the different surroundings of the two C≡N groups at each end of TCNQ, a splitting of the C≡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≡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$_2$NC(CH$_2$OH)$_3$]$_2$(ClO$_4$)$_2$, C$_8$H$_{22}$N$_2$Ni-O$_6^{2+}$.2ClO$_4^-$, $M_r = 499\cdot93$, monoclinic, $P2_1/a$, $a = 11\cdot7249$ (5), $b = 12\cdot2353$ (5), $c = 6\cdot3352$ (2) Å, $\beta = 92\cdot857$ (3)°, $Z = 2$, $V = 907\cdot70$ Å^3, $D_x = 1\cdot829$, $D_m = 1\cdot83$ (1) Mg m^{-3}, μ(Mo $K\alpha$) $= 1\cdot44$ 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.