

Di- μ -chloro-bis{[bis(methoxyethoxy)ethane]cobalt(II)} Hexachloroantimonate(V)

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Abstract. $C_{16}H_{36}Cl_2Co_2O_8^{2+} \cdot 2SbCl_6^-$, $M_r = 1214$, monoclinic, space group $I2/c$, $a = 15.105$ (8), $b = 19.802$ (7), $c = 13.746$ (5) Å, $\beta = 94.15$ (3)°, $Z = 4$, $d_x = 1.95$ (1), $d_c = 1.96$ Mg m⁻³, $V = 4100.8$ Å³. $R = 0.036$ for 2739 observed reflexions. The structure contains a dimeric unit consisting of two Co ions bridged by two Cl atoms. The octahedral coordination of each ion is completed by one molecule of the tetradentate bis(methoxyethoxy)ethane (triethylene glycol dimethyl ether, triglyme).

Introduction. Previous work in this laboratory (van Gils, Zuur & Driessen, 1981) proved the existence of coordination compounds with triglyme (CH₃—O—CH₂—CH₂—O—CH₂—CH₂—O—CH₂—CH₂—O—CH₃) as the ligand and Cu, Ni, Co, Mn, Zn, Sr, Ca or Mg as the central ion. As several ways of coordinating the metal by the ligand are possible, the crystal structure of the title compound was determined.

CoCl₂ and SbCl₅ were dissolved in a 1:1 ratio in nitromethane. To this solution triglyme was added resulting in the title compound (van Gils *et al.*, 1981). Cell parameters were determined using Mo $K\alpha$ radiation ($\lambda = 0.71073$ Å) from 25 hkl reflexions. Systematic absences hkl for $h + k + l$ odd and $h0l$ for $l(h)$ odd indicated the non-standard space group Ic or $I2/c$ (numbers 9 or 15). Since refinement in space group $I2/c$ gave more consistent results this space group was chosen. The transformation from the chosen Bravais lattice to the conventional C lattice is given by: $a' = a + c$, $b' = b$ and $c' = c$. A crystal, $0.1 \times 0.5 \times 0.2$ mm, was mounted on an Enraf–Nonius CAD-4 four-circle diffractometer and 5467 reflexions were measured in the ω - $\frac{2}{3}\theta$ scan mode. After averaging symmetry-related reflexions 4696 independent reflexions were obtained, 2739 of these having an intensity $I > 2\sigma(I)$. $\sigma(I)$ was calculated from counting statistics. Intensities were corrected for absorption [$\mu(\text{Mo } K\alpha) = 3.072$ mm⁻¹] and for Lorentz and polarization factors.

The positions of the metal atoms were determined with MULTAN 78 (Main, 1978). Three high peaks were obtained. The two highest peaks were situated on a twofold axis, while the third peak was about 1.7 Å

from an inversion centre. The two highest peaks were assigned to Sb^V implying that Co^{II} caused the third peak. This information allowed DIRDIF (a program package for solving difference structures by making use of direct methods) (Beurskens, Prick, Doesburg & Gould, 1979) to yield the positions of all other non-H atoms. Cl(2,3) and Cl(2,4) were found on special positions. Scattering factors and anomalous-dispersion corrections were taken from *International Tables for X-ray Crystallography* (1974). Refinement of the structure by full-matrix least-squares calculations minimized $\sum w\Delta F^2$ with $\Delta F = ||F_o| - |F_c||$ and $w =$

Table 1. Fractional coordinates (Sb and Co $\times 10^5$; other atoms $\times 10^4$) (with *e.s.d.*'s in parentheses) and equivalent isotropic thermal parameters for non-H atoms

	$B_{eq} = \frac{2}{3}\pi^2 \text{trace } \tilde{U}$			B_{eq} (Å ² $\times 10$)
	x	y	z	
Sb(1)*	50000	56147 (2)	25000	30
Sb(2)*	0	56772 (3)	25000	37
Co	27162 (4)	73481 (3)	87231 (4)	29
Cl(1,1)	4279 (1)	5610 (1)	3970 (1)	46
Cl(1,2)	4028 (1)	4780 (1)	1840 (2)	61
Cl(1,3)	5979 (1)	6462 (1)	3110 (2)	56
Cl(2,1)	1547 (1)	5662 (1)	2372 (2)	63
Cl(2,2)	-206 (1)	5666 (1)	799 (2)	85
Cl(2,3)*	0	6853 (1)	2500	87
Cl(2,4)*	0	4495 (1)	2500	103
Cl(3,1)	3537 (1)	7331 (1)	7302 (1)	41
O(1)	3843 (2)	6910 (2)	9506 (2)	35
O(2)	2332 (2)	6335 (2)	8952 (2)	39
O(3)	1947 (2)	7429 (2)	9962 (2)	37
O(4)	3065 (2)	8309 (2)	9303 (2)	40
C(1)	4711 (3)	7231 (3)	9599 (4)	54
C(2)	3910 (3)	6220 (3)	9197 (4)	46
C(3)	3036 (4)	5891 (3)	9357 (4)	53
C(4)	1571 (3)	6328 (3)	9535 (4)	47
C(5)	1737 (3)	6783 (3)	10368 (4)	46
C(6)	2322 (4)	7924 (3)	10635 (4)	47
C(7)	2511 (4)	8524 (3)	10041 (4)	51
C(8)	3290 (5)	8854 (3)	8662 (5)	60

* Special positions.

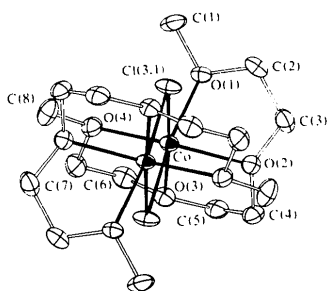


Fig. 1. One dimeric unit. The thermal ellipsoids are shown at the 25% probability level.

$\sigma(F)^{-2}$. H atoms were placed at calculated positions at a distance of 1.0 Å from the parent C atoms. The methyl H atoms could not be calculated and were therefore omitted. Using only the significant reflexions all non-H atoms were refined anisotropically while coupling the positional parameters of the H atoms to those of the corresponding C atoms (C–H = 1.0 Å). The isotropic thermal parameter of an H atom was kept constant at the last value of the isotropic parameter of its parent C atom. Four cycles of this refinement resulted in $R(R_w) = 0.036$ (0.048), where $R = \sum \Delta F / \sum |F_o|$ and $R_w = [\sum w(\Delta F)^2 / \sum wF_o^2]^{1/2}$. Finally, four cycles of refinement, using all reflexions, yielded $R(R_w) = 0.083$ (0.050). Positional parameters and B_{eq} for the non-H atoms are given in Table 1.*

Discussion. The asymmetric unit contains two SbCl₆ octahedra lying on a twofold axis and half a [Co(triglyme)Cl]₂ dimer. Intramolecular distances and selected bond angles and torsion angles are given in Table 2. The abnormally large B_{eq} of Cl(2,1), Cl(2,2), Cl(2,3) and Cl(2,4) are probably caused by disorder, since the anisotropic thermal parameters perpendicular to the twofold axis are extremely large. Fig. 1 shows one dimeric unit and also indicates the atom numbering. The Co^{II} octahedra are distorted (Table 2b). This distortion (the four Co–O bonds are bent towards each other) can be explained by the strain in the triglyme molecule. The bond angles in the ligand are all quite normal (in the range 106–115°) and have not been included in the table. Intermolecular distances are in Table 3. IR and reflexion spectra show that the title compound is isomorphous with similar complexes having Mn, Ni or Zn as the central ion instead of Co.

* Lists of structure factors, anisotropic thermal parameters and H-atom coordinates have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 36732 (15 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 2. Intramolecular distances, angles and torsion angles

(a) Distances (Å)			
Sb(1)–Cl(1,1)	2.364 (1)	Sb(1)–Cl(1,3)	2.351 (1)
Sb(1)–Cl(1,2)	2.349 (1)		
Sb(2)–Cl(2,1)	2.356 (1)	Sb(2)–Cl(2,3)	2.328 (2)
Sb(2)–Cl(2,2)	2.336 (2)	Sb(2)–Cl(2,4)	2.340 (2)
Co–Cl(3,1)	2.388 (1)	Co–Cl(3,1')	2.364 (1)
Co–O(1)	2.132 (3)	Co–O(3)	2.136 (3)
Co–O(2)	2.118 (3)	Co–O(4)	2.115 (5)
C(1)–O(1)	1.453 (6)	C(5)–O(3)	1.441 (6)
O(1)–C(2)	1.437 (6)	O(3)–C(6)	1.436 (6)
C(2)–C(3)	1.502 (8)	C(6)–C(7)	1.481 (8)
C(3)–O(2)	1.460 (6)	C(7)–O(4)	1.425 (6)
O(2)–C(4)	1.448 (6)	O(4)–C(8)	1.449 (6)
C(4)–C(5)	1.465 (8)		

(b) Ligand–metal–ligand angles (°)			
Cl(1,1)–Sb(1)–Cl(1,2)	90.80 (5)	Cl(1,2)–Sb(1)–Cl(1,3)	178.17 (5)
Cl(1,1)–Sb(1)–Cl(1,3)	90.82 (5)		
Cl(2,1)–Sb(2)–Cl(2,2)	89.22 (7)	Cl(2,2)–Sb(2)–Cl(2,3)	90.54 (6)
Cl(2,1)–Sb(2)–Cl(2,3)	90.75 (4)	Cl(2,2)–Sb(2)–Cl(2,4)	89.46 (6)
Cl(2,1)–Sb(2)–Cl(2,4)	89.25 (4)	Cl(2,3)–Sb(2)–Cl(2,4)	179.97 (15)
Cl(3,1)–Co–Cl(3,1')	87.54 (4)	Cl(3,1)–Co–O(3)	176.10 (9)
Cl(3,1)–Co–O(1)	87.93 (9)	Cl(3,1)–Co–O(4)	101.0 (1)
Cl(3,1)–Co–O(2)	105.8 (1)		
O(1)–Co–Cl(3,1')	170.5 (1)	O(1)–Co–O(3)	95.1 (1)
O(1)–Co–O(2)	76.0 (1)	O(1)–Co–O(4)	90.4 (1)
O(2)–Co–Cl(3,1')	97.3 (1)	O(2)–Co–O(4)	149.3 (1)
O(2)–Co–O(3)	77.4 (1)		
O(3)–Co–Cl(3,1')	89.8 (1)	O(3)–Co–O(4)	76.5 (1)
O(4)–Co–Cl(3,1')	98.6 (1)		

(c) Torsion angles in the ligand (°)			
C(1)–O(1)–C(2)–C(3)	166.5 (5)	C(4)–C(5)–O(3)–C(6)	167.0 (4)
O(1)–C(2)–C(3)–O(2)	47.8 (6)	C(5)–O(3)–C(6)–C(7)	177.7 (4)
C(2)–C(3)–O(2)–C(4)	–143.8 (5)	O(3)–C(6)–C(7)–O(4)	–55.5 (6)
C(3)–O(2)–C(4)–C(5)	81.6 (5)	C(6)–C(7)–O(4)–C(8)	179.4 (5)
O(2)–C(4)–C(5)–O(3)	55.1 (5)		

Symmetry code: (i) 0.5 – x, 1.5 – y, 1.5 – z.

Table 3. Intermolecular distances < 4.0 Å

First atoms have coordinates as in Table 1.

Cl(1,1)–C(2 ⁱ)	3.684 (5)	Cl(1,1)–C(7 ⁱⁱⁱ)	3.554 (5)
Cl(1,1)–C(3 ⁱ)	3.577 (5)	Cl(1,1)–C(2 ⁱⁱ)	3.781 (5)
Cl(1,1)–C(6 ⁱⁱⁱ)	3.842 (6)		
Cl(1,2)–C(8 ^{iv})	3.969 (7)	Cl(1,2)–C(2 ⁱ)	3.813 (6)
Cl(1,3)–Cl(2,3 ^v)	3.721 (2)	Cl(1,3)–C(2 ⁱⁱ)	3.724 (6)
Cl(1,3)–O(1 ⁱⁱ)	3.386 (4)	Cl(1,3)–C(3 ⁱⁱⁱ)	3.855 (6)
Cl(1,3)–C(1 ⁱⁱ)	3.714 (6)	Cl(1,3)–C(5 ⁱⁱⁱ)	3.955 (6)
Cl(2,1)–C(8 ^{iv})	3.866 (6)	Cl(2,1)–C(5 ⁱⁱⁱ)	3.565 (6)
Cl(2,2)–Cl(2,2 ^{ix})	3.518 (4)	Cl(2,2)–C(8 ^{vi})	3.704 (7)
Cl(2,2)–O(4 ^{vi})	3.793 (4)	Cl(2,2)–C(4 ^{viii})	3.552 (5)
Cl(2,2)–C(7 ^{vi})	3.876 (7)	Cl(2,2)–C(5 ^{viii})	3.755 (5)
Cl(2,4)–C(4 ⁱ)	3.892 (6)	Cl(2,4)–C(8 ^{iv})	3.381 (6)
O(3)–C(1 ^{vii})	3.445 (6)	C(5)–C(1 ^{vii})	3.718 (8)

Symmetry code: (i) x, 1 – y, –0.5 + z; (ii) 1 – x, y, 1.5 – z; (iii) 0.5 – x, 1.5 – y, 1.5 – z; (iv) 0.5 – x, –0.5 + y, 1 – z; (v) 0.5 + x, 1.5 – y, z; (vi) –0.5 + x, 1.5 – y, –1 + z; (vii) –0.5 + x, 1.5 – y, z; (viii) x, y, z – 1; (ix) –x, 1 – y, –z.

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. $C_{16}H_{10}N_8NiO_4$, $C_4H_6N_4NiO_4 \cdot C_{12}H_4N_4$, $M_r = 437.02$, monoclinic, $P2_1/a$, $a = 7.221(2)$, $b = 15.496(5)$, $c = 8.160(2)$ Å, $\beta = 102.54(2)^\circ$, $V = 891.3$ Å³, $Z = 2$, $d_c = 1.63$ Mg m⁻³. Final $R = 0.041$ 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-Bélobmé, 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 CHCl₃ and 30 ml CH₃CN, 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 CHCl₃ and 25 ml CH₃CN, 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 CHCl₃, 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 $K\alpha$ radiation. Data

* Recommended IUPAC name: 2,2'-(2,5-cyclohexadiene-1,4-diyliidene)dipropanedinitrile.

† Correspondence about preparation and properties should be addressed to M. Mégnamisi-Bélobmé, about the structure to H. Endres.