

The perchlorate ion has standard geometry [mean Cl—O distance 1.42 (2) Å, range: 1.411 (3)–1.442 (3) Å; mean O—Cl—O angle 109 (2)°, range 107.2 (2)–111.4 (2)°].

The molecular packing is due to ionic forces and weak hydrogen bonds (Table 4). Other short intermolecular distances are also shown in Table 4.

This work was sponsored by the Universidad de Barcelona.

References

- ALCOCK, N. W., DE MEESTER, P. & KEMP, T. J. (1978). *Acta Cryst.* **B34**, 3367–3369.
- BEURSKENS, P. T., BOSMAN, W. P., DOESBURG, H. M., GOULD, R. O., VAN DEN HARK, T. E. M. & PRICK, P. A. J. (1980). Tech. Rep. 1980/1. Crystallography Laboratory, Toernooiveld, Nijmegen, The Netherlands.
- BROUTY, C., SPINAT, P. & WHULER, A. (1977). *Acta Cryst.* **B33**, 3453–3460.
- BROUTY, C., SPINAT, P., WHULER, A. & HERPIN, P. (1977). *Acta Cryst.* **B33**, 1913–1920.
- BROUTY, C., WHULER, A., SPINAT, P. & HERPIN, P. (1977). *Acta Cryst.* **B33**, 2563–2572.
- DUESLER, E. N. & RAYMOND, K. N. (1978). *Inorg. Chim. Acta* **30**, 87–95.
- JURNAK, F. A. & RAYMOND, K. N. (1974). *Inorg. Chem.* **13**, 2387–2397.
- MAIN, P., FISKE, S. L., HULL, S. E., LESSINGER, L., GERMAIN, G., DECLERCQ, J. P. & WOOLFSON, M. M. (1980). *MULTAN. A System of Computer Programs for the Automatic Solution of Crystal Structures from X-ray Diffraction Data*. Univs. of York, England, and Louvain, Belgium.
- SHELDRICK, G. M. (1976). *SHELX*. A program for crystal structure determination. Univ. of Cambridge, England.
- WHULER, A., BROUTY, C., SPINAT, P. & HERPIN, P. (1977). *Acta Cryst.* **B33**, 2877–2885.
- WHULER, A., SPINAT, P. & BROUTY, C. (1978). *Acta Cryst.* **B34**, 793–799.

Acta Cryst. (1982). **B38**, 2901–2903

Hexaaquacobalt(II) Bis[dibromobis(ethanedial dioximato)cobaltate(III)] Acetone Solvate

BY GABRIEL O. EGHAREVBA AND MICHEL MÉGNAMISI-BÉLOMBÉ*

Department of Chemistry, University of Ife, Ile-Ife, Nigeria

AND HELMUT ENDRES* AND ELISABETH ROSSATO

Anorganisch-Chemisches Institut der Universität, Im Neuenheimer Feld 270, D-6900 Heidelberg 1, Federal Republic of Germany

(Received 19 April 1982; accepted 7 June 1982)

Abstract. [Co(H₂O)₆][CoBr₂(C₂H₃N₂O₂)₂]₂·2C₃H₆O, 2C₄H₆Br₂CoN₄O₄·CoH₁₂O₆²⁺·2C₃H₆O, *M_r* = 1068.89, monoclinic, *P*2₁/*n*, *a* = 7.005 (3), *b* = 12.964 (5), *c* = 20.134 (10) Å, β = 92.91 (4)°, *V* = 1826 Å³, *Z* = 2, *D_x* = 1.94 Mg m⁻³. Final *R* = 0.036 for 1876 observed diffractometer data. The compound, which decomposes rapidly in the air by loss of acetone, contains cobalt complexes in two different oxidation states: hexaaquacobalt(II) and *trans*-dibromobis(ethanedial dioximato)cobaltate(III). The crystal structure is held together by an extended network of hydrogen bridges.

Introduction. The title compound was prepared in the course of our efforts to synthesize and study sys-

tematically complexes of α,β-dione dioxime ligands with divalent metal halides, *MX*₂ (Andoseh, Douglas, Egharevba & Mégnamisi-Bélobbé, 1982; Mégnamisi-Bélobbé, 1981*a,b*). So far our interest has mainly focused on the dimeric adducts of Cu^{II} halides, in search of a better understanding of their magnetic properties (Mégnamisi-Bélobbé, 1979; Mégnamisi-Bélobbé & Novotny, 1980). Some of these Cu^{II} dimers have been analyzed by X-ray diffraction (Svedung, 1969; Endres, 1978; Endres, Andoseh & Mégnamisi-Bélobbé, 1981). Although complexes of NiCl₂, NiBr₂, and CoCl₂ with ethanedial dioxime (glyoxime, gH₂) have not been structurally characterized so far, their 1:1 composition *MX*₂(gH₂) is confirmed by analytical and IR data (Mégnamisi-Bélobbé, 1981*a*). By contrast, unclear data were obtained for the reaction product of CoBr₂ with gH₂. Hence we performed the X-ray structure determination described below.

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

To prepare the material, 100 mg (~1.14 mmol) gH₂ were dissolved in 50 ml acetone and filtered. While being stirred at 298–323 K, this solution was treated slowly with a filtered solution of 250 mg (~1.14 mmol) of CoBr₂ in 100 ml acetone. After completion of the addition, stirring was continued for another 45–60 min. The blue-green reaction mixture was allowed to cool to room temperature, and a small amount of flocculent green body was discarded by filtration. On concentrating the filtrate by slow evaporation at ambient temperature over a few days, elongated, prismatic dark-green crystals formed. As previous experience showed that the crystals decompose on drying, crystals for the X-ray investigation were picked from the mother liquor and sealed immediately into a glass capillary.

Lattice parameters were derived from the setting angles of 25 reflections centered on a diffractometer (Syntex R3, monochromatic Mo K α radiation). To minimize possible difficulties due to decomposition, a fast room-temperature data collection by ω scans, background–peak–background, $2\theta \leq 50^\circ$, was performed. It took about 14 h to collect 1876 observed [$I > 2.0\sigma(I)$] out of 3217 possible independent reflections (including the systematically absent ones). During this period the intensities of two check reflections dropped by about 3%. Rapid pre-scans had been used to suppress the measurement of reflections with an intensity not significantly higher than local background. An empirical absorption correction (ψ scans) was applied. The reflections were processed in the usual way by subtracting local background from the gross intensity.

A Co atom at a general position and two Br atoms attached to it were located from a Patterson map. A Fourier synthesis revealed a second Co atom at a special position, and subsequent Fourier maps yielded the sites of the other non-H atoms, including a four-atom species interpreted as an acetone molecule. An octahedral CoX₆ species at the inversion center 0.5, 0, 0.5 was identified as a hexaaqua complex. All H positions showed up in the difference map, but they could not be refined reasonably. Thus, in the final cycles the H positions of acetone were refined as rigid CH₃ groups, the other H atoms were inserted as found in the difference map and not refined at all. Fixed isotropic temperature factors for H atoms, rather larger than those of the atoms they were bound to, were used. Refinement by 'cascade-matrix' least squares converged with a weighted (unweighted) $R = 0.036$ (0.043). 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 of the non-H atoms are listed in Table 1,* bond lengths and angles in Table 2. The numbering schemes in the Co complex species are shown in Figs. 1 and 2, where unrefined H atoms from a difference Fourier map are included. The two

* Lists of structure factors, anisotropic thermal parameters, and unrefined or constrained H positions have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 36980 (15 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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

U_{eq} is one third of the trace of the diagonalized U matrix.

	x	y	z	U_{eq} (\AA^2)
Co(1)	10314 (2)	1200 (1)	2399.4 (6)	25.2 (4)
Br(1)	11819 (1)	2425.9 (8)	3149.9 (4)	36.3 (3)
Br(2)	8827 (1)	-27.8 (9)	1659.1 (5)	43.8 (3)
C(1)	12926 (14)	-252 (7)	2802 (4)	36 (3)
C(2)	13714 (13)	249 (8)	2234 (5)	38 (4)
C(3)	6939 (12)	2153 (7)	2586 (4)	36 (3)
C(4)	7719 (12)	2670 (7)	2029 (4)	35 (3)
N(1)	11273 (10)	92 (6)	2950 (3)	32 (3)
N(2)	12665 (10)	972 (6)	1984 (3)	36 (3)
N(3)	7985 (10)	1398 (6)	2822 (3)	32 (3)
N(4)	9350 (11)	2316 (6)	1859 (3)	36 (3)
O(1)	10313 (9)	-288 (5)	3461 (3)	40 (2)
O(2)	13257 (9)	1522 (6)	1450 (3)	55 (3)
O(3)	7481 (9)	807 (5)	3332 (3)	47 (2)
O(4)	10336 (9)	2689 (5)	1359 (3)	45 (2)
Co(2)	5000	0	5000	28.9 (5)
O(6)	6576 (9)	-894 (5)	4382 (3)	41 (2)
O(7)	4804 (9)	1098 (5)	4228 (3)	52 (3)
O(8)	2424 (9)	-639 (5)	4643 (3)	49 (3)
C(5)	6545 (22)	8361 (12)	359 (7)	111 (8)
C(6)	4632 (22)	7919 (10)	139 (5)	71 (6)
C(7)	2953 (21)	8568 (10)	87 (7)	104 (7)
O(5)	4588 (10)	6963 (6)	-1 (4)	63 (3)

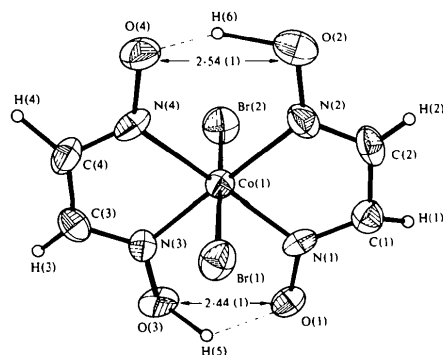


Fig. 1. Numbering scheme and thermal ellipsoids (at 50% probability) in the *trans*-dibromobis(ethanedial dioximato)cobaltate(III) anion, a perspective view. Unrefined H positions from a difference Fourier map are drawn as small spheres with an arbitrary radius. The lengths (\AA) of the intramolecular hydrogen bridges are indicated.

Table 2. Bond lengths (Å) and angles (°)

Co(1)—Br(1)	2.400 (1)	N(1)—O(1)	1.350 (9)
Br(2)	2.384 (2)	Co(1)—N(1)—C(1)	114.7 (6)
N(1)	1.915 (7)	O(1)	122.8 (5)
N(2)	1.908 (7)	C(1)—N(1)—O(1)	122.5 (7)
N(3)	1.895 (7)	N(2)—O(2)	1.372 (9)
N(4)	1.912 (7)	Co(1)—N(2)—C(2)	115.6 (6)
Br(1)—Co(1)—Br(2)	179.6 (1)	O(2)	124.4 (5)
N(1)	90.1 (2)	C(2)—N(2)—O(2)	120.0 (7)
N(2)	91.0 (2)	N(3)—O(3)	1.343 (9)
N(3)	89.3 (2)	Co(1)—N(3)—C(3)	114.9 (6)
N(4)	89.3 (2)	O(3)	122.1 (5)
Br(2)—Co(1)—N(1)	89.5 (2)	C(3)—N(3)—O(3)	123.0 (7)
N(2)	89.0 (2)	N(4)—O(4)	1.341 (9)
N(3)	90.7 (2)	Co(1)—N(4)—C(4)	114.2 (6)
N(4)	91.1 (2)	O(4)	121.4 (6)
N(1)—Co(1)—N(2)	81.5 (3)	C(4)—N(4)—O(4)	124.4 (7)
N(3)	97.3 (3)	Co(2)—O(6)	2.061 (6)
N(4)	179.3 (3)	O(7)	2.108 (6)
N(2)—Co(1)—N(3)	178.8 (3)	O(8)	2.080 (6)
N(4)	98.9 (3)	O(6)—Co(2)—O(7)	87.2 (2)
N(3)—Co(1)—N(4)	82.3 (3)	O(8)	92.8 (2)
C(1)—C(2)	1.449 (13)	O(7)—Co(2)—O(8)	89.5 (2)
N(1)	1.290 (12)	C(6)—C(5)	1.503 (21)
C(2)—C(1)—N(1)	114.2 (8)	C(7)	1.445 (20)
C(2)—N(2)	1.278 (12)	O(5)	1.271 (15)
C(1)—C(2)—N(2)	113.9 (8)	C(5)—C(6)—C(7)	120.7 (12)
C(3)—C(4)	1.439 (12)	O(5)	116.6 (12)
N(3)	1.298 (11)	C(7)—C(6)—O(5)	122.7 (13)
C(4)—C(3)—N(3)	114.0 (8)		
C(4)—N(4)	1.293 (12)		
C(3)—C(4)—N(4)	114.6 (8)		

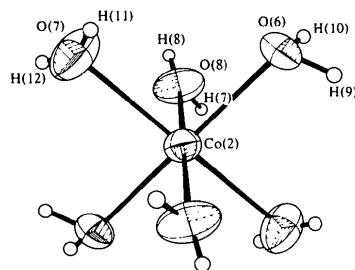


Fig. 2. The centrosymmetric hexaaquacobalt(II) cation, analogous to Fig. 1.

ethanedial dioxime ligands are present as mononegative gH⁻ species and form the usual intramolecular H bridges. Octahedral coordination is completed by the two Br⁻ anions in *trans* positions. For two of these complex species the unit cell contains one octahedral Co(H₂O)₆ cation with Co at a crystallographic inversion center. Charge neutrality requires that the

Co(H₂O)₆ moiety is a dipositive cation, and that each of the chelate complexes is a mononegative anion. This means that the hexaaqua species contains Co^{II}, and the chelate complex Co^{III}, most likely formed by air oxidation of the parent CoBr₂ during the preparation. The presence of acetone in the crystals explains the observed decomposition on drying.

The structure is held together by an extended network of hydrogen bridges. Each of the water molecules of the [Co(H₂O)₆]²⁺ cation forms hydrogen bridges, extending to the O atoms of the acetone and the oxime groups. The acetone O accepts two hydrogen bridges from two different [Co(H₂O)₆]²⁺ cations.

This structure determination performed with a rapidly collected data set is a further example of the statement of Hope & Nichols (1981) that fast data collection yields acceptable results in routine structure determinations. This holds even if the data are collected at room temperature (Endres, 1982). In the present case standard deviations of bond lengths between light atoms are around 0.01 Å, of angles 0.8°.

This work was supported by Stiftung Volkswagenwerk *via* its 'Partnership Program'.

References

- ANDOSEH, I. N., DOUGLAS, I., EGHAREVBA, G. O. & MÉGNAMISI-BÉLOMBÉ, M. (1982). *Z. Anorg. Allg. Chem.* **484**, 203–209.
- ENDRES, H. (1978). *Acta Cryst.* **B34**, 3736–3739.
- ENDRES, H. (1982). *Acta Cryst.* **B38**, 1313–1315.
- ENDRES, H., ANDOSEH, I. N. & MÉGNAMISI-BÉLOMBÉ, M. (1981). *Acta Cryst.* **B37**, 681–683.
- HOPE, H. & NICHOLS, B. G. (1981). *Acta Cryst.* **B37**, 158–161.
- International Tables for X-ray Crystallography* (1974). Vol. IV. Birmingham: Kynoch Press.
- MÉGNAMISI-BÉLOMBÉ, M. (1979). *Bull. Chem. Soc. Jpn.* **52**, 3424–3430.
- MÉGNAMISI-BÉLOMBÉ, M. (1981a). 19. *Gesellschaft Deutscher Chemiker Hauptversammlung*, pp. 129–130. Weinheim: Verlag Chemie.
- MÉGNAMISI-BÉLOMBÉ, M. (1981b). *International Conference on the Chemistry of Platinum Group Metals*, organized by R. Soc. Chem., School of Chemistry, Bristol, England, C26.
- MÉGNAMISI-BÉLOMBÉ, M. & NOVOTNY, M. A. (1980). *Inorg. Chem.* **19**, 2470–2473.
- 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.
- SVEDUNG, D. H. (1969). *Acta Chem. Scand.* **23**, 2863–2878.