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## Tetrahedral and Octahedral Cobalt(II) in Hexaaquacobalt Tetrachlorocobaltate–18-Crown-6–Acetone\*

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**Abstract.** [Co(H<sub>2</sub>O)<sub>6</sub>][CoCl<sub>4</sub>].C<sub>12</sub>H<sub>24</sub>O<sub>6</sub>.C<sub>3</sub>H<sub>6</sub>O, triclinic, *P*1̄, *a* = 10.251 (4), *b* = 11.619 (5), *c* = 13.603 (7) Å, α = 92.64 (4), β = 95.05 (4), γ = 112.38 (3)°, *V* = 1487 (1) Å<sup>3</sup>, *Z* = 2, *D<sub>m</sub>* = 1.53 (1), *D<sub>c</sub>* = 1.54 Mg m<sup>-3</sup>, μ(Mo *K*α) = 1.57 mm<sup>-1</sup>. The structure of [Co(H<sub>2</sub>O)<sub>6</sub>][CoCl<sub>4</sub>].18-crown-6.acetone, determined by heavy-atom techniques and refined by least-squares methods using diffractometer data to *R*<sub>1</sub> = 4.3% (4246 observed reflections), includes cobalt(II) in two coordination geometries: a tetrachlorocobaltate anion and a hexaaquacobalt cation. The crown ether ring does not incorporate the metal into its cavity.

**Introduction.** Su & Weiher (1968) reported the isolation of a blue material from acetic acid which they formulated as 2CoCl<sub>2</sub>.dicyclohexyl-18-crown-6, a 2:1 complex. Based on the physical properties of this material, two possible structures were proposed (Fig. 1). A more recent report (Knöchel, Klimes, Oehler & Rudolph, 1975) described the formation of transition-metal complexes of unsubstituted 18-crown-6; these

were 2:1 complexes containing nitrate or chloride. Farago (1977) has reported complexes of varying stoichiometries including a series of five complexes of CoBr<sub>2</sub> and 18-crown-6.

Structural investigations have been limited to: [Mn(H<sub>2</sub>O)<sub>5</sub>(NO<sub>3</sub>)]<sup>+</sup>.18-crown-6.NO<sub>3</sub><sup>-</sup>.H<sub>2</sub>O (Knöchel, Kopf, Oehler & Rudolph, 1978) where octahedral Mn is coordinated to five water molecules and one nitrate ion, and CuCl<sub>2</sub>.12-crown-4 where the metal is directly bound to the polyether O atoms (van Remoortere, Boer & Steiner, 1975). We have determined the structures of a series of transition-metal complexes with crown ethers to examine the structural consequences of change of ring size and metal ion (part II: Vance, Holt, Varie & Holt, 1980; Vance, 1978).

Hexaaquacobalt(II) tetrachlorocobaltate(II)–18-crown-6–acetone (Farago, 1977) was crystallized in a form suitable for X-ray diffraction studies. A crystal (approximately 0.5 × 0.5 × 0.5 mm) was coated with epoxy glue and mounted on a Syntex *P*1̄ diffractometer with graphite-monochromatized radiation (Mo *K*α, λ = 0.71069 Å). Least-squares refinement of the angular coordinates of fifteen independent reflections gave the unit-cell parameters and their standard deviations. The θ/2θ scan mode, at an invariant scan

\* Transition-Metal–Crown Ether Complexes. I.

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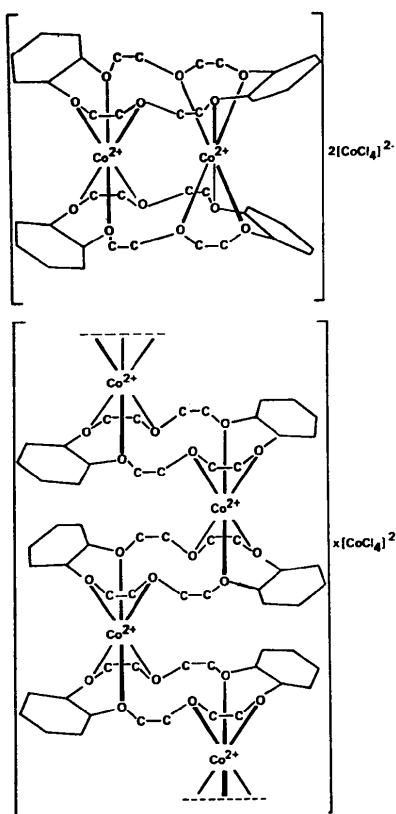


Fig. 1. Proposed structures of dicyclohexyl-18-crown-6 and  $\text{CoCl}_2$  (Su & Weiher, 1968), reproduced by permission from Pedersen (1978) and amended to remove one incorrect C atom.

rate of  $4^\circ \text{ min}^{-1}$ , was used to measure 5593 intensities ( $2\theta < 50^\circ$ ), of which 4246 were considered observed [ $F_o^2 > 3\sigma(F_o^2)$ ]. Backgrounds were measured at each end of the scan range for a time equal to 50% of the scan time. Three standard reflections were remeasured after every 97 reflections; decay corrections were deemed unnecessary. Lorentz and polarization corrections were made, but absorption corrections were not applied as the epoxy coating precluded precise measurement of the crystal.

A Patterson synthesis followed by successive least-squares cycles [function minimized:  $\sum w(|F_o| - |F_c|)^2$ ] and difference Fourier syntheses allowed location of all other atoms. The H atoms attached to C(15), C(16), C(19) and C(21) could not be satisfactorily located. The H atoms of the acetone are not included. Three cycles of refinement of scale factor, positional coordinates and anisotropic thermal parameters (isotropic thermal parameters for crown ether H atoms were refined; those for water H atoms were not varied) yielded the final discrepancy index:  $R_1 = \sum (|F_o| - |F_c|) / \sum |F_o| = 0.043$ .

Atomic scattering factors for  $\text{Co}^{2+}$ , Cl, O, C, and H were taken from Cromer & Mann (1968) and

anomalous-dispersion corrections were made for Co and Cl (*International Tables for X-ray Crystallography*, 1974). The XRAY 76 system (Stewart, 1976) was used for all calculations.\* The fractional atomic coordinates are given in Table 1.

\* Lists of structure factors and thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 34728 (19 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 1. Fractional atomic coordinates and standard deviations [for Co,  $\times 10^5$ ; H(11)–H(182),  $\times 10^3$ ; others,  $\times 10^4$ ]

	x	y	z
Co(1)	16061 (7)	13120 (5)	27995 (4)
O(30)	3206 (4)	610 (3)	2816 (2)
O(31)	3020 (4)	2782 (3)	3820 (2)
O(32)	799 (4)	296 (3)	3961 (2)
O(33)	2382 (4)	2425 (3)	1694 (2)
O(34)	352 (4)	-145 (3)	1756 (2)
O(35)	-35 (4)	1956 (3)	2851 (2)
Co(2)	28131 (8)	59175 (6)	26487 (5)
Cl(1)	4023 (2)	5254 (1)	1590 (1)
Cl(2)	3633 (2)	5693 (1)	4198 (1)
Cl(3)	3226 (2)	7926 (1)	2374 (1)
Cl(4)	458 (2)	4719 (1)	2387 (1)
C(1)	512 (6)	3006 (4)	9521 (4)
O(2)	1412 (3)	2354 (3)	9744 (2)
C(3)	2621 (6)	2751 (4)	9224 (4)
C(4)	3380 (5)	1889 (4)	9342 (4)
O(5)	2440 (3)	680 (3)	8895 (2)
C(6)	2990 (5)	-268 (5)	9048 (4)
C(7)	2931 (6)	-664 (4)	86 (4)
O(8)	1529 (4)	-1193 (3)	355 (2)
C(9)	788 (6)	-2468 (5)	9978 (4)
C(10)	332 (14)	7110 (7)	4541 (6)
O(11)	-496 (6)	7802 (4)	4175 (3)
C(12)	-1921 (10)	7080 (6)	3779 (5)
C(13)	-2675 (8)	7888 (8)	3524 (5)
O(14)	-2756 (5)	8540 (4)	4399 (3)
C(15)	3728 (10)	818 (10)	5640 (8)
C(16)	3263 (8)	9750 (9)	6114 (8)
O(17)	1864 (6)	8782 (5)	5691 (4)
C(18)	1865 (12)	8033 (10)	4895 (6)
C(19)	3255 (7)	6101 (6)	8761 (5)
C(20)	3875 (6)	6966 (5)	7986 (4)
C(21)	3567 (9)	6420 (6)	6919 (5)
O(22)	4624 (4)	8055 (3)	8213 (3)
H(301)	2846	-269	2638
H(302)	4053	1019	2452
H(311)	3302	2670	4416
H(312)	3264	3608	3812
H(321)	1269	562	4595
H(322)	269	-477	3971
H(331)	1980	2280	1026
H(332)	2893	3228	1770
H(341)	-594	-202	1449
H(342)	905	-428	1414
H(351)	106	2728	2764
H(352)	-598	1627	3393
H(11)	90 (5)	372 (4)	975 (4)
H(12)	20 (7)	285 (5)	865 (4)
H(31)	323 (4)	377 (4)	943 (3)
H(32)	215 (7)	268 (5)	833 (4)

Table 1 (cont.)

	x	y	z
H(41)	429 (6)	214 (5)	901 (4)
H(42)	370 (6)	175 (5)	3 (4)
H(61)	399 (5)	4 (4)	893 (3)
H(62)	234 (5)	-100 (4)	852 (3)
H(71)	343 (5)	4 (4)	55 (3)
H(72)	351 (6)	-123 (5)	20 (4)
H(91)	59 (6)	-240 (5)	930 (4)
H(92)	142 (6)	-290 (5)	11 (4)
H(101)	30 (8)	662 (6)	396 (5)
H(102)	-13 (6)	667 (5)	498 (4)
H(121)	-214 (6)	659 (5)	433 (4)
H(122)	-172 (8)	659 (6)	310 (5)
H(131)	-220 (5)	851 (4)	314 (3)
H(132)	-358 (7)	742 (6)	327 (5)
H(181)	221 (8)	845 (6)	431 (5)
H(182)	252 (8)	760 (7)	505 (5)

**Discussion.** Co adopts two coordination geometries in the asymmetric unit (Fig. 2): a minimally distorted octahedral coordination sphere of water molecules [right angles 86.2 (2)–93.1 (2)°, bond lengths 2.042 (3)–2.118 (3) Å] and tetrahedral coordination to four Cl atoms [Co–Cl bonds, 2.262 (2)–2.269 (2) Å; Cl–Co–Cl angles, 106.72 (7)–113.33 (6)°]. Co was also found in two coordination geometries in  $\text{CoCl}_2 \cdot 2.5\text{C}_2\text{H}_5\text{OH}$  (Bkouche-Waksman & L'Haridon, 1977), where isolated  $[\text{Co}(\text{C}_2\text{H}_5\text{OH})_6]^{2+}$  octahedra [average Co–O distance, 2.096 (4) Å] and trinuclear  $[\text{Cl}_3\text{CoCl}-\text{Co}(\text{C}_2\text{H}_5\text{OH})_4-\text{ClCoCl}_3]^{2-}$  chains were found.

The crown ether exists as two crystallographically unique rings about centers of inversion at 0,0,0 and 0,0,½ (crown A and B, Table 2) (Fig. 3). Attempts to describe the disorder apparent in C(15) and C(16) with partial-occupancy positions were unsuccessful. A

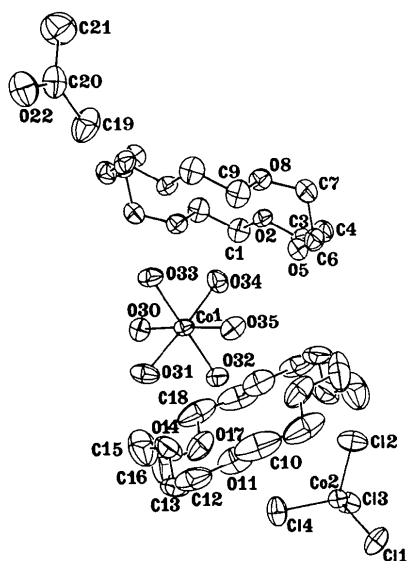
Fig. 2.  $[\text{Co}(\text{H}_2\text{O})_6][\text{CoCl}_4] \cdot 18\text{-crown-6} \cdot \text{acetone}$ .

Table 2. Selected distances (Å) and angles (°)

$[\text{Co}(\text{H}_2\text{O})_6]^{2+}$			
Co(1)–O(30)	2.091 (4)	Co(1)–O(31)	2.118 (3)
Co(1)–O(32)	2.057 (3)	Co(1)–O(33)	2.042 (3)
Co(1)–O(34)	2.082 (3)	Co(1)–O(35)	2.090 (5)
$[\text{CoCl}_4]^{2-}$			
Co(2)–Cl(1)	2.269 (2)	Co(2)–Cl(3)	2.262 (2)
Co(2)–Cl(2)	2.263 (2)	Co(2)–Cl(4)	2.266 (2)
Crown A			
C(1)–O(2)	1.420 (8)	O(5)–C(6)	1.432 (7)
O(2)–C(3)	1.414 (6)	C(6)–C(7)	1.504 (7)
C(3)–C(4)	1.490 (9)	C(7)–O(8)	1.420 (6)
C(4)–O(5)	1.435 (5)	O(8)–C(9)	1.427 (6)
		C(9)–C(1')	1.482 (8)
C(1)–O(2)–C(3)	112.5 (4)	C(6)–C(7)–O(8)	113.4 (4)
O(2)–C(3)–C(4)	109.9 (4)	C(7)–O(8)–C(9)	113.1 (4)
C(3)–C(4)–O(5)	107.6 (4)	O(8)–C(9)–C(1')	108.6 (5)
C(4)–O(5)–C(6)	113.1 (4)	C(9)–C(1')–O(2')	109.4 (4)
O(5)–C(6)–C(7)	113.2 (4)		
Crown B			
C(10)–O(11)	1.45 (1)	O(14)–C(15)	1.45 (1)
O(11)–C(12)	1.42 (1)	C(15)–C(16)	1.36 (2)
C(12)–C(13)	1.46 (1)	C(16)–O(17)	1.49 (1)
C(13)–O(14)	1.41 (1)	O(17)–C(18)	1.36 (1)
		C(18)–C(10')	1.54 (1)
C(10)–O(11)–C(12)	116.1 (6)	C(15)–C(16)–O(17)	115.7 (8)
O(11)–C(12)–C(13)	110.7 (5)	C(16)–O(17)–C(18)	116.7 (8)
C(12)–C(13)–O(14)	108.5 (6)	O(17)–C(18)–C(10')	109.8 (9)
C(13)–O(14)–C(15)	118.0 (6)	C(18)–C(10')–O(11')	109.1 (7)
O(14)–C(15)–C(16)	113.5 (8)		

Table 3. Contact distances (Å)

H(302)–O(22)	1.735 (4)	O(30)–O(22)	2.726 (5)
H(311)–O(14)	2.158 (4)	O(31)–O(14)	2.905 (6)
H(321)–O(14)	1.891 (4)	O(32)–O(14)	2.775 (5)
H(322)–O(11)	1.894 (4)	O(32)–O(11)	2.732 (5)
H(331)–O(2)	1.805 (3)	O(33)–O(2)	2.736 (4)
H(341)–O(5)	1.761 (3)	O(34)–O(5)	2.741 (5)
H(342)–O(8)	1.937 (4)	O(34)–O(8)	2.807 (6)
H(352)–O(17)	1.825 (6)	O(35)–O(17)	2.788 (7)

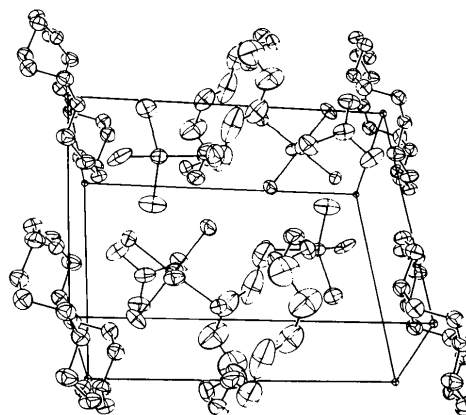


Fig. 3. Packing of molecules within the cell.

similar disorder was observed in  $[\text{Mn}(\text{H}_2\text{O})_6](\text{ClO}_4)_2 \cdot 18\text{-crown-6}$  (Vance, Holt, Varie & Holt, 1980). The distances of Table 3 indicate a network of hydrogen bonding between polyether O atoms and the  $[\text{Co}(\text{H}_2\text{O})_6]$  group.

The molecule of acetone shows normal bond angles and distances. An infrared spectrum shows a peak at  $1691\text{ cm}^{-1}$ , a shift of  $22\text{ cm}^{-1}$  to lower frequency as compared to the spectrum of free acetone, confirming the H(302)–O(22) hydrogen bond indicated in Table 3.

The 18-crown-6 thus fails to form the direct Co–O (polyether) bonds proposed by Su & Weiher (1968).

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## Structure of Hexaaquamanganese(II) Perchlorate–18-Crown-6\*

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**Abstract.**  $[\text{Mn}(\text{H}_2\text{O})_6](\text{ClO}_4)_2 \cdot \text{C}_{12}\text{H}_{24}\text{O}_6$ , monoclinic,  $P2_1/c$ ,  $a = 14.099$  (5),  $b = 10.619$  (6),  $c = 17.956$  (8) Å,  $\beta = 91.37$  (3)°,  $V = 2688$  (2) Å<sup>3</sup>,  $Z = 4$ ,  $D_m = 1.62$  (1),  $D_c = 1.55\text{ Mg m}^{-3}$ ,  $\mu(\text{Mo } K\alpha) = 0.80\text{ mm}^{-1}$ . Least-squares refinement of diffractometer data (1593 observed reflections) to  $R_1 = 7.5\%$  shows Mn with an octahedral coordination sphere of water molecules. Hydrogen bonding appears to tether the hexaaquamanganese cation between two crystallographically nonequivalent crown ether rings.

**Introduction.** Transition-metal complexes with crown ethers have received little attention in the literature (Vance, Holt, Pierpont & Holt, 1980; and references therein). We have determined the structures of a series of these complexes to examine structural consequences of change of ring size and metal ion.

\* Transition-Metal–Crown Ether Complexes. II.

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The title compound was prepared by addition of a dilute acetic acid solution of hexaaquamanganese(II) perchlorate to a dilute acetic acid solution of 18-crown-6 (1:1). Colorless crystalline rods were formed on evaporation. These were observed to decompose in air. (Analysis: calculated for  $\text{C}_{12}\text{H}_{36}\text{Cl}_2\text{MnO}_{20}$ : Mn, 8.77; C, 23.02; H, 5.79; Cl, 11.32%; found: Mn, 8.55; C, 22.95; H, 5.80; Cl, 11.27%.)

A single crystal of average diameter 0.21 mm and 0.54 mm in length was mounted in a glass capillary. A Syntex  $P\bar{1}$  four-circle automated diffractometer with a pulse-height analyzer and graphite-monochromatized radiation were used for data collection. Least-squares refinement of the angular coordinates of 15 independent reflections ( $4.5^\circ < 2\theta < 17.9^\circ$ ) allowed determination of cell constants and standard deviations. Room-temperature measurement of 2705 reflections ( $2\theta_{\text{max}} = 40^\circ$ ) using a  $\theta/2\theta$  scan produced 1593 observed data [ $I > 3\sigma(I)$ ]. A fixed scan rate of  $3^\circ\text{ min}^{-1}$  and a background to scan time ratio of 0.8:1 were employed. The intensities of three check reflec-