

Transition-Metal–Crown-Ether Complexes. III.* Seven-Coordinate Co^{II} in Dinitratocobalt(II)–12-Crown-4 and Diaquacobalt(II) Dinitrate–15-Crown-5

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Abstract

The structures of Co^{II}(NO₃)₂(12-crown-4), [Co(C₈H₁₆O₄)(NO₃)₂], (I), and Co^{II}(H₂O)₂(15-crown-5)(NO₃)₂, [Co(C₁₀H₂₀O₅)(H₂O)₂](NO₃)₂, (II), have been determined from single-crystal X-ray diffractometer data at 291 (2) K and refined by least-squares methods to $R = 2.7$ and 4.7% respectively. (I) crystallizes in orthorhombic space group $Pna2_1$, $a = 12.478$ (3), $b = 7.567$ (2), $c = 14.231$ (6) Å, $V = 1343.7$ (8) Å³, $Z = 4$, $D_m = 1.75$, $D_c = 1.775$ Mg m⁻³ and (II) crystallizes in tetragonal space group $P4_12_12$, $a = b = 8.079$ (1), $c = 27.231$ (5) Å, $Z = 4$, $V = 1777.4$ (5) Å³, $D_m = 1.66$ and $D_c = 1.641$ Mg m⁻³. The oxygen atoms of each crown-ether ring are directly coordinated to Co^{II}, which is seven coordinate in each structure by additional coordination to two oxygens of one nitrate group and one oxygen of the other nitrate group in (I) and coordination to two water oxygens in (II).

Introduction

While the structural chemistry of crown-ether complexes with alkali-metal ions has been investigated at some length, the structures of transition-metal complexes with crown ethers have received little attention. Those complexes which have been examined structurally have shown a wide variety of modes of involvement with the crown ether. Some structures have shown that the transition metal achieves normal coordination geometry with water or nitrate ions which

are then hydrogen bonded to the crown ether: Mn(NO₃)₂·6H₂O·18-crown-6 (Knöchel, Kopf, Oehler & Rudolph, 1978), [Mn(H₂O)₆](ClO₄)₂·18-crown-6 (Vance, Holt, Varie & Holt, 1980), and [Co(H₂O)₆][CoCl₄]·18-crown-6·acetone (Vance, Holt, Pierpont & Holt, 1980) where two coordination geometries were observed for Co^{II}. Other structures have shown direct involvement of the transition metal with the polyether oxygens, either completing the coordination sphere of the metal: Mn(12-crown-4)₂(Br₃)₂ (Pierpont & Blackmer, 1979), or partially completing it: CuCl₂·(12-crown-4) (van Remoortere, Boer & Steiner, 1975). We have determined the structures of a series of transition-metal–crown-ether complexes to observe the effects of change of polyether ring size on coordination geometry and structure.

Experimental

Preparation of Co^{II}(NO₃)₂(12-crown-4) (I)

190 μl of 12-crown-4 ($d = 1.1$ g/ml) were added to 15 ml of a 0.04 mol dm⁻³ solution of Co(H₂O)₆(NO₃)₂ in dioxane (mole ratio Co:12-crown-4 = 1:2). After filtration, the solution was allowed to evaporate slowly under nitrogen. Rose-red plates formed after 1–2 d which were collected by filtration and washed with small amounts of dioxane under a nitrogen atmosphere. Analysis: found, C 26.54; H 4.47; N 7.63; calc., C 26.75; H 4.49; N 7.80%.

Characterization: m.p. 503–510 K, decomp.; $\mu_{\text{eff}} = 4.21 \times 10^{-23}$ J T⁻¹ (room temp.); IR spectrum (720–740 cm⁻¹) characteristic of monodentate NO₃⁻, the 50 cm⁻¹ splitting of this band, characteristic of bidentate NO₃⁻ is not observed. Other bands typical of coordinated NO₃⁻ are seen at 809, 1020, 1280 and 1490 cm⁻¹ (Curtis & Curtis, 1965).

* Part I: Vance, Holt, Pierpont & Holt (1980). Part II: Vance, Holt, Varie & Holt (1980).

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Preparation of $\text{Co}^{\text{II}}(\text{H}_2\text{O})_2(15\text{-crown-5})(\text{NO}_3)_2$ (II)

To 3 ml of a 0.04 mol dm^{-3} dioxane solution of $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ were added 0.256 g (tenfold molar excess) of 15-crown-5 (Parrish Chemical Co.). The solution was evaporated slowly under N_2 and small, transparent, violet needles were observed after 24 h. These were collected by filtration in a dry N_2 environment. M.p. 462–463 K. Analysis: found, C 27.28; H 5.46; N 5.73; calc., C 27.34; H 5.51; N 6.38%. The nitrogen analysis is somewhat low but was reproducible to within 0.02% on five successive analyses.

X-ray diffraction

Crystals suitable for X-ray diffraction study (I, $0.7 \times 0.5 \times 0.1 \text{ mm}$; II, $0.4 \times 0.4 \times 0.6 \text{ mm}$) were mounted on a Syntex $P2_1$ diffractometer. Cell dimensions (Table 1) and their standard deviations were determined by least-squares fit to the 2θ , ω and χ settings for twelve independent reflections. Data were measured ($+h, +k, +l$) at 291 (2) K using graphite-monochromatized molybdenum $K\alpha$ radiation, a θ – 2θ scan with speed of 2.0 – $29.3^\circ \text{ min}^{-1}$, depending upon the intensity of a 2 s prescan and a 2θ scan range of $(1.6 + 0.692 \tan \theta)^\circ$ starting the scan from 0.8° below the calculated $K\alpha_1$ position. (I) was measured in a stream of dry nitrogen gas. Background measurements were made at each end of the scan range for a time period equal to $\frac{1}{4}$ of the scan time with crystal and counter stationary. Reflections were measured to $2\theta_{\text{max}} = 45^\circ$. Three standard reflections were measured after every 100 reflections and their intensities showed deviations

of less than 4% during the course of data collection. Independent, observed reflections (I, 1399; II, 1090) were judged to be those with $I > 3\sigma(I)$ and were used for structure solution and refinement after correction for background, Lorentz, polarization and absorption effects.

Atomic coordinates were determined by direct methods and refined by least-squares techniques. For (II), the initial solution ($R = 13\%$) showed Co surrounded by a planar ring of ten oxygen atoms, each approximately 2.2 \AA from Co. Each adjacent pair of oxygen atoms was bridged by a carbon atom, the ten carbons forming a second planar ring about Co with an average Co–C distance of 3.1 \AA . The two halves of the concentric ring systems were related by a twofold axis in the plane of the rings. None of the oxygen atoms of the initial solution lay on the twofold axis, but two of the carbon atoms were on that axis. The disorder was resolved into two half-occupancy 15-crown-5 rings by selecting one set of five alternating oxygens and viewing the carbon positions of the original solution as composite positions of carbons bridging the selected set of five oxygen atoms and those bridging the other set. Thus, appropriate positions for carbon atoms were calculated by fitting a model with reasonable angles and distances to the observed positions. This 50% occupancy ring (A), whose halves are not related by the twofold axis, generates the other 50% occupancy ring (B) when the twofold symmetry operation is applied (Fig. 1). This approximation allowed refinement of the structure to a point of good agreement of observed and calculated data; however, the difficulty of refining a set of atoms which generates another set in close spatial proximity upon application of a space-group symmetry element must be recognized in the appearance of the thermal ellipsoids. C(10) (ring A), for example, is 0.4 \AA from C(10) (ring B); C(1) (ring A) must interfere with the refinement of C(9) as C(1) (ring A) and C(9) (ring B) are 0.7 \AA apart (Figs. 1 and 2).

Table 1. *Crystal data*

	(I)	(II)
	$\text{C}_9\text{H}_{16}\text{CoN}_2\text{O}_{10}$	$\text{C}_{10}\text{H}_{24}\text{CoN}_2\text{O}_{13}$
M_r	359.16	439.25
Space group	$Pna2_1$	$P4_12_12$
Systematic absences	hkl none $0kl$ $k + l \neq 2n$ $h0l$ $h \neq 2n$ $hk0$ none $h00$ ($h \neq 2n$) $0k0$ ($k \neq 2n$) $00l$ ($l \neq 2n$)	hkl none $00l$ $l \neq 4n$ $h00$ $h \neq 2n$
a	12.478 (3) \AA	8.079 (1) \AA
b	7.567 (2)	8.079 (1)
c	14.231 (6)	27.231 (5)
V	1343.7 (8) \AA^3	1777.4 (5) \AA^3
Z	4	4
$F(000)$	740	916
D_m	1.75 (2) Mg m^{-3} (floatation)	1.66 (2) Mg m^{-3} (floatation)
D_c	1.775	1.641
$\mu(\text{Mo } K\alpha)$	1.325 mm^{-1}	1.075 mm^{-1}
Transmission factors	0.61–0.84	0.77–0.82

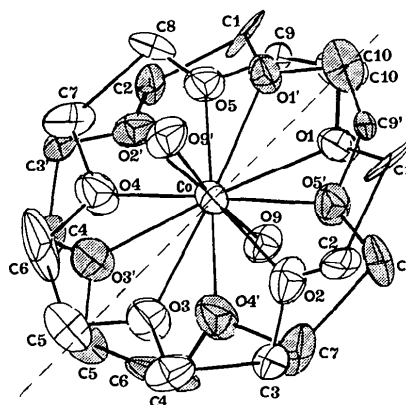
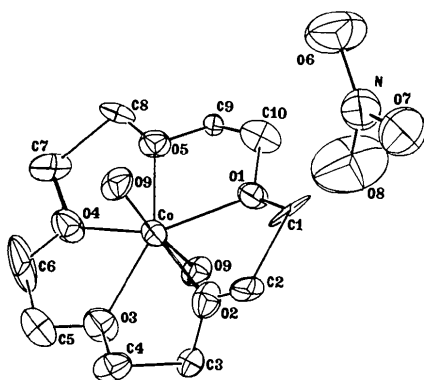


Fig. 1. $\text{Co}^{\text{II}}(15\text{-crown-5})$ (II) with ring A (50% occupancy), ring B (shaded atoms numbered as C' and O', 50% occupancy) and twofold axis (dashed line).

Fig. 2. $\text{Co}^{\text{II}}(\text{H}_2\text{O})_2(15\text{-crown-5})(\text{NO}_3)_2$ (II).Table 2. Positional parameters for $\text{Co}^{\text{II}}(\text{NO}_3)_2(12\text{-crown-4})$ (I)

The z coordinate for Co(I) was held constant during refinement. For non-H atoms $U_{\text{eq}} = U_{11} + U_{22} + U_{33}$, $\sigma(U_{\text{eq}}) = \frac{1}{2}\{[\sigma(U_{11})]^2 + [\sigma(U_{22})]^2 + [\sigma(U_{33})]^2\}^{1/2}$. H atom U values are in the form $\exp[-2\pi^2 U (2 \sin \theta/\lambda)^2]$.

	x	y	z	$U_{\text{eq}}/U (\text{\AA}^2)$
Co(1)	0.08845 (4)	0.07757 (6)	0.44000	0.0977 (2)
O(1)	0.4432 (3)	0.5623 (4)	0.4870 (2)	0.149 (2)
O(2)	0.4731 (2)	0.3834 (5)	0.3286 (2)	0.145 (2)
O(3)	0.5903 (2)	0.1395 (4)	0.4158 (2)	0.119 (1)
O(4)	0.5448 (3)	0.3035 (4)	0.5766 (2)	0.142 (2)
O(5)	0.1362 (3)	-0.1637 (5)	0.3644 (3)	0.154 (2)
O(6)	0.2032 (3)	0.0787 (5)	0.3184 (3)	0.170 (2)
O(7)	0.2622 (4)	-0.1625 (7)	0.2584 (3)	0.248 (3)
O(8)	0.2360 (2)	0.0615 (4)	0.5108 (2)	0.138 (2)
O(9)	0.1682 (3)	-0.1658 (6)	0.5810 (3)	0.198 (2)
O(10)	0.3230 (3)	-0.0696 (6)	0.6210 (3)	0.216 (2)
N(1)	0.2031 (3)	-0.0872 (6)	0.3122 (3)	0.129 (2)
N(2)	0.2425 (3)	-0.0594 (6)	0.5729 (3)	0.132 (2)
C(1)	0.3501 (5)	0.5189 (11)	0.4298 (7)	0.242 (4)
C(2)	0.3834 (5)	0.5000 (12)	0.3337 (6)	0.248 (4)
C(3)	0.4476 (5)	0.2013 (8)	0.3089 (4)	0.170 (3)
C(4)	0.5473 (6)	0.1012 (8)	0.3238 (4)	0.158 (3)
C(5)	0.5416 (4)	0.0339 (7)	0.4886 (4)	0.153 (3)
C(6)	0.5725 (5)	0.1185 (8)	0.5792 (4)	0.150 (3)
C(7)	0.4406 (5)	0.3436 (8)	0.6109 (4)	0.179 (3)
C(8)	0.4215 (5)	0.5348 (8)	0.5846 (4)	0.171 (3)
H(11)	0.312 (4)	0.635 (7)	0.422 (5)	0.08 (2)
H(12)	0.325 (5)	0.372 (9)	0.482 (5)	0.09 (2)
H(21)	0.377 (10)	0.664 (17)	0.315 (9)	0.09 (2)
H(22)	0.334 (6)	0.466 (11)	0.292 (5)	0.06 (2)
H(31)	0.409 (6)	0.180 (9)	0.244 (5)	0.09 (2)
H(32)	0.386 (6)	0.158 (10)	0.361 (5)	0.09 (2)
H(41)	0.038 (5)	0.530 (9)	0.314 (5)	0.08 (2)
H(42)	0.106 (4)	0.363 (8)	0.270 (4)	0.09 (2)
H(51)	0.066 (4)	0.579 (7)	0.492 (3)	0.05 (1)
H(52)	0.460 (4)	0.032 (7)	0.477 (3)	0.07 (2)
H(61)	0.357 (3)	0.885 (6)	0.077 (3)	0.04 (1)
H(62)	0.468 (4)	0.917 (7)	0.133 (4)	0.06 (2)
H(71)	0.047 (5)	0.802 (9)	0.179 (4)	0.10 (2)
H(72)	0.119 (5)	0.756 (9)	0.077 (5)	0.09 (2)
H(81)	0.028 (5)	0.108 (9)	0.119 (5)	0.07 (2)
H(82)	0.143 (8)	0.066 (13)	0.086 (8)	0.07 (4)

Three cycles of refinement [function minimized, $\sum(|F_o| - |F_c|)^2$] of positional and anisotropic thermal parameters and including anomalous-dispersion corrections for Co (*International Tables for X-ray Crystallography*, 1974) were carried out for the 21 nonhydrogen atoms in each structure giving a final R of 4.7% for (II) [$R = (\sum|F_o| - |F_c|)/\sum|F_o| \times 100$]. A difference-Fourier map calculated at this stage allowed location of 16 hydrogen atoms attached to the polyether ring of (I). Two further cycles of refinement (positional parameters for all atoms, anisotropic thermal parameters for 21 nonhydrogen atoms and isotropic thermal parameters for hydrogens) gave a final R of 2.7% for (I).

The chiral character of structure (II) was established by examining refinement of the x, y, z modification of atomic coordinates of space group $P4_12_12$ (No. 92) in space group $P4_32_12$ (No. 96) which gave a final R of 5.6%. Tabulation of ΔF for those reflections for which $h \neq 0$, $h \neq k$, $k \neq 0$ and $l \neq 0$ confirmed that the enantiomorph is correctly represented by $P4_12_12$.

Scattering factors for all atoms were taken from Cromer & Mann (1968). Unit weights were used throughout. All calculations were performed using the XRAY system (Stewart, 1976).* The fractional atomic coordinates are shown in Tables 2 and 3.

* Lists of structure factors, anisotropic thermal parameters and an alternative view of $\text{Co}^{\text{II}}(\text{NO}_3)_2(12\text{-crown-4})$ (I) have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 35277 (19 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 3. Positional coordinates for $\text{Co}^{\text{II}}(\text{H}_2\text{O})_2(15\text{-crown-5})(\text{NO}_3)_2$ (II)

Co(1) is situated on the twofold symmetry axis, $x, x, 0$. See Table 2 for definition of U_{eq} and $\sigma(U_{\text{eq}})$.

	x	y	z	$U_{\text{eq}} (\text{\AA}^2)$
Co(1)	0.0848 (1)	0.0848 (1)	0.0000	0.0985 (4)
N(1)	0.5069 (9)	0.3079 (9)	0.4064 (3)	0.133 (4)
O(1)	0.3389 (15)	0.1943 (15)	0.0087 (4)	0.122 (6)
O(2)	0.2325 (18)	-0.0776 (21)	0.0565 (4)	0.136 (8)
O(3)	-0.0424 (16)	-0.1600 (19)	0.0122 (5)	0.167 (8)
O(4)	-0.1530 (16)	0.0936 (19)	-0.0338 (5)	0.175 (8)
O(5)	0.0712 (18)	0.3235 (14)	-0.0331 (5)	0.131 (7)
O(6)	0.5718 (8)	0.2599 (8)	0.4473 (2)	0.161 (3)
O(7)	0.4541 (9)	0.4504 (8)	0.4033 (2)	0.222 (4)
O(8)	0.4988 (11)	0.2138 (10)	0.3724 (3)	0.293 (6)
O(9)	-0.0076 (7)	0.1991 (7)	0.0628 (2)	0.135 (3)
C(1)	0.429 (3)	0.155 (3)	0.0548 (8)	0.16 (1)
C(2)	0.332 (3)	-0.044 (3)	0.0736 (9)	0.13 (1)
C(3)	0.199 (4)	-0.235 (4)	0.0589 (15)	0.16 (1)
C(4)	0.0001 (4)	-0.260 (3)	0.0514 (7)	0.14 (1)
C(5)	-0.208 (4)	-0.176 (4)	0.0099 (7)	0.14 (1)
C(6)	-0.268 (4)	-0.014 (5)	-0.0207 (13)	0.30 (2)
C(7)	-0.217 (5)	0.248 (4)	-0.0502 (16)	0.22 (2)
C(8)	-0.034 (4)	0.408 (3)	-0.0600 (14)	0.26 (2)
C(9)	0.226 (2)	0.386 (2)	-0.0461 (9)	0.11 (1)
C(10)	0.354 (11)	0.350 (9)	-0.0081 (17)	0.13 (2)

Discussion

Cobalt(II) is seven coordinate and directly bound to the crown ether in both $\text{Co}(\text{NO}_3)_2(12\text{-crown-4})$ (I) and $\text{Co}(\text{H}_2\text{O})_2(15\text{-crown-5})(\text{NO}_3)_2$ (II) (Figs. 2 and 3). In (I) (Table 4) the binding sphere shows coordination to the tetradentate polyether [Co—O, 2.161 (4) and 2.210 (4) Å], one bidentate NO_3^- (Co—O, 2.202 (4), 2.246 (4) Å) and one monodentate NO_3^- [Co—O, 2.210 (4) Å; nonbonded Co—O(9), 2.900 (5) Å]. In (II) (Table 5), 15-crown-5 serves as a pentadentate ligand [Co—O, 2.131 (11)–2.347 (14) Å] and two water oxygen atoms [Co—O, 2.082 (5) Å] complete the seven sites, NO_3^- being uninvolved with the metal. The Co—O distances are longer than the five Co—O distances [av. 2.177 (4) Å] observed in the seven-coordinate Co—cryptate complex, $[\text{Co}(\text{C}_{16}\text{H}_{32}\text{N}_2\text{O}_5)]\text{[Co}(\text{SCN})_4]$ (Mathieu & Weiss, 1973).

The ionic diameter of Co^{II} is 1.48 Å (Pauling, 1960) compared to the cavity diameter of 1.2–1.5 Å for 12-crown-4 and 1.7–2.2 Å for 15-crown-5 (Dalley, 1978). Ion diameter/cavity diameter ratios of 0.75–0.90 (Christensen, Hill & Izatt, 1971) have been observed to be favorable for direct ion–crown-ether bonding in alkali metals. Thus, it is not surprising that Co^{II} is able to coordinate directly to these smaller crown ethers, whereas the complex $[\text{Co}(\text{H}_2\text{O})_6]\text{[CoCl}_4]$. 18-crown-6. acetone (Vance, Holt, Pierpont & Holt, 1980) displays Co^{II} in octahedral $\text{Co}(\text{H}_2\text{O})_6$ and tetrahedral CoCl_4 ions, both uninvolved with 18-crown-6 (cavity diameter, 2.6–3.2 Å).

Seven coordination has been previously observed for Co^{II} in two general situations: in structures with planar pentadentate ligands such as $[\text{Co}(\text{DAPSC})\text{Cl}(\text{H}_2\text{O})]\text{Cl}\cdot 2\text{H}_2\text{O}$ [DAPSC = 2,6-diacetylpyridine bis(semicarbazone)] (Wester & Palenik, 1973; Palenik & Wester, 1978), $[\text{Co}(\text{DAPBH})(\text{H}_2\text{O})(\text{NO}_3)]^+$ (DAPBH = 2,6-diacetylpyridine dibenzoylhydrazone) (Giordano, Palenik, Palenik & Sullivan, 1979) and $[\text{Co}(\text{H}_2\text{DAPP})(\text{H}_2\text{O})_2]\text{Cl}_2$ (H_2DAPP = 2,6-diacetylpyridine di-2-pyridylhydrazone) (Wester & Palenik, 1975, 1976) where two additional axial ligands complete the pentagonal bipyramidal geometry; and with bidentate nitrate groups which subtend very small O—metal—O bond angles, for example seven-coordinate

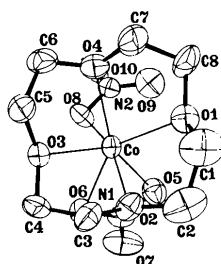


Fig. 3. View of $\text{Co}^{II}(\text{NO}_3)_2(12\text{-crown-4})$ (I).

Table 4. Selected bond angles ($^\circ$) and distances (Å) for $\text{Co}^{II}(\text{NO}_3)_2(12\text{-crown-4})$ (I)

Co(1)—O(1)	2.203 (3)	C(1)—O(1)	1.457 (8)
Co(1)—O(2)	2.161 (4)	C(1)—C(2)	1.436 (13)
Co(1)—O(3)	2.169 (3)	C(2)—O(2)	1.428 (9)
Co(1)—O(4)	2.210 (4)	O(2)—C(3)	1.442 (7)
Co(1)—O(5)	2.202 (4)	C(3)—C(4)	1.472 (9)
Co(1)—O(6)	2.246 (4)	C(4)—O(3)	1.445 (7)
Co(1)—O(8)	2.102 (3)	O(3)—C(5)	1.442 (6)
N(1)—O(5)	1.258 (6)	C(5)—C(6)	1.491 (8)
N(1)—O(6)	1.259 (6)	C(6)—O(4)	1.442 (7)
N(1)—O(7)	1.206 (6)	O(4)—C(7)	1.422 (7)
N(2)—O(8)	1.274 (6)	C(7)—C(8)	1.513 (8)
N(2)—O(9)	1.233 (6)	C(8)—O(1)	1.430 (7)
N(2)—O(10)	1.218 (6)		
O(1)—Co(1)—O(2)	75.0 (1)	O(3)—Co(1)—O(4)	74.9 (1)
O(1)—Co(1)—O(3)	122.1 (1)	O(3)—Co(1)—O(5)	137.6 (1)
O(1)—Co(1)—O(4)	74.1 (1)	O(3)—Co(1)—O(6)	82.4 (1)
O(1)—Co(1)—O(5)	88.4 (1)	O(3)—Co(1)—O(8)	97.1 (1)
O(1)—Co(1)—O(6)	139.5 (1)	O(4)—Co(1)—O(5)	146.5 (1)
O(1)—Co(1)—O(8)	123.2 (1)	O(4)—Co(1)—O(6)	146.4 (1)
O(2)—Co(1)—O(3)	75.9 (1)	O(4)—Co(1)—O(8)	79.5 (1)
O(2)—Co(1)—O(4)	115.2 (1)	O(5)—Co(1)—O(6)	56.9 (1)
O(2)—Co(1)—O(5)	86.3 (1)	O(5)—Co(1)—O(8)	87.1 (1)
O(2)—Co(1)—O(6)	81.9 (1)	O(6)—Co(1)—O(8)	79.1 (1)
O(2)—Co(1)—O(8)	160.5 (1)		
C(8)—O(1)—C(1)	111.0 (5)	C(4)—O(3)—C(5)	112.5 (4)
O(1)—C(1)—C(2)	108.9 (5)	O(3)—C(5)—C(6)	105.9 (4)
C(1)—C(2)—O(2)	109.7 (6)	C(5)—C(6)—O(4)	109.4 (5)
C(2)—O(2)—C(3)	115.2 (5)	C(6)—O(4)—C(7)	114.7 (4)
O(2)—C(3)—C(4)	106.1 (5)	O(4)—C(7)—C(8)	105.3 (4)
C(3)—C(4)—O(3)	109.9 (5)	C(7)—C(8)—O(1)	110.5 (4)
O(5)—N(1)—O(6)	114.7 (4)	O(8)—N(2)—O(9)	119.1 (4)
O(6)—N(1)—O(7)	121.0 (5)	O(9)—N(2)—O(10)	121.7 (5)
O(7)—N(1)—O(5)	124.2 (5)	O(10)—N(2)—O(8)	119.2 (4)

Table 5. Selected bond angles ($^\circ$) and distances (Å) for $\text{Co}^{II}(\text{H}_2\text{O})_2(15\text{-crown-5})(\text{NO}_3)_2$ (II)

Co(1)—O(1)	2.248 (12)	Co(1)—O(4)	2.131 (13)
Co(1)—O(2)	2.347 (14)	Co(1)—O(5)	2.131 (11)
Co(1)—O(3)	2.254 (15)	Co(1)—O(9)	2.082 (5)
O(1)—Co(1)—O(2)	71.7 (5)	O(3)—Co(1)—O(5)	146.4 (5)
O(1)—Co(1)—O(3)	138.3 (5)	O(4)—Co(1)—O(5)	75.0 (6)
O(1)—Co(1)—O(4)	148.8 (5)	O(9)—Co(1)—O(1)	93.8 (3)
O(1)—Co(1)—O(5)	74.7 (5)	O(9)—Co(1)—O(2)	83.8 (4)
O(2)—Co(1)—O(3)	69.2 (5)	O(9)—Co(1)—O(3)	96.0 (4)
O(2)—Co(1)—O(4)	139.4 (5)	O(9)—Co(1)—O(4)	90.9 (4)
O(2)—Co(1)—O(5)	144.0 (5)	O(9)—Co(1)—O(5)	85.8 (4)
O(3)—Co(1)—O(4)	71.4 (5)		

$\text{Co}(\text{pyridine})_3(\text{NO}_3)_2$ where the O—Co—O angle is 55.8° [Co—O distances 2.207 (9)–2.311 (9) Å (Cameron, Taylor & Nuttall, 1972)]. The geometry of highly coordinated systems involving NO_3^- has sometimes been simplified by considering the midpoint between the bonding bidentate nitrate oxygens as the site of a single ligand (Bergman & Cotton, 1966). $\text{Co}(\text{NO}_3)_4$, an eight-coordinate Co^{II} species, may be viewed as a tetrahedral Co group if this simplification is made.

Structure (II) is an example of the first of these general types of Co^{II} seven coordination with the five oxygens of 15-crown-5 close to planar (deviation 0.20 Å) with cobalt on that plane and the water oxygens axial to that plane ($\text{O}_{\text{p-ether}}-\text{Co}-\text{O}_{\text{p-ether}}$ bond angles close to 72 or 144°; $\text{O}_{\text{water}}-\text{Co}-\text{O}_{\text{p-ether}}$ bond angles close to 90°) confirming the pentagonal bipyramidal geometry.

Structure (I) (Figs. 3 and 4) does not display either of the other common seven-coordinate geometries: capped octahedral or capped trigonal prismatic, unless large distortions are admitted (Drew, 1977). Octahedral geometry does not result from simplification of the bidentate NO_3^- group using Cotton's method. (I) might be described as a 4:3 system with the four polyether oxygens planar (deviation 0.06 Å) and subtending a dihedral angle of 58.5° to the plane of the three bonded nitrate oxygen atoms (Muetterties & Wright, 1967).

Examination of the torsion angles for a wide range of crown-ether structures shows O-C-C-O angles of about 60° and C-C-O-C angles of about 180° are to be expected for the smaller crowns. The torsion angles for (I) (Table 6) compared to those observed in $\text{CuCl}_2(12\text{-crown-4})$ (van Remoortere, Boer & Steiner, 1975) seem to indicate less deformation strain in the Co^{II} complex. Furthermore, in (I), bonding to the metal occurs through four lone-pair orbitals on the same side of the polyether ring whereas that in the octahedral Cu complex occurs with three lone pairs from one side of the ring and one lone pair from the opposite side to fill

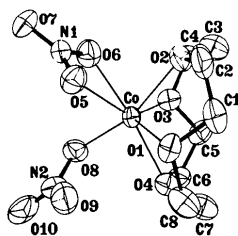


Fig. 4. View of $\text{Co}^{\text{II}}(\text{NO}_3)_2(12\text{-crown-4})$ (I).

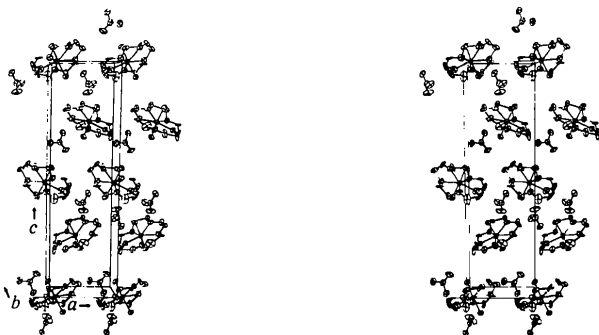


Fig. 5. Stereoview of $\text{Co}^{\text{II}}(\text{H}_2\text{O})_2(15\text{-crown-5})(\text{NO}_3)_2$ (II) packing.

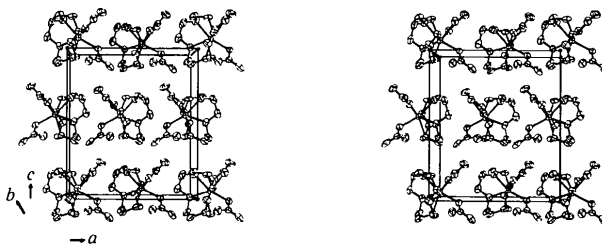


Fig. 6. Stereoview of $\text{Co}^{\text{II}}(\text{NO}_3)_2(12\text{-crown-4})$ (I) packing.

Table 6. Torsion angles (°) for $\text{Co}^{\text{II}}(\text{NO}_3)_2(12\text{-crown-4})$ (I)

O(1)-C(1)-C(2)	O(2)	50.5 (8)
C(1)-C(2)-O(2)-C(3)		94.9 (6)
C(2)-O(2)-C(3)-C(4)		-170.0 (5)
O(2)-C(3)-C(4)-O(3)		52.9 (6)
C(3)-C(4)-O(3)-C(5)		83.5 (5)
C(4)-O(3)-C(5)-C(6)		-165.9 (4)
O(3)-C(5)-C(6)-O(4)		53.2 (5)
C(5)-C(6)-O(4)-C(7)		90.0 (5)
C(6)-O(4)-C(7)-C(8)		-168.8 (4)
O(4)-C(7)-C(8)-O(1)		51.6 (6)
C(7)-C(8)-O(1)-C(1)		84.9 (6)
C(8)-O(1)-C(1)-C(2)		-163.9 (6)

two axial and two equatorial binding sites. Since we lack structural information on uncomplexed 12-crown-4, it is difficult to evaluate further the deformation of the polyether ring. Certainly, greater deformation is seen in the bonding orbitals of Co^{II} than is observed in the 12-crown-4. Torsion angles of the complexed 15-crown-5 are not meaningful due to the disorder of the carbon atoms of the polyether.

Structure (II) belongs to that group of nonbiaxial crystals whose enantiomorphism derives solely from crystal packing and which contain no active chiral units. Other examples are $\text{NiSO}_4 \cdot 6\text{H}_2\text{O}$ (Beevers & Lipson, 1932; O'Conner & Dale, 1966) and $\alpha\text{-}[(\text{Zn}, \text{Co})\text{(H}_2\text{O})_6][\text{SeO}_4]$ (Palmer & Giles, 1978). Packing diagrams of (II) show the polyether rings stacked with alternating tilt into columns which parallel the c axis. Hydrogen bonding of the NO_3^- species to coordinated water molecules secures it in the intervening space (Fig. 5) [$\text{O}(9)-\text{O}(7')$, 2.778 (8) Å; $\text{O}(9)-\text{O}(6')$, 2.767 (9) Å]. The placement of the atoms in the cell of structure (I) is shown in Fig. 6.

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