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cis-Diaquobis(ethylenediamine)cobalt(III) Hexacyanocobaltate(III) Trihydrate

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Abstract. $[Co(H_2O)_2en_2][Co(CN)_6].3H_2O$, monoclinic, $P2_1/c$, $a=12{\cdot}702$ (2), $b=11{\cdot}285$ (1), $c=17{\cdot}277$ (3) Å, $\beta=125{\cdot}87$ (1)°, $Z=4$, $D_m=1{\cdot}59$, $D_x=1{\cdot}60$ g cm^{-3}. The structure is characterized by a distorted NaCl-type arrangement of the complex cation $[Co(H_2O)_2en_2]^{3+}$ and the complex anion $[Co(CN)_6]^{3-}$. Two ethylenediamine chelate rings about the Co atoms of the complex cation are in *cis* positions. One chelate ring takes the usual *gauche* conformation, but the other ring is unsymmetrical and statistically disordered.

Introduction. The crystals were prepared by Tsuchiya, Nakagawa, Uehara & Kyuno (1973) and were kindly supplied by Professor R. Tsuchiya of Kanazawa University. They are brittle, fine, red tabular prisms elongated along **c**. It was shown that this complex salt loses five moles of water in the region 50–120 °C and yields a binuclear complex salt $[en_2Co(CN)_2Co(CN)_4]$ having two bridging cyano groups.

A single crystal with a maximum dimension of 0·22 mm was used for intensity measurement. Intensities were obtained by the ω–2θ scan technique with Zr-filtered Mo $K\alpha$ ($\lambda=0{\cdot}7107$ Å) radiation on a Rigaku automatic four-circle diffractometer, and corrected for Lorentz–polarization factors but not for absorption. Of the 1729 measured intensities ($2\theta \leq 70°$), 1633 with $|F_o| > 3\sigma$ were used for structure analysis.

The positions of the Co atoms were determined from a Patterson function. The positions of all remaining atoms, except H, were found from successive Fourier syntheses calculated with the program *RSSFR*-5 written by Dr T. Sakurai. The structure was refined by the block-diagonal least-squares method with the *HBLS*-IV program written by Dr T. Ashida. The final R value is 0·079 for the 1633 observed reflexions. A weighting scheme, $w=15{\cdot}53/|F_o|$ for $|F_o| > 15{\cdot}53$ and otherwise $w=1$, was used. Atomic scattering factors were taken from *International Tables for X-ray Crystal-*

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Table 1. *Final atomic parameters* ($\times 10^4$) *and estimated standard deviations*

The temperature factor is of the form $\exp\{-(h^2B_{11}+k^2B_{22}+l^2B_{33}+klB_{23}+lhB_{13}+hkB_{12})\}$.

	x	y	z	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
Co(1)	2457 (2)	2006 (3)	3909 (2)	67 (2)	37 (2)	25 (1)	−5 (5)	58 (3)	−5 (3)
Co(2)	7072 (2)	3004 (3)	4179 (2)	59 (2)	33 (1)	23 (1)	4 (5)	52 (3)	1 (3)
O(1)	3154 (13)	601 (12)	3709 (9)	97 (17)	71 (12)	39 (7)	9 (24)	89 (20)	−10 (15)
O(2)	2439 (14)	2781 (13)	2900 (9)	147 (20)	58 (13)	38 (7)	−22 (25)	105 (21)	38 (15)
O(3)	1878 (13)	1900 (13)	759 (9)	72 (15)	111 (15)	53 (8)	−42 (29)	87 (19)	1 (20)
O(4)	7132 (15)	72 (14)	1824 (11)	128 (21)	85 (15)	59 (10)	29 (31)	70 (25)	−16 (20)
O(5)	9865 (15)	4547 (14)	1114 (11)	140 (22)	91 (15)	77 (11)	−67 (31)	152 (28)	−39 (21)
N(1)	2557 (14)	1221 (13)	4956 (10)	64 (17)	58 (14)	27 (8)	19 (25)	59 (20)	4 (17)
N(2)	4242 (15)	2552 (13)	4869 (10)	96 (20)	38 (11)	25 (8)	32 (25)	51 (22)	3 (15)
N(3)	691 (16)	1489 (15)	2958 (11)	77 (18)	50 (13)	40 (9)	−33 (26)	71 (22)	22 (18)
N(4)	1701 (15)	3436 (13)	4026 (10)	80 (18)	47 (12)	32 (8)	40 (25)	55 (22)	10 (16)
N(5)	4335 (19)	2210 (17)	2680 (13)	94 (23)	107 (22)	51 (11)	−24 (38)	52 (27)	10 (25)
N(6)	5787 (16)	4972 (15)	4541 (11)	108 (21)	41 (13)	57 (10)	−21 (28)	123 (26)	−30 (20)
N(7)	7000 (16)	1400 (16)	5547 (12)	150 (25)	41 (14)	61 (11)	3 (32)	143 (29)	12 (20)
N(8)	9755 (18)	3746 (16)	5872 (13)	105 (22)	92 (18)	49 (10)	36 (34)	99 (27)	−8 (22)
N(9)	8095 (19)	910 (18)	3707 (13)	211 (35)	69 (17)	85 (15)	44 (42)	200 (41)	−16 (26)
N(10)	7240 (16)	4584 (15)	2843 (12)	97 (21)	72 (16)	40 (9)	−23 (30)	90 (24)	18 (19)
C(1)	3975 (19)	1069 (17)	5775 (14)	102 (25)	77 (18)	28 (10)	8 (37)	71 (28)	6 (22)
C(2)	4623 (19)	2238 (17)	5846 (13)	91 (24)	69 (20)	23 (9)	35 (33)	44 (25)	1 (20)
C(3)	−261 (26)	2341 (24)	2827 (18)	110 (31)	56 (21)	116 (21)	2 (39)	131 (44)	18 (32)
C(4)	310 (33)	3429 (29)	3296 (22)	125 (35)	175 (36)	88 (20)	102 (65)	2 (45)	−152 (45)
C(5)	5394 (20)	2499 (18)	3212 (13)	54 (20)	68 (16)	42 (10)	−39 (29)	82 (26)	−39 (20)
C(6)	6317 (18)	4242 (16)	4414 (13)	77 (22)	32 (13)	43 (10)	−12 (28)	88 (27)	−2 (19)
C(7)	7028 (16)	2060 (17)	5035 (11)	52 (17)	43 (12)	23 (7)	−2 (31)	49 (20)	21 (20)
C(8)	8730 (21)	3448 (18)	5207 (14)	85 (24)	95 (20)	34 (10)	−59 (37)	70 (27)	−30 (24)
C(9)	7769 (20)	1721 (19)	3901 (14)	88 (23)	59 (18)	49 (11)	32 (30)	103 (29)	31 (20)
C(10)	7154 (19)	4025 (17)	3325 (13)	55 (20)	61 (16)	30 (9)	−24 (31)	30 (24)	6 (20)

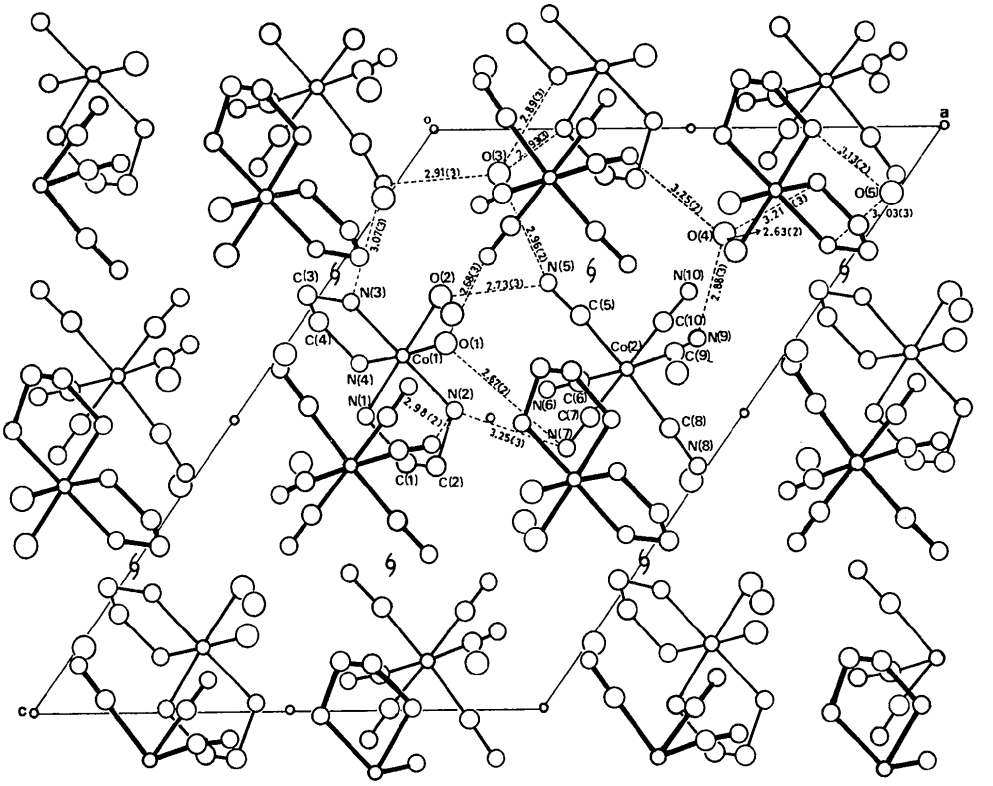

Fig. 1. The structure viewed down **b**. Broken lines indicate hydrogen bonds.

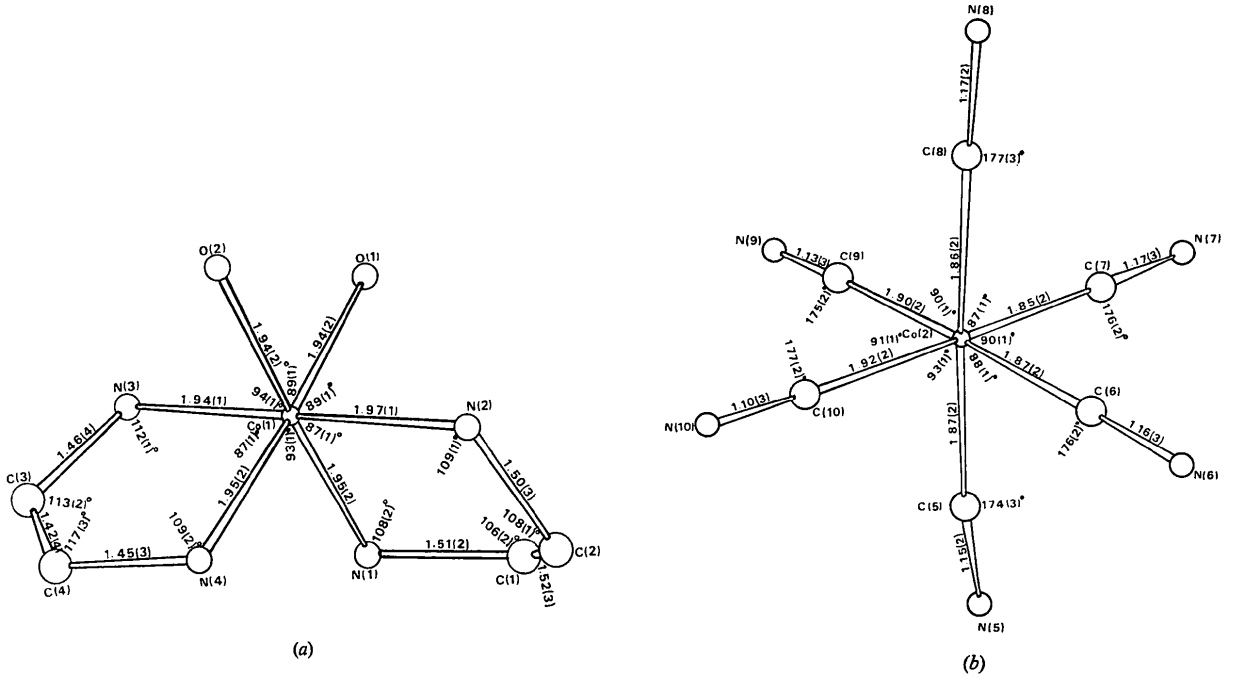

Fig. 2. The structure of the complex ion: (*a*) *cis*-$[Co(H_2O)_2en_2]^{3+}$ and (*b*) $[Co(CN)_6]^{3-}$.

lography (1962). A difference synthesis was calculated to find the H positions, but only obscure broad peaks appeared around the ethylenediamine skeletons. The final atomic parameters with their estimated standard deviations are listed in Table 1.*

Discussion. A view of the structure along **b** is shown in Fig. 1. The structure is characterized by the distorted NaCl-type arrangement of the complex ions. Water molecules connect the complex ions together through hydrogen bonds. A similar close-packed structure of complex ions has been reported in a double complex salt, $(+)_D$-[Co(penten)] $[Co(CN)_6].2H_2O$ (Muto, Marumo & Saito, 1970).

The configurations of the complex ions, *cis*-$[Co(H_2O)_2en_2]^{3+}$ and $[Co(CN)_6]^{3-}$, are illustrated in Fig. 2 (*a*) and (*b*). In the complex cation, the four N and two O atoms of the ligand molecules form a slightly distorted octahedron around the Co atom. Both kinds of ethylenediamine molecules are of the *gauche* form and the conformations of the chelate rings are of the type *lel-lel*. Two ethylenediamine chelate rings are shown parallel to N–Co–N plane in Fig. 3. One ethylenediamine chelate ring, Co(1)–N(1)–C(1)–C(2)–N(2), forms the usual *gauche* conformation and the bond distances and angles in the ligand are normal. However, another ethylenediamine group, N(3)–C(3)–C(4)–N(4), is nearly planar. The dihedral angles between the N(1)–C(1)–C(2) and N(2)–C(2)–C(1) planes and between the N(3)–C(3)–C(4) and N(4)–C(4)–C(3) are 51·2° and 15·6°, respectively. The C(3)–C(4) bond distance of 1·41 Å is especially short in comparison with the usual single C–C bond distance. Furthermore, C(3) and C(4) have large temperature factors, which are thought to result from the positional disorder of the ethylenediamine chelate rings. Similar anomalous conformations of the ethylenediamine chelate rings have been reported [for example, $Co(en)_2SO_3NCS.2H_2O$,

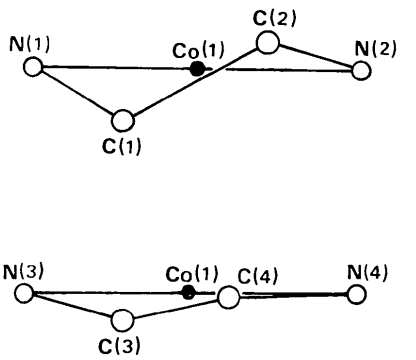

Fig. 3. Projections of ethylenediamine chelate rings parallel to the N–Co–N plane.

Baggio & Becka (1969) and $Cu_3(en)_2(CN)_4.H_2O$, Williams, Larson & Cromer (1972)]. The shape and the size of the complex anions are normal.

Two water O atoms, O(3) and O(4), have approximately tetrahedral coordinations with hydrogen bonds. The other water O atom, O(5), is coordinated by three N atoms, N(1), N(3) and N(9).

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References

BAGGIO, S. & BECKA, C. J. (1969). *Acta Cryst.* B**25**, 946–954.

International Tables for X-ray Crystallography (1962). Vol. III. Birmingham: Kynoch Press.

MUTO, A., MARUMO, F. & SAITO, Y. (1970). *Acta Cryst.* B**26**, 226–233.

TSUCHIYA, R., NAKAGAWA, S., UEHARA, A. & KYUNO, E. (1973). *Bull. Chem. Soc. Japan*, **46**, 169–175.

WILLIAMS, R. J., LARSON, A. C. & CROMER, D. T. (1972). *Acta Cryst.* B**28**, 858–864.

* A table of structure factors has been deposited with the British Library Lending Division as Supplementary Publication No. SUP 31348 (9 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.