

La Fig. 6 est la projection selon l'axe *a* de l'édifice cristallin. Aucune distance n'est inférieure à la somme des rayons de van der Waals.

Les calculs ont été effectués au CIRCE à Orsay sur les ordinateurs IBM 360/75 et CDC 3600, en utilisant les principaux programmes suivants:

- pour les calculs préliminaires, *PHOTO* (Riche & Lanier, communication particulière).
- pour les calculs de facteur de structure et d'affinement: une modification de *ORFLS* (Busing, Martin & Levy, 1962),
- pour les calculs de distances, angles et plans moyens, la série de programmes NRC de Ahmed, Hall, Pippy & Huber (1966),
- pour les Fig. 5 et 6 le programme *ORTEP* de Johnson (1965).

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The Crystal Structure of Potassium (-)₅₄₆-Trimethylenediaminetetra-acetatocobaltate(III) Dihydrate

BY RUMIKA NAGAO, FUMIYUKI MARUMO AND YOSHIHIKO SAITO

Institute for Solid State Physics, The University of Tokyo, Roppongi-7, Minato-ku, Tokyo 106, Japan

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The crystal structure of potassium (-)₅₄₆-trimethylenediaminetetra-acetatocobaltate(III) dihydrate, (-)₅₄₆-K{Co[(OOCCH₂)₂N(CH₂)₃N(CH₂COO)₂]}·2H₂O, has been determined and refined on the basis of three-dimensional intensity data collected on a diffractometer using Mo K α radiation. The crystals are orthorhombic, space group *B*2₂2, with cell dimensions: *a* = 10·984, *b* = 16·638, *c* = 8·851 Å, and *Z* = 4. The structure was refined by the anisotropic, block-diagonal, least-squares method to an *R* value of 0·098 for 888 observed reflexions. The ligand functions as a sexidentate. The cobalt atom is bonded octahedrally to the two nitrogen atoms and to one oxygen atom from each of the four carboxylate groups of the ligand. The central six-membered trimethylenediaminecobalt ring takes a twist-boat form. The complex anion has a twofold axis of rotation through the central methylene carbon atom of the six-membered ring and the cobalt atom. The absolute configuration of the complex anion can be designated as skew chelate pairs, *AAA*.

Introduction

Cobalt(III) and chromium(III) complexes with trimethylenediaminetetra-acetic acid, H₄(trdta), have been synthesized and the quadrivalent ligand has been shown to act as a sexidentate in both cases (Tanaka & Ogino, 1964; Weyh & Hamm, 1968). Recently potassium trimethylenediaminetetra-acetatocobaltate(III) dihydrate, K[Co(trdta)]·2H₂O, was found to resolve spontaneously. The absolute configuration of (-)₅₄₆-[Co(trdta)]⁻ was determined by the measurement of its optical properties and the conformation of the central six-membered chelate ring was deduced from the proton nuclear magnetic resonance spectrum. In the present paper the crystal structure of (-)₅₄₆-K[Co(trdta)]·2H₂O is reported.

Experimental

Reddish-violet crystals of potassium (-)₅₄₆-trimethylenediaminetetra-acetatocobaltate(III) dihydrate, (-)₅₄₆-K[Co(trdta)]·2H₂O, were kindly supplied by Professor H. Ogino of Tohoku University. They were recrystallized from an aqueous solution containing alcohol. The cell dimensions were obtained from zero-level Weissenberg photographs. The crystal data are:

C₁₁H₁₈N₂O₁₀CoK, M.W. 436·31
 Orthorhombic; *a* = 10·984 ± 0·004,
b = 16·638 ± 0·004,
c = 8·851 ± 0·003 Å
U = 1617·6 Å³; *D_m* = 1·81 g·cm⁻³, *Z* = 4, *D_x* = 1·79 g·cm⁻³

$\mu(\text{Mo } K\alpha) = 36.97 \text{ cm}^{-1}$

Absent reflexions: hkl for $h+l$ odd, $0k0$ for k odd.

Space group $B22_12$ (No. 20).

For the intensity measurement a manual Rigaku four-circle diffractometer was used. The crystal was mounted on the goniometer head with the c axis roughly parallel to the φ axis. The ω -scan technique was employed with the scanning speed of 1.0° per min. Zr-filtered Mo $K\alpha$ radiation was used. The background was counted both at the beginning and at the end of each scan for 20 sec. The intensity measurements were carried out up to $2\theta = 60^\circ$. The 210 reflexion was measured every thirty reflexions during the data collection to check the stability of the instrument and to check for any deterioration of the crystal. The intensity of this reflexion was found to change appreciably owing to radiation damage of the specimen, and the intensity data were corrected

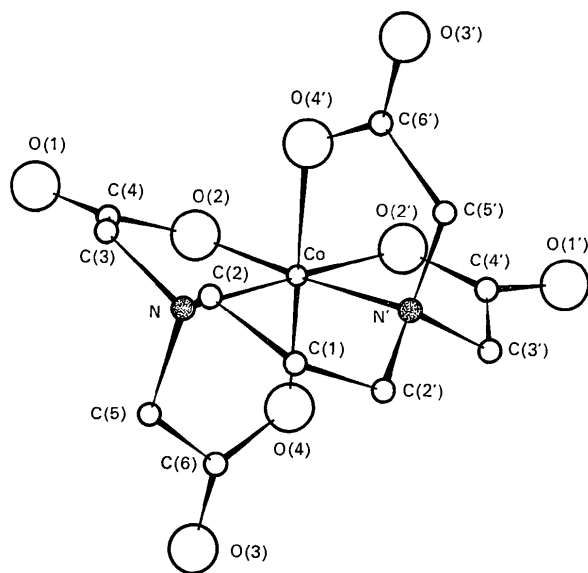


Fig. 1. A perspective drawing of the complex ion, $(-)_546$ - $[\text{Co}(\text{trdta})]^-$.

for this effect with the intensity *versus* time curve of the standard reflexion. The 888 independent reflexions collected were corrected for Lorentz and polarization effects. The observed structure amplitudes were brought on to an absolute scale by comparing them with the corresponding calculated values at a later stage.

Determination and refinement of the structure

The general positions of the space group $B22_12$ are eightfold. The potassium and cobalt atoms must be on fourfold special positions, since there are four formula units in the unit cell. Consequently the complex anion is required to have a twofold axis of rotation. The coordinates of the potassium and cobalt atoms were readily derived from the prominent peaks on three-dimensional Patterson maps and all the remaining lighter atoms, except hydrogen, could be located on subsequent three-dimensional electron-density maps. Structure factors calculated at this stage gave an R value ($R = \frac{\sum |F_o|}{\sum |F_c|}$) of 0.22.

The coordinates of all the non-hydrogen atoms were refined by the least-squares method, initially assuming isotropic and later anisotropic thermal motion. The R value decreased to 0.11.

A difference map was evaluated and six out of the nine hydrogen atoms were revealed. A second difference map, calculated with the inclusion of the hydrogen atoms revealed by the first synthesis, fixed the positions of all the remaining hydrogen atoms.

The positional parameters of the hydrogen atoms were included in the refinement with isotropic temperature factors. After five strong reflexions were corrected for extinction, according to the formula: $I_o = I_{\text{corr}} \exp(-g \cdot I_{\text{corr}})$, four more cycles of least-squares refinement were carried out. The final R value was 0.098 for 888 observed reflexions. The atomic scattering factors were taken from *International Tables for X-ray Crystallography* (1962). In the final stage of the refinement, the following weighting scheme was employed: $1/w = a|F_o|^2 + b|F_o| + c$, where $a = 0.00166$, $b = -0.195$ and $c = 6.68$.

Table 1. Final positional and thermal parameters with their standard deviations ($\times 10^4$)

The anisotropic thermal parameters are of the form: $\exp[-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + \beta_{12}hk + \beta_{13}hl + \beta_{23}kl)]$.

	x	y	z	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
K	5000 (0)	7500 (0)	9123 (5)	57 (3)	31 (1)	136 (6)	-1 (4)	0 (0)	0 (0)
Co	6567 (2)	5000 (0)	5000 (0)	29 (1)	23 (1)	81 (2)	0 (0)	0 (0)	-2 (3)
N	5404 (8)	4387 (6)	6235 (12)	32 (7)	28 (4)	99 (14)	19 (9)	-12 (16)	43 (13)
O(1)	8003 (8)	3270 (6)	7397 (11)	75 (8)	41 (4)	112 (13)	24 (10)	-17 (19)	13 (14)
O(2)	7764 (7)	4401 (5)	6072 (11)	51 (7)	31 (4)	135 (14)	-1 (8)	-2 (18)	24 (13)
O(3)	5973 (8)	6013 (6)	8890 (10)	77 (8)	45 (4)	71 (11)	15 (11)	-8 (16)	-17 (12)
O(4)	6576 (8)	5777 (5)	6511 (9)	55 (7)	33 (3)	97 (11)	-19 (10)	20 (18)	-19 (11)
O(5)	8403 (11)	7028 (6)	6380 (13)	99 (10)	37 (4)	185 (17)	-32 (13)	28 (28)	-21 (15)
C(1)	3514 (14)	5000 (0)	5000 (0)	42 (10)	36 (6)	139 (24)	0 (0)	0 (0)	69 (30)
C(2)	4234 (10)	4242 (8)	5445 (13)	46 (9)	36 (5)	86 (15)	-26 (12)	-40 (19)	5 (15)
C(3)	6028 (11)	3596 (7)	6486 (19)	52 (10)	23 (4)	185 (24)	26 (12)	-44 (27)	29 (18)
C(4)	7378 (11)	3762 (7)	6672 (15)	53 (9)	27 (5)	112 (17)	27 (12)	-50 (22)	-41 (16)
C(5)	5248 (9)	4817 (7)	7707 (13)	43 (8)	27 (5)	96 (15)	10 (9)	-7 (19)	-36 (14)
C(6)	5981 (11)	5608 (7)	7739 (14)	53 (9)	20 (4)	110 (18)	29 (10)	-91 (23)	-2 (14)

Table 3. *The relationship between $I(hkl)$ and $I(\bar{h}\bar{k}\bar{l})$ in their calculated and observed values*

<i>h</i>	<i>k</i>	<i>l</i>	$F_0^2(hkl)$	Observed	$F_0^2(\bar{h}\bar{k}\bar{l})$
1	7	1	2123	<	4369
1	8	1	5730	>	4436
1	9	1	151	<	812
1	10	1	1310	>	864
1	11	1	835	<	2061
3	2	1	12056	>	7974
3	4	1	15006	>	12034
3	10	1	756	<	1656
3	14	1	253	<	562
5	3	1	3540	>	1875
5	7	1	708	<	1109
7	8	1	454	>	108
1	1	3	3136	>	1282
1	2	3	2294	<	3226
1	4	3	10712	>	8612
1	6	3	2034	>	1600
1	7	3	7762	>	9506
1	9	3	4720	>	3318
1	11	3	1764	>	870
1	12	3	1082	<	1689
1	13	3	3318	>	1998
1	14	3	169	<	497
3	2	3	2460	>	1731
3	4	3	10712	>	8668
3	8	3	1142	<	2333
3	12	3	900	>	292
3	14	3	853	>	534
5	5	3	4638	<	8190
5	9	3	1505	<	2401
5	11	3	1789	>	581
5	13	3	534	>	188
5	17	3	912	<	1505

Description of the structure and discussion

The crystal is built up of $(-)_546-[\text{Co}(\text{trdta})]^-$ and K^+ ions, and water molecules. A perspective drawing of the complex ion $(-)_546-[\text{Co}(\text{trdta})]^-$ is illustrated in Fig. 1, which also represents the ion's absolute configuration correctly. The ligand functions as a sexidentate like ethylenediaminetetra-acetic acid (H_4edta). The shape of the complex ion is broadly similar to that of $[\text{Co}(\text{edta})]^-$ (Weakliem & Hoard, 1959). The interatomic distances and bond angles within the complex ion are listed in Table 4, in which some of the bond angles are compared with the mean values of the corresponding angles observed in the crystal structure of $\text{NH}_4[\text{Co}(\text{edta})]\cdot 2\text{H}_2\text{O}$. The cobalt atom is bonded octahedrally to the two nitrogen atoms and to one oxygen atom from each of the four carboxylate groups of trdta. The complex ion has a twofold axis of rotation through the cobalt atom and the carbon atom of the central methylene group. Little difference was observed in the shape and size of the four glycinic rings between $[\text{Co}(\text{trdta})]^-$ and $[\text{Co}(\text{edta})]^-$. There are two crystallographically independent glycinic rings: one is in the plane of the six-membered chelate ring and forms part of a girdle about the cobalt atom; the other lies in plane nearly perpendicular to the plane of the girdle. The latter glycinic ring $[\text{Co}, \text{N}, \text{C}(5), \text{C}(6), \text{O}(4)]$ is nearly planar and O(3) deviates by about 0.11 Å from the

least-squares plane (see Table 5), while the former ring $[\text{Co}, \text{N}, \text{C}(3), \text{C}(4), \text{O}(2)]$ shows significant departure from planarity and O(1) is 0.18 Å out of the plane of the chelate ring. In addition, the Co–O(2) distance is slightly longer than Co–O(4). These observations suggest that the glycinic ring forming the girdle about the cobalt atom is more strained than the one perpendicular to it. A similar tendency has also been observed in the structure of the complex ion, $[\text{Co}(\text{edta})]^-$.

Table 4. *Bond distances and angles within the complex anion*

Bond distances			
Co–N	1.966 (9) Å	C(1)–C(2)	1.540 (15) Å
Co–O(2)	1.904 (9)	C(3)–C(4)	1.518 (17)
Co–O(4)	1.861 (8)	C(4)–O(1)	1.247 (15)
N–C(2)	1.483 (15)	C(4)–O(2)	1.261 (15)
N–C(3)	1.501 (15)	C(5)–C(6)	1.542 (15)
N–C(5)	1.496 (15)	C(6)–O(3)	1.222 (15)
		C(6)–O(4)	1.299 (15)

Bond angles		$\text{K}[\text{Co}(\text{trdta})]\cdot 2\text{H}_2\text{O}$	$\text{NH}_4[\text{Co}(\text{edta})]\cdot 2\text{H}_2\text{O}^*$
N—Co—N'	99.0 (3)°		89.7°
O(2)—Co—O(2')	92.6 (3)		104.0
N—Co—O(2)	84.3 (3)		83.2
O(2)—Co—O(4)	90.1 (3)		93.1
O(2)—Co—O(4')	89.5 (3)		86.0
N—Co—O(4)	87.9 (3)		88.6
N'—Co—O(4)	92.4 (3)		92.5
C(2)—N—C(3)	108.8 (6)		116.1
C(2)—N—C(5)	112.9 (8)		108.6
C(3)—N—C(5)	110.0 (8)		110.4
C(2)—N—Co	112.7 (7)		107.5
C(3)—N—Co	103.9 (5)		105.9
C(5)—N—Co	108.1 (5)		108.1
C(2)—C(1)—C(2')	118.2 (11)		
C(1)—C(2)—N	115.6 (5)		108.1
C(4)—C(3)—N	107.6 (6)		106.4
C(3)—C(4)—O(2)	115.9 (9)		115.1
C(3)—C(4)—O(1)	118.3 (8)		121.4
O(1)—C(4)—O(2)	125.8 (10)		123.2
C(6)—C(5)—N	111.3 (8)		111.1
C(5)—C(6)—O(4)	115.6 (8)		116.9
C(5)—C(6)—O(3)	118.8 (9)		121.3
O(3)—C(6)—O(4)	125.5 (7)		121.7
Co—O(2)—C(4)	114.8 (6)		112.9
Co—O(4)—C(6)	116.6 (6)		113.1

* Mean value (Weakliem & Hoard, 1959).

Table 5. *Deviations from the least-squares planes*

Atom		Atoms out of the plane	
Co	−0.033 Å	O(3)	−0.108 Å
N	0.037		
O(4)	0.037		
C(5)	−0.014		
C(6)	−0.025		
Co	0.164	O(1)	−0.182
N	−0.213		
O(2)	−0.154		
C(3)	0.268		
C(4)	−0.046		

The six-membered chelate ring takes a twist-boat form in agreement with the result of the proton nuclear magnetic resonance studies (Ogino, Takahashi & Tanaka, 1970). The carbon atoms C(2) and C(2') are 0.65 Å out of the plane defined by Co, N and N'. A similar twist-boat conformation has been observed in crystals of bis-(2-hydroxyacetophenone)trimethylenedi-imine-copper(II) (Iida, Oonishi, Nakahara & Komiyama, 1970) and $(+)_546$ -tris-(*R,R*-2,4-diaminopentane)cobalt(III) chloride monohydrate (Kobayashi, Marumo, Saito, Fujita & Mizukami, 1971). The angle N–Co–N' of 99° is larger than the corresponding angles (93° and 87.9°) in the Cu(II) and Co(III) complexes mentioned above. This expansion of the angle N–Co–N' is evidently due to the fused ring formation. The distortion of the octahedron formed by the six corresponding atoms is not so marked as that observed in [Co(penten)]³⁺ (Muto, Marumo & Saito, 1970). The bonds Co–O(4) and Co–O(4') are collinear but the bonds Co–O(2) and Co–N' make an angle of 175.9°. In the crystals of [Co(penten)] [Co(CN₆)]·2H₂O, the corresponding angles are 175 and 170° (mean). The absolute configuration of the complex ion, $(-)_546\text{-}[\text{Co}(\text{trdta})]^-$, can be designated as *AAA* (IUPAC Information Bulletin, 1968), in agreement with that predicted by optical measurements and the chemical reaction with ethylenediamine (Ogino *et al.* 1970). The conformation of the six-membered chelate ring can be designated as *δ*, providing the helicity is defined by the line joining the two coordinating atoms and by the line joining the two carbon atoms that are the neighbours to each coordinating atom.

A projection of the structure along the *a* axis is shown in Fig. 2. The complex anions are on the two-fold axes of rotation parallel to the *a* axis. An interesting feature of the packing of the complex anions is that they lie in layers parallel to the plane (010). Between these layers of complex ions, potassium ions and water molecules are arranged. A potassium ion is surrounded by four carboxylate oxygen atoms, which are not coordinated to the cobalt atom, and by the oxygen atoms of two water molecules. The potassium to oxygen atom distances range from 2.70 to 2.87 Å. These distances are illustrated in Fig. 2. A water oxygen atom O(5) is linked by hydrogen bonding to two carboxylate oxygen atoms of the complex ions belonging to adjacent layers. Thus the (010) layers of the complex anions are held together by electrostatic attraction between the cations and carboxylate oxygen atoms not coordinated to the cobalt atom, and by O–H...O hydrogen bonds.

The calculations were performed on the FACOM 270–30 computer at this Institute.

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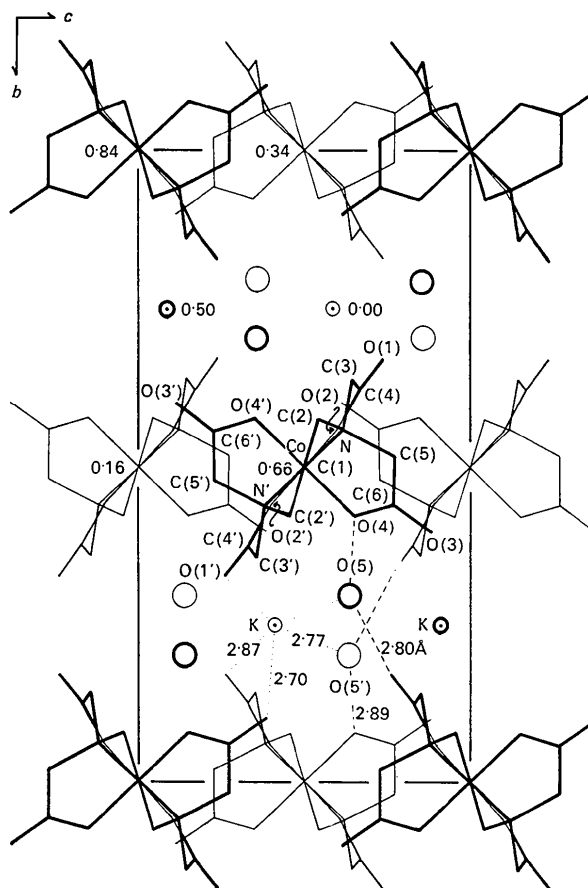


Fig. 2. A projection of the structure along the *a* axis.

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