THE CRYSTAL AND MOLECULAR STRUCTURE OF POTASSIUM 2-HYDROXY-1,3-PROPANEDIAMINE-N,N,N′,N′-TETRA-ACETATOCOBALTATE

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The substance crystallizes in a monoclinic lattice with a space group of $P2_1/c$ with lattice parameters: a 12·120, b 10·969, c 16·613 Å, β 141·13° and $Z = 4$. The structure was solved by the heavy atom method. Anisotropic refinement using the full matrix and the least squares method yielded R 0·078. The cobalt coordination polyhedron is octahedral. The central six-membered 1,3-propanediamine ring has a skew-boat shape and its hydroxyl group does not take part in the coordination but is hydrogen bonded to the oxygen atom of the carboxyl group of the neighbouring complex unit. The oxygen atom of the hydroxyl group interacts with the K^+ cation (3·03 Å).

Bersworth prepared 2-hydroxy-1,3-propanediamine-N,N,N′,N′-tetraacetic acid (HPDTA) and it has been described in a patent[1]. Špringer, Majer and Kopecká[2] proposed a simple and better preparation procedure. Novomeský[3] prepared potassium 2-hydroxy-1,3-propanediamine-N,N,N′,N′-tetraacetatecobaltate K[Co(HPDTA)] and this work describes its crystal and molecular structure.

EXPERIMENTAL

Basic crystallographic data were obtained from Weissenberg goniometric patterns. The crystal density was found by the flotation method. The following crystal data were found: $C_{11}H_{14}CoK.N_2O_9$ (M.w. 416·3), monoclinic system, $a = 12{\cdot}120$ (5), $b = 10{\cdot}969$ (9), $c = 16{\cdot}613$ (8) Å, $\beta = 141{\cdot}13$ (2)°, $U = 1385{\cdot}9$ Å^3, $D_m = 1{\cdot}95$ gcm^{-3}, $Z = 4$, $D_x = 2{\cdot}00$ gcm^{-3}, μ(MoKα) = = 16·4 cm^{-1}, MoKα (0·70926, 0·71354 Å), reflections absent: $h01$ $1 = 2n + 1$, $0k0$ $k = 2n + 1$, space group $P2_1/c$ No 14(ref.[4]).

The crystal employed for the structural analysis was a roughly tetragonal prism with base dimensions 0·2 × 0·2 mm^2 and height 0·35 mm (Maximal $\mu R = 0{\cdot}6$). The intensities were measured on a four-cycle automatic diffractometer $P2_1$ SYNTEX using MoKα radiation (controlled by the NOVA 1200 computer) over the range $0 < 2\Theta < 50°$ by the $\Theta - 2\Theta$ method. The scan speed was varied automatically in the range 4·88—29·30 min^{-1} according to two-second preliminary measurement of the intensity at the centre of the peak. The scan range was from 1° less than the calculated diffraction angle for Kα_1 radiation to 1° above the calculated value for Kα_2. The background was measured at each end of the reflection range over half the exposure

time. MoKα radiation rendered monochromatic with graphite was employed. After each 94 reflections, the intensities of two selected reflections were measured and after 480 reflections recentering was carried out. No significant change in the intensities of the control reflections was found during the measurement. The intensities were corrected for the Lorentz and the polarization factors and were converted into the absolute scale using the Wilson statistical method[5] on an XTL computing model from SYNTEX. No correction for the extinction and absorption was made. Altogether 2054 symmetrically independent reflections were obtained, of which 1048 reflections were considered as observed $I > 1{\cdot}96\sigma$ (I). The absolute values of the structural factors resulted in an approximately absolute scale and formed a basis for the crystal structure calculations.

Solution and Refinement of the Structure

The structure of K[Co(HPDTA)] was solved by the heavy atom method. The coordinates of the cobalt atom were determined from a three-dimensional Patterson map and those of all lighter atoms from three-dimensional maps of the electron density using Fourier synthesis obtained by the DRF program[6]. The computed structural factors yielded $R = 0{\cdot}33$ at this stage ($R = \sum||F_0| - |F_c||/|F_0|$).

The coordinates of all 24 atoms were refined by the least-squares method using the full-matrix program[7], first assuming isotropic and then anisotropic thermal motion of the atoms. The atomic scattering curves were taken from standard tables[8]. In this refinement stage, the weight scheme, $1/w = \sigma^2(F)$, $R = 0{\cdot}109$, was employed. The differential map of the electron density yielded approximate positions of the hydrogen atoms which were in agreement with the calculated positions (assuming d(N—H) = 1·0, d(C—H) = 1·09, H—X—Y = 109·5°). In the final refinement of the atom coordinates, the weight scheme, $1/w = \sigma^2(F) + (0{\cdot}025 \,.\, F_{obs})^2$, $R = 0{\cdot}078$, was used for the observed reflections. The final position and temperature parameters of the atoms in the independent part of the unit cell and their standard deviations are given in Table I.

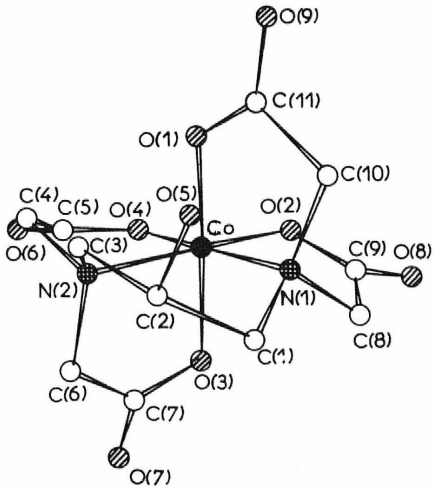

FIG. 1
Perspective Model of the Co(HPDTA)$^-$ Complex Anion

TABLE I

Final Positional and Temperature Parameters[a] of the Atoms and Their Standard Deviations (. 10^4)

Atom	x	y	z	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
K	1 259 (5)	5 759 (3)	3 940 (3)	127 (8)	43 (3)	67 (4)	10 (9)	156 (11)	8 (6)
Co	3 626 (3)	1 889 (2)	894 (2)	63 (4)	30 (2)	31 (2)	4 (5)	69 (5)	3 (4)
N(1)	4 425 (13)	3 028 (11)	545 (10)	64 (21)	43 (12)	36 (12)	− 11 (29)	58 (28)	7 (22)
N(2)	2 290 (14)	3 019 (12)	817 (10)	96 (24)	64 (13)	32 (12)	55 (32)	82 (31)	22 (22)
O(1)	1 638 (11)	3 371 (7)	4 105 (8)	107 (20)	16 (8)	53 (10)	37 (21)	124 (26)	15 (15)
O(2)	4 935 (11)	751 (9)	1 058 (9)	91 (20)	64 (11)	56 (11)	37 (25)	105 (28)	27 (18)
O(3)	4 441 (11)	7 159 (9)	2 320 (9)	103 (20)	52 (11)	50 (10)	9 (24)	111 (27)	− 8 (18)
O(4)	2 899 (12)	648 (8)	1 193 (9)	131 (21)	43 (10)	60 (11)	8 (24)	157 (29)	9 (17)
O(5)	2 899 (12)	−162 (10)	3 796 (9)	178 (25)	66 (11)	60 (12)	− 38 (29)	169 (32)	−37 (19)
O(6)	1 301 (12)	409 (9)	1 413 (9)	165 (24)	64 (11)	87 (13)	− 9 (27)	212 (34)	9 (20)
O(7)	3 857 (13)	7 774 (9)	749 (9)	169 (25)	70 (12)	39 (10)	8 (28)	120 (29)	8 (18)
O(8)	2 483 (13)	5 678 (11)	3 124 (10)	155 (24)	118 (15)	100 (14)	−128 (31)	222 (34)	−84 (23)
O(9)	512 (12)	2 916 (9)	2 255 (8)	146 (21)	47 (11)	47 (10)	20 (25)	124 (27)	11 (18)
C(1)	4 439 (20)	4 343 (13)	854 (15)	169 (36)	34 (14)	107 (20)	− 9 (38)	241 (51)	− 8 (29)
C(2)	2 645 (21)	4 825 (14)	76 (14)	179 (37)	46 (15)	53 (17)	10 (42)	152 (46)	15 (28)
C(3)	1 405 (20)	4 020 (14)	−135 (14)	179 (36)	54 (16)	78 (18)	58 (39)	227 (49)	38 (28)
C(4)	911 (18)	2 232 (14)	414 (15)	100 (30)	57 (17)	85 (18)	6 (37)	157 (43)	30 (28)
C(5)	1 754 (18)	1 004 (13)	1 084 (13)	137 (33)	61 (16)	31 (14)	− 88 (38)	117 (40)	−32 (26)
C(6)	3 546 (19)	3 507 (15)	2 169 (14)	127 (33)	80 (19)	65 (18)	23 (40)	144 (46)	−25 (29)
C(7)	4 808 (18)	7 748 (12)	1 887 (13)	103 (29)	32 (14)	31 (13)	71 (33)	85 (36)	34 (22)
C(8)	3 718 (19)	7 638 (14)	3 562 (14)	69 (30)	53 (17)	56 (18)	− 54 (35)	70 (42)	−54 (27)
C(9)	3 712 (19)	6 265 (15)	3 519 (13)	108 (33)	106 (20)	37 (16)	− 70 (42)	120 (44)	−36 (29)
C(10)	3 362 (17)	2 138 (15)	4 181 (12)	89 (28)	87 (19)	28 (14)	79 (39)	75 (36)	13 (26)
C(11)	1 704 (18)	2 840 (12)	3 445 (13)	125 (30)	7 (13)	59 (15)	− 27 (32)	118 (39)	−35 (23)

[a] Anisotropic temperature parameters have the form: $\exp[-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + \beta_{12}hk + \beta_{13}hl + \beta_{23}kl)]$.

Description of the Structure and Discussion

The crystals consist of $[Co(HPDTA)]^-$ anions and K^+ cations. A perspective model of the complex anion and the atomic notation are depicted in Fig. 1. HPDTA is a hexadentate ligand, bound to the cobalt atom through two nitrogen atoms and one oxygen atom from each of the four carboxyl groups. The cobalt coordination polyhedron is octahedral. The stereochemistry of the complex anion is similar

TABLE II

Interatomic Distances in the K[Co(HPDTA)] Complex Anion, Compared with Those for K[Co(TRDTA)].2 H_2O[a] and the Appropriate Standard Deviations

Atoms	K[Co(HPDTA)] Å	K[Co(TRDTA)][b] . 2 H_2O Å
Co—N(1)	1·926 (11)[c]	1·966 (9)
Co—N(2)	1·963 (12)	
Co—O(1)	1·889 (9)	1·860 (8)
Co—O(2)	1·864 (9)	1·904 (9)
Co—O(3)	1·885 (9)	1·861 (8)
Co—O(4)	1·886 (9)	1·904 (9)
N(1)—C(1)	1·527 (19)	1·483 (15)
N(1)—C(8)	1·500 (18)	1·501 (15)
N(1)—C(10)	1·510 (16)	1·496 (15)
N(2)—C(3)	1·492 (19)	1·483 (15)
N(2)—C(4)	1·498 (18)	1·501 (15)
N(2)—C(6)	1·525 (18)	1·496 (15)
C(1)—C(2)	1·517 (22)	1·540(15)
C(2)—C(3)	1·528 (22)	—
C(4)—C(5)	1·526 (21)	1·518 (17)
C(5)—O(6)	1·223 (17)	1·247 (15)
C(5)—O(4)	1·311 (17)	1·261 (15)
C(8)—C(9)	1·508 (23)	1·518 (17)
C(9)—O(8)	1·242 (18)	1·247 (15)
C(9)—O(2)	1·305 (17)	1·261 (15)
C(6)—C(7)	1·503 (20)	1·542 (15)
C(7)—O(7)	1·229 (16)	1·222 (15)
C7(7)—O(3)	1·277 (16)	1·299 (15)
C(10)—C(11)	1·516 (19)	1·542 (15)
C(11)—O(9)	1·246 (16)	1·222 (15)
C(11)—O(1)	1·298 (16)	1·299 (15)
C(2)—O(5)	1·466 (17)	—

[a] K [Co(TRDTA)] . 2 H_2O potassium trimethylenediaminetetraacetatocobaltate(III) dihydrate; [b] see ref.[9]; [c] standard deviations (. 10^3) are given in parenthesis.

TABLE III

Interatomic Angles (deg) in the K[Co(HPDTA)] Complex Anion Compared with Those in K[Co(TRDTA)] . 2 H_2O[a] and the Corresponding Standard Deviations

Atoms	K[Co(HPDTA)]	K[Co(TRDTA)] . 2 H_2O
N(1)—Co—N(2)	98·8 (5)[b]	99·0 (3)
N(1)—Co—O(1)	87·0 (4)	—
N(1)—Co—O(2)	84·7 (4)	—
N(1)—Co—O(3)	94·1 (4)	92·4 (3)
N(1)—Co—O(4)	174·2 (4)	—
N(2)—Co—O(1)	91·0 (4)	—
N(2)—Co—O(2)	175·8 (4)	—
N(2)—Co—O(3)	87·4 (4)	87·9 (3)
N(2)—Co—O(4)	86·7 (5)	84·3 (3)
O(1)—Co—O(2)	91·6 (4)	—
O(1)—Co—O(3)	178·1 (4)	—
O(1)—Co—O(4)	91·2 (4)	89·5 (3)
O(2)—Co—O(3)	90·1 (4)	—
O(2)—Co—O(4)	89·8 (4)	92·6 (3)
O(3)—Co—O(4)	87·8 (4)	90·1 (3)
Co—N(1)—C(1)	112·8 (8)	—
Co—N(1)—C(8)	103·7 (8)	—
Co—N(1)—C(10)	109·4 (8)	—
C(1)—N(1)—C(8)	108·7 (11)	—
C(1)—N(1)—C(10)	113·1 (11)	—
C(8)—N(1)—C(10)	108·6 (10)	—
Co—N(2)—C(3)	114·3 (8)	112·7 (7)
Co—N(2)—C(4)	104·0 (9)	103·9 (5)
Co—N(2)—C(6)	107·4 (8)	108·1 (5)
C(3)—N(2)—C(4)	108·7 (10)	108·8 (6)
C(3)—N(2)—C(6)	111·8 (12)	112·9 (8)
C(4)—N(2)—C(6)	110·3 (10)	110·0 (8)
C(2)—C(1)—N(1)	114·2 (12)	—
C(1)—C(2)—C(3)	119·7 (12)	118·2 (11)
C(1)—C(2)—O(5)	108·7 (12)	—
C(3)—C(2)—O(5)	106·2 (12)	—
C(2)—C(3)—N(2)	114·5 (12)	115·6 (5)
C(5)—C(4)—N(2)	107·6 (11)	107·6 (6)
C(4)—C(5)—O(4)	113·6 (12)	115·9 (9)
C(4)—C(5)—O(6)	121·2 (13)	118·3 (8)
O(6)—C(5)—O(4)	125·1 (13)	125·8 (10)
C(7)—C(6)—N(2)	109·5 (12)	111·3 (8)
C(6)—C(7)—O(3)	117·0 (12)	115·6 (8)
C(6)—C(7)—O(7)	119·0 (12)	118·8 (9)
C(9)—C(8)—N(1)	106·2 (12)	—

TABLE III
(*Continued*)

Atoms	K[Co(HPDTA)]	K[Co(TRDTA)] . 2 H_2O
C(8)—C(9)—O(2)	116·7 (13)	—
O(8)—C(9)—O(2)	123·2 (15)	—
C(11)—C(10)—N(1)	108·6 (10)	—
C(10)—C(11)—O(1)	117·4 (12)	—
C(10)—C(11)—O(9)	119·0 (12)	—
O(9)—C(11)—O(1)	123·5 (12)	—
O(7)—C(7)—O(3)	123·9 (13)	125·5 (7)
C(8)—C(9)—O(8)	120·1 (13)	—
Co—O(1)—C(11)	114·8 (8)	—
Co—O(2)—C(9)	111·0 (9)	—
Co—O(3)—C(7)	114·5 (8)	116·6 (6)
Co—O(4)—C(5)	114·2 (9)	114·8 (6)

[a] See ref.[9]; [b] standard deviations (. 10) are given in parentheses.

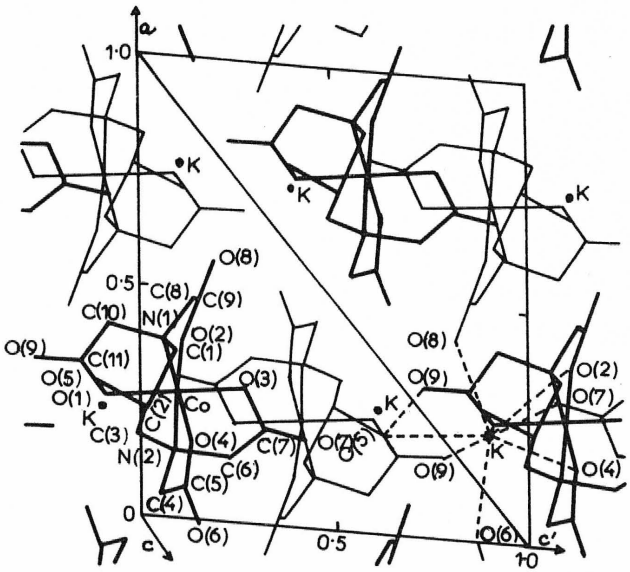

FIG. 2

Projection of the Structure in the Direction of the *b*-Axis

For the sake of lucidity, part of the unit cell is limited by axes *a* and *c*′, where $\vec{c'} = \vec{c} + \vec{a}$.

to $[Co(TRDTA)]^-$ (where TRDTA is trimethylenediaminetetraacetic acid), as can be seen in Tables II and III summarizing the interatomic distances and bond angles of the $K[Co(HPDTA)]$ crystal structure, compared with some corresponding values for the crystal structure[9] of $K[Co(TRDTA)].2\ H_2O$.

The ligand forms five chelate rings during coordination (Fig. 2), one six-membered, 1,3-propanediamine, and four five-membered, crystallographically independent glycine rings, which represent two pairs of chemically virtually equivalent rings. The latter are pseudosymmetrically dependent, with symmetry axis passing through the cobalt atom and through the centre of the line connecting N(1)...N(2). In the $[Co(TRDTA)]^-$ complex anion the pseudoaxis becomes the real symmetry axis, which results in chemical and crystallochemical equivalence of the rings. The glycine rings lying in the six-membered ring plane (G-rings) are deformed more than those perpendicular to the equatorial plane consisting of the Co, N(1), N(2), O(2) and O(4) atoms (R-rings), which are almost planar. This can be seen from Table IV, giving the distances from the individual planes. A similar situation was encountered with the $[Co(TRDTA)]^-$ and $[Co(EDTA]^-$ complexes, where the central diamine ring is five-membered. This is caused by the formation of a girdle around the cobalt atom

TABLE IV

Deviations of the Atoms from Planes No 1, 2, 3, 4 (No 2 — the least square plane)

Plane, No	Atoms defining the plane	Out-of-plane atoms	Distances between out-of-plane atoms, Å
	N(2)	C(3)	0·76
1	Co	C(2)	0·27
	N(1)	C(1)	−0·55
	Co	C(4)	0·62
	N(2)	C(5)	0·17
2	N(1)	C(2)	0·26
	O(4)	C(8)	−0·89
	O(2)	C(9)	−0·64
	Co	C(10)	−0·33
3	N(1)	C(11)	−0·14
	O(1)		
	Co	C(6)	0·08
4	O(3)	C(7)	−0·20
	N(2)		

consisting of the fused rings in the equatorial plane, which forces the N—C bonds between the band atoms to form approximately identical angles with the equatorial plane. An N—C bond in the R-ring is then in a plane almost perpendicular to the equatorial plane and the R-ring becomes nearly planar. The G-rings have a pronounced asymmetrical envelope conformation, the deviations of the C(8) and C(9) atoms from the equatorial plane, 0·89 and 0·64 Å, respectively, being anomalously large. The six-membered 1,3-propanediamine ring has a skew-boat conformation and the C(1) and C(3) atoms lie out of the plane defined by the Co N(1) and N(2) atoms by 0·55 and 0·76 Å, respectively. A similar conformation was observed[9] in the K[Co(TRDTA)].2 H_2O crystals, where the corresponding carbon atoms were 0·65 Å out of the plane.

The structure has an ionic character and exhibits bond interactions between the K^+ cation and the complex anion van der Waals forces. The strong intermolecular hydrogen bond between the hydroxyl group and the O(9) oxygen of a carboxyl group from the neighbouring complex unit is exceptional. The O(5)···(9) distance amounts to 2·71 Å. The fractional negative charges located practically only on the oxygen atoms in the carboxyl groups can be saturated in the absence of water of crystallization only by interaction with the K^+ cation, which results in a complicated spacial arrangement around the potassium atom. The K^+ ion also interacts with the O(5) atom in the hydroxyl group (3·03 Å). Eight oxygen atoms are located in the vicinity of the K^+ cation at a distance smaller than 3·25 Å, whose spacial arrangement can be described by no defined polyhedron. The overall crystal arrangement and significant bond interactions are evident from the crystal projection given in Fig. 2.

All computations were carried out on a SIEMENS 4 004/150 computer in the Institute for Computing Techniques of the universities and on an XTL module from SYNTEX.

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