Crystal and Molecular Structure of Potassium *cis*-Bis(iminodiacetato)-cobaltate(III)–2·5 Water

By **A. Bonamartini Corradi, C. Grasselli Palmieri, M. Nardelli,* M. A. Pellinghelli,** and **M. E. Vidoni Tani,** Istituto di Chimica Generale ed Inorganica, Centro di Studio per la Strutturistica Diffrattometrica del C.N.R., Parma, Italy

The crystal structure of the title compound has been determined from diffractometer data by Patterson and Fourier methods and refined by least-squares techniques to *R* 5·4% for 1884 observed reflections. Crystals are orthorhombic, space group *Pbcn*, with $a = 18{\cdot}366(9)$, $b = 10{\cdot}143(8)$, $c = 15{\cdot}317(9)$ Å, $Z = 8$. Co-ordination around Co^{III} is octahedral and involves two iminodiacetate ions which behave as terdentate ligands through the nitrogen atom [Co–N 1·937(4), 1·946(4) Å] and two oxygen atoms of the carboxylic groups [Co–O 1·875(4), 1·883(4), 1·896(4), 1·902(4) Å].

IMINODIACETIC acid is a terdentate ligand which forms several 2 : 1 octahedral metal complexes.[1] We report the *X*-ray crystal structure determination of potassium *cis*-bis(iminodiacetato)cobaltate(III)–2·5 water. This analysis was carried out as part of a study of metal–amino-acid interactions.

EXPERIMENTAL

Crystals of the compound show no pleochroic effects. They were prepared by the method of ref. 2 by the addition of cobalt dichloride hexahydrate to an aqueous solution of $NH(CH_2CO_2H)_2$ and $KHCO_3$. The solution was cooled in an ice bath, and 30% hydrogen peroxide was added dropwise, to give a violet microcrystalline precipitate with traces of a brown product. Prismatic crystals of the violet compound elongated along [010] were obtained and separated from hot water containing potassium acetate.

Crystal data were determined by use of a single-crystal Siemens automated diffractometer and Mo-K_α radiation.

Crystal Data.—$C_8H_{10}CoKN_2O_8,2{\cdot}5H_2O$, $M = 505{\cdot}1$, Orthorhombic, $a = 18{\cdot}366(9)$, $b = 10{\cdot}143(8)$, $c = 15{\cdot}317(9)$ Å, $U = 2853$ Å^3, $D_m = 1{\cdot}88$, $Z = 8$, $D_c = 1{\cdot}89$, $F(000) = 1691$. Mo-K_α radiation, $\lambda = 0{\cdot}7107$ Å, $\mu(\text{Mo-}K_\alpha) = 16{\cdot}0$ cm^{-1}. Space group *Pbcn*, from systematic absences.

Three-dimensional intensity data were collected with Mo-K_α radiation by use of the ω–2θ scan technique. 2884 Reflections were measured, of which 1884 were observed and used for the analysis. Intensities were corrected for Lorentz and polarization factors; no absorption correction was applied since the sample was rather small (cross-section dimensions 0·08 and 0·04 mm). Data were placed on an absolute scale first by Wilson's method and later by correlation of observed and calculated values.

Structure Analysis and Refinement.—The heavy atom was located by Patterson methods. The Fourier synthesis obtained by using the observed structure factors phased by the heavy-atom contributions gave all the non-hydrogen atom positions. The model was refined with isotropic

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[1] B. B. Smith and D. T. Sawyer, *Inorg. Chem.*, 1968, **7**, 922.

[2] J. Hidaka, Y. Schimura, and R. Tsuchida, *Bull. Chem. Soc. Japan*, 1962, **35**, 567.

thermal parameters by block-diagonal least-squares calculations to R 15% which was improved by the subsequent anisotropic refinement to 6·6%. The function minimized was $\Sigma w|\Delta F|^2$, at first with unit weights, then with the weighting scheme $w = 1/(A + BF_o)^2$ with $A = 1{\cdot}35$ and $B = 0{\cdot}033$; this further reduced R to 6·2%. At this stage a three-dimensional difference Fourier synthesis showed the position of all the hydrogen atoms whose co-ordinates were afterwards improved by a least-squares isotropic refinement, giving the final R of 5·4%.

TABLE 1

Final fractional co-ordinates (× 10^4) and thermal parameters * (× 10 Å^2) for non-hydrogen atoms, with estimated standard deviations in parentheses

	x/a	y/b	z/c	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
Co	2409(1)	28(1)	992(1)	18(0)	12(0)	15(0)	−2(0)	−1(0)	0(0)
K	4404(1)	2241(1)	3539(1)	25(0)	40(0)	26(0)	4(0)	0(0)	−6(0)
O(1)	1815(2)	156(3)	1984(2)	28(1)	20(1)	23(1)	−2(1)	3(1)	−1(1)
O(2)	1594(2)	−749(5)	3278(2)	45(2)	52(2)	25(1)	−15(2)	11(1)	−1(1)
O(3)	3070(2)	1320(3)	1407(2)	25(1)	16(1)	27(1)	−4(1)	−2(1)	−2(1)
O(4)	4214(2)	1537(4)	1829(2)	27(1)	40(2)	35(1)	−13(1)	−2(1)	−5(1)
O(5)	1828(2)	1375(3)	482(2)	24(1)	17(1)	27(1)	3(1)	−4(1)	2(1)
O(6)	666(3)	1760(4)	155(2)	26(1)	41(2)	36(2)	13(1)	−4(1)	4(1)
O(7)	2990(2)	−134(3)	−15(2)	26(1)	14(1)	23(1)	−4(1)	1(1)	1(1)
O(8)	3056(2)	−1088(4)	−1318(2)	33(1)	37(1)	21(1)	4(1)	3(1)	−5(1)
O(9)	4684(4)	2582(7)	−1602(5)	64(3)	100(5)	123(6)	−14(3)	11(3)	−42(4)
O(10)	5000(—)	4391(8)	2500(—)	78(5)	51(4)	85(5)		0(4)	
O(11)	4458(3)	−362(8)	4423(4)	49(2)	142(6)	78(4)	40(3)	12(3)	20(4)
N(1)	2996(2)	−1235(3)	1640(2)	28(1)	11(1)	17(1)	0(1)	−2(1)	0(1)
N(2)	1740(2)	−1199(4)	448(2)	24(1)	18(1)	21(1)	−2(1)	0(1)	0(1)
C(1)	3695(2)	842(4)	1654(3)	24(2)	20(2)	18(2)	−4(1)	2(1)	0(1)
C(2)	3734(2)	−648(5)	1678(3)	21(2)	28(2)	30(2)	1(1)	−6(1)	6(2)
C(3)	2656(3)	−1446(4)	2521(3)	38(2)	21(2)	19(2)	−4(2)	0(2)	2(1)
C(4)	1974(3)	−636(6)	2616(3)	30(2)	42(2)	16(2)	−18(2)	2(1)	−2(2)
C(5)	1168(2)	983(5)	332(3)	24(2)	19(2)	19(2)	2(1)	0(1)	−3(1)
C(6)	1041(2)	−485(5)	386(4)	19(2)	14(1)	52(3)	−3(1)	−3(2)	−7(2)
C(7)	2039(2)	−1614(5)	−406(3)	26(2)	18(2)	23(2)	−2(1)	−2(1)	−4(1)
C(8)	2743(2)	−912(4)	−616(3)	27(2)	16(1)	20(1)	6(1)	−4(1)	−1(1)

* The anisotropic temperature factor is expressed in the form: $\exp[-\frac{1}{4}(B_{11}h^2a^{*2} + B_{22}k^2b^{*2} + B_{33}l^2c^{*2} + 2B_{12}hka^*b^* + 2B_{13}hla^*c^* + 2B_{23}klb^*c^*)]$.

Final positional and thermal parameters with estimated standard deviations [3,4] are given in Tables 1 and 2. Observed and calculated structure factors are listed in Supplementary Publication No. SUP 20577 (17 pp., 1 microfiche).†

TABLE 2

Final atomic fractional co-ordinates (× 10^3) and isotropic thermal parameters (Å^2) for the hydrogen atoms, with estimated standard deviations in parentheses

	x/a	y/b	z/c	B
H(1)	300(2)	−198(5)	136(3)	2·3(1·0)
H(2)	166(3)	−191(5)	76(3)	2·7(1·0)
H(3)	410(3)	−73(5)	219(3)	3·7(1·2)
H(4)	400(3)	−74(5)	109(3)	3·7(1·2)
H(5)	291(2)	−128(5)	300(3)	1·8(1·0)
H(6)	257(3)	−233(5)	263(3)	2·6(1·0)
H(7)	81(3)	−72(5)	102(3)	3·2(1·1)
H(8)	74(3)	−75(5)	−1(3)	3·9(1·2)
H(9)	168(3)	−156(5)	−86(3)	2·7(1·1)
H(10)	202(3)	−254(5)	−38(3)	3·2(1·1)
H(11)	434(5)	325(8)	−200(5)	8·2(2·5)
H(12)	500(5)	324(9)	−150(6)	9·7(2·9)
H(13)	548(4)	488(7)	242(6)	8·6(2·3)
H(14)	400(5)	−25(9)	466(6)	12·3(2·7)
H(15)	450(5)	−125(9)	433(6)	12·0(2·9)

H(11) and (12) are on O(9), H(13) is on O(10), and H(14) and (15) are on O(11).

Atomic scattering factors were taken from ref. 5 for all non-hydrogen atoms, and from ref. 6 for hydrogen atoms.

Calculations were performed on a CDC 6600 computer at the Centro di Calcolo Elettronico Interuniversitario dell'Italia Nord-Orientale with the programs of Immirzi.[7]

DESCRIPTION OF THE STRUCTURE AND DISCUSSION

Figure 1 shows the clinographic projection of the anion and Table 3 gives bond distances and angles. The co-ordination around cobalt is distorted octahedral and involves two molecules of the imino-acid which

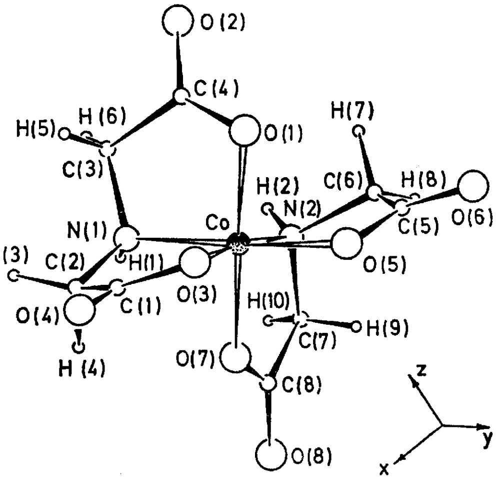

FIGURE 1 Clinographic projection of the anion $[Co\{NH(CH_2{\cdot}CO_2)_2\}_2]^+$

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† For details see Notice to Authors No. 7 in *J. Chem. Soc. (A)*, 1970, Issue No. 20.

[3] D. W. J. Cruickshank, *Acta Cryst.*, 1949, **2**, 65.
[4] D. W. J. Cruickshank, *Acta Cryst.*, 1956, **9**, 748.
[5] D. T. Cromer and J. B. Mann, *Acta Cryst.*, 1968, **A24**, 321.
[6] R. F. Stewart, E. R. Davidson, and W. T. Simpson, *J. Chem. Phys.*, 1965, **42**, 3175.
[7] A. Immirzi, *Ricerca sci.*, 1967, **37**, 743.

behaves as a terdentate ligand. Each of these molecules form two roughly perpendicular five-membered co-ordination rings [dihedral angles Co–O(3)–C(1)–C(2)–N(1), Co–O(1)–C(4)–C(3)–N(1) 80·0°; Co–O(7)–C(8)–C(7)–N(2), Co–O(5)–C(5)–C(6)–N(2) 80·2°]. The ligands are *cis* and this result confirms the suggestions

TABLE 3

Bond distances (Å) and angles (°) with standard deviations in parentheses

(*a*) In the co-ordination polyhedron

Co–O(1)	1·875(4)	Co–O(7)	1·883(4)
Co–O(3)	1·896(4)	Co–N(1)	1·946(4)
Co–O(5)	1·902(4)	Co–N(2)	1·937(4)
O(1)–Co–O(3)	93·0(2)	O(3)–Co–N(2)	173·9(2)
O(1)–Co–O(5)	87·5(2)	O(5)–Co–O(7)	92·3(2)
O(1)–Co–O(7)	178·6(2)	O(5)–Co–N(1)	173·3(2)
O(1)–Co–N(1)	87·4(2)	O(5)–Co–N(2)	85·9(2)
O(1)–Co–N(2)	91·4(2)	O(7)–Co–N(1)	92·7(2)
O(3)–Co–O(5)	90·0(2)	O(7)–Co–N(2)	87·2(2)
O(3)–Co–O(7)	88·4(2)	N(1)–Co–N(2)	98·5(2)
O(3)–Co–N(1)	85·9(2)		

(*b*) In the ligands

O(1)–C(4)	1·291(6)	O(7)–C(8)	1·295(5)
O(2)–C(4)	1·236(6)	C(8)–O(8)	1·232(6)
C(4)–C(3)	1·505(8)	C(8)–C(7)	1·511(6)
C(3)–N(1)	1·502(6)	C(7)–N(2)	1·480(6)
N(1)–C(2)	1·482(5)	N(2)–C(6)	1·477(6)
C(2)–C(1)	1·513(7)	C(6)–C(5)	1·509(7)
C(1)–O(4)	1·216(5)	C(5)–O(6)	1·243(6)
C(1)–O(3)	1·302(5)	C(5)–O(5)	1·296(5)
Co–O(1)–C(4)	115·6(3)	Co–O(7)–C(8)	115·9(3)
O(1)–C(4)–O(2)	123·0(5)	O(7)–C(8)–O(8)	123·0(4)
O(2)–C(4)–C(3)	119·9(5)	O(8)–C(8)–C(7)	121·1(4)
O(1)–C(4)–C(3)	117·1(4)	O(7)–C(8)–C(7)	115·8(4)
C(4)–C(3)–N(1)	110·8(4)	C(8)–C(7)–N(2)	111·8(4)
C(3)–N(1)–Co	108·8(3)	Co–N(2)–C(7)	109·1(3)
Co–N(1)–C(2)	105·2(2)	Co–N(2)–C(6)	105·3(3)
C(2)–N(1)–C(3)	113·7(3)	C(6)–N(2)–C(7)	113·9(3)
N(1)–C(2)–C(1)	110·9(3)	N(2)–C(6)–C(5)	110·7(3)
C(2)–C(1)–O(3)	114·9(3)	C(6)–C(5)–O(5)	115·9(4)
C(2)–C(1)–O(4)	122·4(4)	O(6)–C(5)–O(5)	122·5(5)
O(3)–C(1)–O(4)	122·6(4)	C(6)–C(5)–O(6)	121·5(4)
Co–O(3)–C(1)	113·8(3)	Co–O(5)–C(5)	112·2(3)

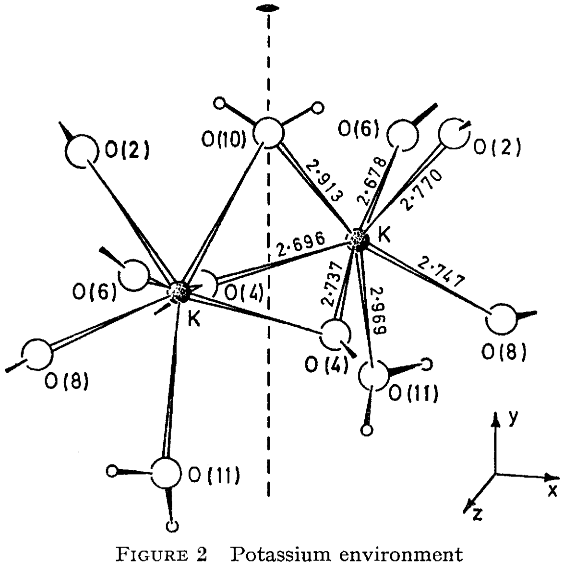

FIGURE 2 Potassium environment

TABLE 4

Co–N and Co–O distances (Å) in Co^{III} amine complexes

	Co–N	Co–O
$K[Co\{NH(CH_2CO_2)_2\}_2],2{\cdot}5H_2O$	1·937, 1·946	1·875, 1·883 1·896, 1·902
$[Co(Et)(salen)]_2$ [a]	1·88, 1·89	1·90, 1·94
$[Co(CH_2{=}CH)(py)(salen)]$ [b]	1·86	1·879
$[Co(CH_2{=}CH)(bae)(H_2O)]$ [c]	1·89, 1·89	1·91, 1·93
$[Co(Ph)(bae)(H_2O)]$ [d]	1·89	1·91
$(-)_{546}$*cis*-β-$[Co(NO_2)_2$(L-dmdd)]-ClO_4 [e]	1·923, 1·941 1·943, 1·969 1·983, 1·994	
$[Co(dmg)_2(NH_3)_2]NO_3$ [f]	1·94, 1·96 1·97	
$(+)_{589}$*cis*-$[Co\{(-)_{589}pn\}_2(NO_2)_2]Cl$ [g]	1·88, 1·92 1·94, 1·96 1·97, 2·01	
[(saldp)(Co·O_2·Co(saldp)],-$C_6H_5CH_3$ [h]	1·92, 1·96 1·99	1·89, 1·91 1·93
[Co(salen)] [i]	1·89	1·90

salen = *NN'*-Ethylenebis(salicylideneiminato); py = pyridine; bae = *NN'*-ethylenebis(acetylacetoneiminato); dmdd = 2,7-dimethyl-3,6-diazaoctane-1,8-diamine; dmg = dimethylglyoximinato; pn = 1,2-propylenediamine; and saldp = 3,3'-bis(salicylideneimino)di-n-propylamine

[a] M. Calligaris, G. Nardin, and L. Randaccio, personal communication. [b] M. Calligaris, G. Nardin, and L. Randaccio, personal communication. [c] S. Bückner, M. Calligaris, G. Nardin, and L. Randaccio, *Inorg. Chim. Acta*, 1968, **2**, 416; 1969, **2**, 278. [d] S. Bückner, M. Calligaris, G. Nardin, and L. Randaccio, *Chem. Comm.*, 1970, 152. [e] M. Ito, F. Marumo, and Y. Saito, *Acta Cryst.*, 1970, **B26**, 1408. [f] K. S. Viswanathan and N. R. Kunchur, *Acta Cryst.*, 1961, **B14**, 675. [g] G. A. Barclay, E. Goldschmied, and N. C. Stephenson, *Acta Cryst.*, 1970, **B26**, 1559. [h] L. A. Lindholm, W. P. Schaeffer, and R. E. Marsh, *Acta Cryst.*, 1971, **B27**, 1461. [i] M. Cesari, C. Neri, G. Perego, E. Perrotti, and A. Zazzetta, *Chem. Comm.*, 1970, 276.

TABLE 5

C–O distances (Å) involving co-ordinated and unco-ordinated oxygen atoms of carboxylic groups

	C–O · · · M	C–O
$K[Co\{NH(CH_2CO_2)_2\}_2],2{\cdot}5H_2O$	1·291, 1·295 1·296, 1·302	1·216, 1·232
$[Cu(Hphthal)_2(H_2O)_2]$ [a]	1·273	1·264
$[Cu(phthal)(NH_3)_2]$ [b]	1·275, 1·282	1·241, 1·249
$[Cu(ClCH_2CO_2)_2(\alpha\text{-pic})_2]$ [c]	1·286	1·215

Hphthal = Hydrogen *o*-phthalato; phthal = *o*-phthalato; and α-pic = α-picoline

[a] M. Biagini Cingi, C. Guastini, A. Musatti, and M. Nardelli, *Acta Cryst.*, 1969, **B25**, 1833. [b] M. Biagini Cingi, C. Guastini, A. Musatti, and M. Nardelli, *Acta Cryst.*, 1970, **B26**, 1836. [c] G. Davey and F. S. Stephens, *J. Chem. Soc.*, (*A*) 1971, 1917.

TABLE 6

Distances (Å) and angles (°) in the potassium environment, with standard deviations in parentheses

K–O(4)	2·737(4)	$K–O(2^{II})$	2·770(5)
K–O(10)	2·913(6)	$K–O(8^{III})$	2·747(4)
K–O(11)	2·969(8)	$K–O(4^{IV})$	2·696(4)
$K–O(6^{I})$	2·678(4)		
O(4)–K–O(11)	102·0(1)	$O(6^{I})–K–O(8^{III})$	92·5(1)
O(4)–K–O(10)	73 8(1)	$O(6^{I})–K–O(4^{IV})$	109·8(1)
$O(4)–K–O(2^{II})$	88·2(1)	$O(11)–K–O(8^{III})$	67·4(1)
$O(4)–K–O(8^{III})$	81·4(1)	$O(10)–K–O(2^{II})$	67·6(1)
$O(4)–K–O(4^{IV})$	81·4(1)	$O(2^{II})–K–O(8^{III})$	74·2(1)
$O(11)–K–O(6^{I})$	85·2(2)	$O(11)–K–O(4^{IV})$	80·1(1)
$O(10)–K–O(6^{I})$	103·9(1)	$O(10)–K–O(4^{IV})$	74·3(1)
$O(6^{I})–K–O(2^{II})$	79·8(1)	$O(4)–K–O(6^{I})$	167·7(1)

Roman numerals as superscripts refer to the following equivalent positions relative to the reference molecule at *x*, *y*, *z*:

I $\frac{1}{2} - x, \frac{1}{2} - y, \frac{1}{2} + z$
II $\frac{1}{2} - x, \frac{1}{2} + y, z$
III $x, \bar{y}, \frac{1}{2} + z$
IV $1 - x, y, \frac{1}{2} - z$
V $\frac{1}{2} + x, \frac{1}{2} - y, \bar{z}$

made [8] on the basis of electronic spectra. The cobalt–nitrogen distances [Co–N(1) 1·946(4), Co–N(2) 1·937(4) Å] are in agreement with those found in other cobalt(III)-amine complexes as are the cobalt–oxygen distance (Table 4).

The C–O bond lengths in each carboxylic group are not equal: the one involving the co-ordinating oxygen is longer (1·29, 1·30 Å), while the other is shorter (1·21, 1·24 Å) and corresponds to a double bond. A similar situation is observed in other compounds (Table 5).

Potassium is surrounded by seven oxygen atoms within 3·0 Å, at the corners of a distorted pentagonal bipyramid; five of these atoms are from the carboxylic groups and two from the water molecules, O(10), O(11) (Figure 2 and Table 6). The K$^+ \cdots$ O distances concerning the carboxylic oxygen atoms correspond fairly well to the sum of the ionic radii (2·73 Å) while those involving the water oxygen atoms are longer.

Packing is determined by the K$^+ \cdots$ O interactions and by water–water and water–carboxylic oxygen contacts. Some of these, O(9)–H(12) $\cdots$ O(6$^{\text{V}}$), O(11)–H(15) $\cdots$ O(9$^{\text{III}}$), and O(11)–H(14) $\cdots$ O(7$^{\text{III}}$), can be interpreted as possible hydrogen bonds.

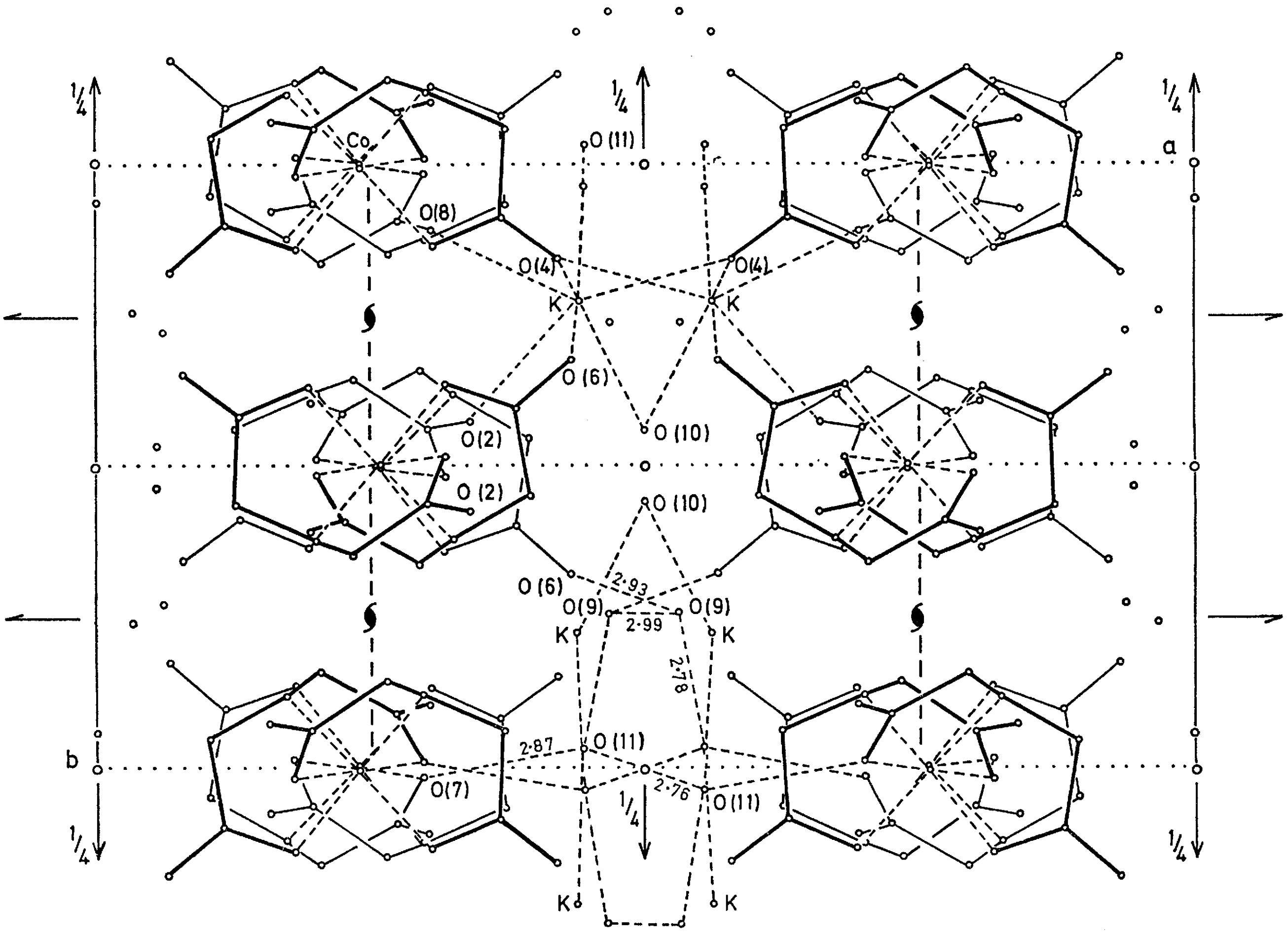

FIGURE 3 Projection of the structure along [001]

The whole structure is built up by layers of complex anions running parallel to (100) and held together by the K$^+$ cations and the water molecules which interact with carboxylic oxygens (Figure 3).

Bond distances involving hydrogen atoms are in the usual range.

[2/1735 *Received*, *24th July*, 1972]

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[8] A. Uehara, E. Kyumo, and R. Tsuchida, *Bull. Chem. Soc. Japan*, 1970, **43**, 1394.