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X-ray Studies of Cobaltate Aminomethylphosphonic Acid Polymeric Complex

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The structure of diaquo-bis(aminomethylphosphonate)cobaltate(II) monohydrate has been determined as one of a series of α-aminomethylphosphonic and -phosphinic acids with divalent metal ions. In the area of transition metal chemistry the following metal complexes with α-aminomethylphosphonic acid (AMP) and α-aminomethylmethylphosphinic acid (AMMP) have been investigated: [Mn(AMMP$_2$·2H$_2$O]Br$_2$·2H$_2$O [1], [MnCl$_2$(AMMP)$_2$·2H$_2$O] [2], [Cu(AMP)$_2$] [3], [Zn(AMP)$_2$]4H$_2$O [4]. Crystallographic studies showed a typical feature of these complexes which is their polymeric nature. Of the four investigated complexes only one is monomer and the three others are polymers. In this group of compounds the metal ions are linked by single or double phosphate bridges.

In this communication we report the X-ray data of the new polymeric cobaltate complex formed during the reaction between CoCl$_2$·6H$_2$O and α-aminomethylphosphonic acid.

Experimental

Crystals suitable for X-ray analysis were obtained from an aqueous solution containing CoCl$_2$·6H$_2$O and α-aminomethylphosphonic acid at 1:2 molar ratio. All measurements were made on a Syntex P2$_1$ diffractometer using MoK radiation. Crystallization from water gave stable brown crystals which were monoclinic, space group P2$_1$/c with a = 9.666(4), b = 6.890(4), c = 9.868(4) Å, β = 115.41(6)°, Z = 2, V = 593.6 Å^3, d$_x$ = 1.96, d$_m$ = 1.96 g cm^{-3} (by flotation), μ(MoKα) = 18.2 cm^{-1}. The structure was solved using the Syntex XTL system programs on a Nova 1200 computer.

The structure was solved by the heavy-atom technique and refined by a full-matrix least squares procedure with anisotropic thermal parameters for all non-hydrogen atoms. The structure was refined to R = 0.051 for 1784 counter reflexions for which F > 3.92σ(F). The coordinates of the H atoms and their isotropic thermal factor (B = 3.6 Å^2) were not refined. Scattering factors for neutral atoms were taken from International Tables for X-ray Crystallography [5].

TABLE I. Fractional Atomic Coordinates ×10^4 and Anisotropic Thermal Parameters ×10^3 with Estimated Standard Deviations in Parentheses.

Atom	x	y	z	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
Co	0	0	0	148(3)	107(3)	58(3)	−7(3)	55(2)	−5(3)
P	1707(1)	3531(2)	−1206(1)	140(4)	101(4)	67(8)	2(4)	58(3)	−3(3)
O(1)	902(4)	2645(5)	−327(4)	205(14)	184(13)	105(11)	−6(11)	108(11)	0(10)
O(2)	585(4)	4181(5)	−2752(4)	219(15)	205(14)	73(11)	57(12)	77(11)	32(10)
O(3)	2822(4)	5105(5)	−278(4)	186(14)	149(13)	169(18)	−41(12)	92(11)	−70(11)
O(4)w	2134(4)	−1326(5)	451(4)	191(14)	156(14)	171(13)	15(12)	79(12)	−21(11)
O(5)w	5651(5)	3356(6)	1710(4)	218(16)	350(20)	165(14)	−33(16)	37(18)	84(14)
N	2022(5)	226(6)	−2588(4)	229(17)	146(16)	121(13)	−6(14)	104(18)	−25(12)
C	2943(6)	1727(7)	−1484(5)	160(18)	130(17)	121(15)	5(14)	70(14)	−19(18)
H(1)	3619	2377	−1865						
H(2)	3584	1099	−532						
H(3)	2670	−710	−2570						
H(4)	1550	840	−3480						
H(5)	1186	−411	−2374						
H(6)	2800	−120	470						
H(7)	2390	−249	310						
H(8)	4780	3900	1290						

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

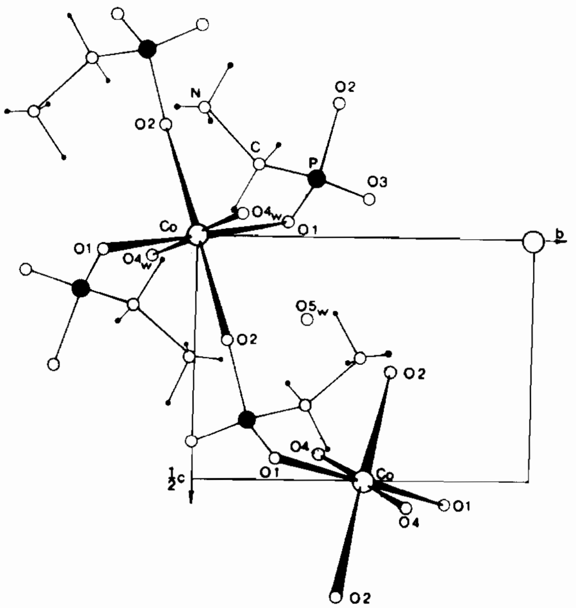

Fig. 1. Projection of the structure of diaquo-bis(aminomethylphosphonate)cobaltate(II) monohydrate along the *a* axis. Bond lengths and angles are: Co–O(1) 2.104(4); Co–O(2) 2.118(3) Co–O(4)$_w$ 2.121(4); P–O(1) 1.520(4); P–O(2) 1.511(3); P–O(3) 1.526(4); P–C 1.824(5); C–N 1.489(6) Å; O(1)–Co–O(4)$_w$ 91.4(1), –O(2) 90.7(1); O(4)$_w$–Co–O(2) 84.5(1); O(1)–P–O(3) 110.2(2), –C 109.9 2, –O(2) 111.9(2); O(3)–P–C 108.6(2), –O(2) 114.2(2); O(2)–P–C 106.5(2); C–P–N 111.0(3)°.

A table of the observed and calculated structure factors may be obtained from the authors. The final positional and isotropic thermal parameters are listed in Table I.

Discussion

The crystal structure viewed down *a* is shown in Fig. 1. The complex is centrosymmetric and the Co atom at the centre of symmetry is coordinated to four O atoms from four phosphonic groups and two water molecules. The coordination about the Co atom is a slightly distorted octahedron. Bond distances and angles in the coordination polyhedron are given in Fig. 1, and agree well with those found in other octahedral Co(II) complexes containing oxygen as ligand atoms. The two phosphonic O atoms are bonded to different Co atoms, forming Co–O–P–O–Co bridge. These bridges are linked in polymeric chain, running along of the *bc* plane. The torsion angles Co–O(1)–P–C(1) and Co–O(2)–P–C(1) are –32.6(4)° and –41.1(5)° respectively.

In this compound the ligand exists as NH_3^+–CH_2–PO_3^{2-}. The phosphonic group is negatively charged, the charge being distributed between O(1), O(2) and O(3) atoms. The mean values of the bond lengths and angles in the aminomethylphosphonic molecule are presented in Fig. 1 and agree well with those found in [Cu(AMP)$_2$] [3], [Zn(AMP)$_2$]4H$_2$O [4] and in α-aminomethylphosphonic acid [6].

The investigation complex contains a network of hydrogen bonds which plays an important role in stabilization. All water molecules enter hydrogen-bond formation. O(4)$_w$ and O(1), O(2) of the phosphonic groups are coordinated to Co and also form hydrogen bonds. O(4)$_w$ of the water molecules forms two hydrogen bonds with O(1) (2.724(5) Å) and O(5)$_w$ (2.709(6) Å). Uncoordinated O(5)$_w$ of the second water molecule takes part in the hydrogen bonds with the O(3) atoms of the phosphonic groups (2.859(6), 2.662(6) Å). All of the hydrogen atoms attached to nitrogen atom are also involved as donors to O(5)$_w$ (3.198(6) Å), O(1) (2.849(5) Å) and O(2) (2.776(7) Å).

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References

1 T. Głowiak and W. Sawka-Dobrowolska, *Acta Cryst., B33,* 325 (1977).
2 T. Głowiak and W. Sawka-Dobrowolska, *Acta Cryst., B33,* 2765 (1977).
3 T. Głowiak, W. Sawka-Dobrowolska, B. Jeżowska-Trzebiatowska and A. Antonów, *J. Cryst. Mol. Struc.,* to be published (1980).
4 P. Fenot, J. Darriet and C. Garrigou-Lagrange, *J. Mol. Struct., 43,* 49 (1978).
5 International Tables for X-ray Crystallography, Vol. IV, Kynoch Press, Birmingham (1974).
6 H. Darriet, J. Darriet, A. Cassaigne and E. Neuzil, *Acta Cryst., B31,* 469 (1975).