Synthesis and crystal structure of a novel cobalt phosphonate containing the $[Co(H_2O)_6]^{2+}$ cation

Guo-Li Zheng, Jian-Fang Ma* and Jin Yang

Department of Chemistry, Northeast Normal University, Changchun 130024, P. R. China

Reaction of hexamethylenediaminetetrakis(methylphosphonic acid), $[(H_2O_3PCH_2)_2N(CH_2)_6N(CH_2PO_3H_2)_2]$ (H_8L), with cobalt nitrate affords a novel phosphonate, $[Co(H_2O)_6][Co(H_2O)_4(H_6L)_2]\cdot 12H_2O$ (**1**), and its structure was determined by X-ray diffraction analysis.

Keywords: phosphonate, cobalt, crystal structure

Recently, more work has been focused on the metal phosphonate chemistry due to their novel structures and their potential applications in the areas of catalysis, sensors, non-linear optics, sorption and ion exchange.[1-7] In addition, phosphonic acids can be employed as building blocks in supramolecular chemistry.[7] Many layered structures, three-dimensional networks and porous materials have been prepared, among them compounds with diphosphonic acid have been most investigated.[5-7] But few compounds with tetraphosphonic acid have been reported.[8] In this paper, we report the synthesis and crystal structure of a novel cobalt compound with tetraphosphonic acid.

Selected bond lengths and angles of compound **1** are listed in Table 1. As shown in Fig.1, there is one H_6L^{2-} ligand, $[(^-HO_3P–CH_2)_2–NH^+–(CH_2)_6–NH^+–(CH_2–PO_3H^-)_2]$, in the asymmetric unit, the P–O bond lengths range from 1.497(8) to 1.572(2) Å, and the O–P–O angles vary from 108.3(1) to 118.3(1)°. One –OH group of each phosphonate group is deprontonated while the remaining –OH group stays in the prontonated form. The P(1)–O(3), P(2)–O(6), P(3)–O(8) and P(4)–O(10) bonds are longer than the other P-O bonds, which indicates that oxygen atoms O3, O6, O8 and O10 are protonated. Thus the nitrogen atoms N1 and N2 are also protonated, as required by the charge balance of the formula. This is the same as the previously reported cobalt tetraphosphonate compound,[8] where each phosphonate group is partly deprontonated, and each N atom is protonated. Each H_6L^{2-} ligand bonds to one cobalt atom through one of its deprontonated –OH oxygen donor atoms O(1). There are two kinds of cobalt atoms in the asymmetric unit, and each cobalt atom lies at an inversion centre. Co(1) is coordinated by four water molecules and two deprontonated –OH oxygen atoms from two H_6L^{2-} groups; Co(2) is six-coordinated by six water molecules. The Co–O distances of 1 are similar to the values found in other reported octahedral Co(II) compounds: $[Co(H_2O)_4(H_2O_3P(CH_2)_8PO_3H_2)](HO_3P(CH_2)_8PO_3H)\cdot 2H_2O$ (2.035(1)–2.138(1) Å),[9] $[Co\{(HO_3PCH_2)NH_2(CH_2PO_3H)\}_2(H_2O)_2]$ (2.067(2)–2.132(2) Å),[10] $[Co\{OOCCH_2CH(OH)COO\}]\cdot 3H_2O$ (2.067(3)–2.136(3) Å),[11] $[Co(NH_3CH_2PO_3)_2(H_2O)_2]_n\cdot mH_2O$ (2.104(4)–2.121(4) Å),[12] and $[NH_2(C_2H_5)_2]_2$ $[Co(HO_3PC(CH_3)(OH)PO_3H)_2(H_2O)_2]$ (2.064(2)–2.179(2) Å).[13] The positive charges of $[Co(H_2O)_6]^{2+}$ are balanced by $[Co(H_2O)_4(H_6L)_2]^{2-}$ anions. This is different from the previous reported 3D structure of the cobalt tetraphosphonate compound,[8] which is composed of Co^{2+} ions and zwitter ions $[(HO_3PCH_2)_2–NH–(CH_2)_4–NH–(CH_2PO_3H)_2]^2$.

Note that there is a $[Co(H_2O)_6]^{2+}$ cation in **1**. Generally, the phosphonate group is a much stronger ligand for transition metal ions than the water molecule, and transition metal ions are commonly bridged by phosphonate groups to form polymeric frameworks.[14] The existence of $[M(H_2O)_6]^{2+}$ cations in metal phosphonates has been reported very rarely.[15] The reason why the uncoordinating phosphonate group do not replace the coordinated water molecules of $[Co(H_2O)_6]^{2+}$ is not clear.

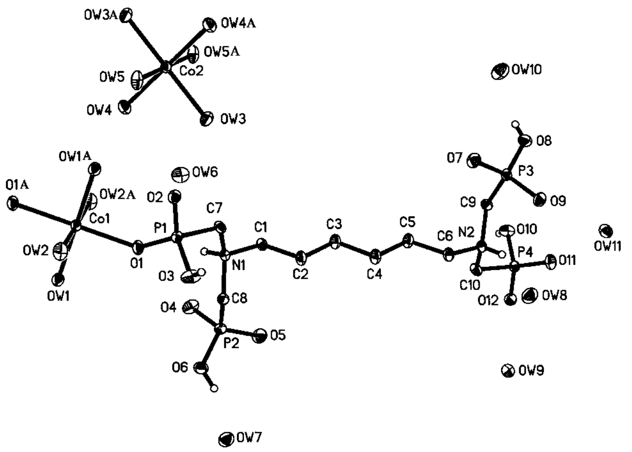

Fig. 1 A view of coordination environments of cobalt atoms in **1** with the atomic numbering scheme. Displacement ellipsoids are drawn at the 50% probability level. The H atoms on the N and PO_3H are shown as small spheres of arbitrary radii and the other H atoms are omitted for clarity.

Table 1 Selected bond lengths (/Å) and angles (/°) for **1**

Co(1)–O(1)	2.106(2)	Co(1)–Ow(1)	2.099(2)
Co(1)–Ow(2)	2.119(2)	Co(2)–Ow(3)	2.121(2)
Co(2)–Ow(4)	2.127(2)	Co(2)–Ow(5)	2.044(2)
N(1)–H(1)	0.91(3)	N(2)–H(2)	0.85(3)
O(1)–P(1)	1.507(2)	O(2)–P(1)	1.510(2)
O(3)–P(1)	1.550(2)	O(4)–P(2)	1.510(2)
O(5)–P(2)	1.497(2)	O(6)–P(2)	1.562(2)
O(7)–P(3)	1.499(2)	O(8)–P(3)	1.563(2)
O(9)–P(3)	1.507(2)	O(10)–P(4)	1.572(2)
O(11)–P(4)	1.502(2)	O(12)–P(4)	1.502(2)
P(1)–O(1)–Co(1)	130.69(9)	O(1)–P(1)–O(2)	116.04(9)
O(1)–P(1)–O(3)	108.7(1)	O(2)–P(1)–O(3)	113.0(1)
O(5)–P(2)–O(4)	117.1(1)	O(5)–P(2)–O(6)	112.6(1)
O(4)–P(2)–O(6)	109.7(1)	O(7)–P(3)–O(9)	116.8(1)
O(7)–P(3)–O(8)	112.5(1)	O(9)–P(3)–O(8)	108.9(1)
O(11)–P(4)–O(12)	118.3(1)	O(11)–P(4)–O(10)	108.3(1)
O(12)–P(4)–O(10)	109.7(1)		

$[Co(H_2O)_4(H_6L)_2]^{2-}$ anions, $[Co(H_2O)_6]^{2+}$ cations and lattice water molecules are held together by complicated hydrogen-bonding interaction, resulting in a complex three-dimensional structure (Fig.2). The hydrogen bonds in this study have been considered with liberal distance cut-off criteria of $2.4<D\cdots A<3.0$Å and angle cut-off criteria of $120<D\cdots A<180°$. Hydrogen bond distances and angles are listed in Table 2.

In the IR spectrum of **1**, the broad bands at 3461–3121 cm^{-1} can be attribute to the stretching vibrations of hydrogen-bonded lattice water molecules superimposed on vibrations of coordinated water. The corresponding δ(HOH) band appears at 1663 cm^{-1}. The strong peak at 1165 cm^{-1} may be assigned to the υ(P=O) band. Symmetrical and asymmetrical stretching vibrations of P–OH groups (υ(P-OH)) appear at 1160

---

* Correspondence.

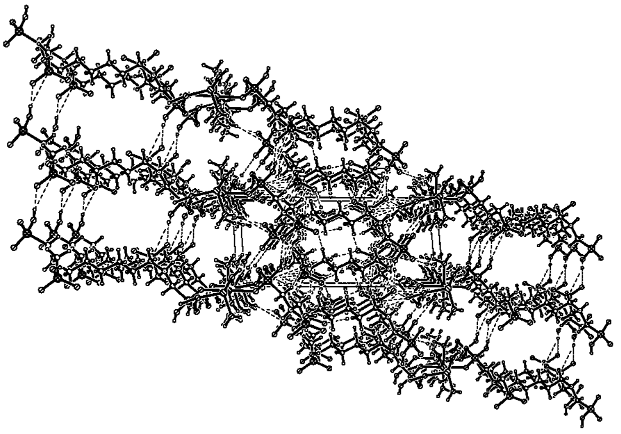

Fig. 2 The packing diagram of **1** (hydrogen bonds are represented with dashed lines) along the *b* axis.

Table 2 Hydrogen bonds for **1**

D–H...A	d(D-H)	d(H...A)	d(D...A)	<(DHA)
OW1–H(1C)...O(2)#1	0.85(4)	1.85(4)	2.683(2)	167(4)
OW1–H(1D)...OW9#3	0.76(3)	2.06(3)	2.823(3)	176(3)
OW2–H(2C)...OW6#4	0.97(4)	1.98(4)	2.944(3)	168(3)
OW2–H(2D)...OW9#5	0.88(3)	1.94(3)	2.816(3)	170(3)
OW4–H(4D)...O(11)#6	0.78(3)	1.97(3)	2.736(3)	167(3)
OW4–H(4C)...OW1#1	0.82(4)	2.17(4)	2.981(3)	171(3)
OW5–H(5C)...O(12)#7	0.68(3)	2.00(3)	2.678(3)	171(4)
OW5–H(5D)...OW11#8	0.88(4)	1.88(4)	2.751(3)	169(3)
OW6–H(6C)...O(2)	0.81(3)	2.01(3)	2.795(2)	161(3)
OW6–H(6D)...OW11#8	0.89(4)	1.80(4)	2.682(3)	170(4)
OW7–H(7D)...O(7)#9	0.94(4)	1.82(4)	2.716(3)	158(3)
OW7–H(7C)...O(7)#5	0.85(4)	1.92(4)	2.768(3)	176(3)
OW8–H(8C)...O(12)#10	0.81(4)	2.16(4)	2.963(3)	170(4)
OW9–H(9D)...O(4)#3	0.79(4)	2.26(4)	2.968(3)	149(4)
OW9–H(9C)...O(12)	0.94(4)	1.73(4)	2.656(3)	168(3)
OW10–H(10D)...O(5)#11	0.88(4)	1.89(4)	2.752(3)	166(4)
OW10–H(10C)...O(5)#12	0.86(4)	1.94(4)	2.793(3)	174(4)
OW11–H(11D)...O(11)	0.92(4)	1.80(4)	2.706(3)	167(3)
OW11–H(11C)...OW4#12	0.71(3)	2.28(3)	2.973(3)	166(3)
O(3–H(3)...O(4)#10	0.71(4)	1.78(4)	2.459(2)	158(5)
O(6)–H(4)...OW7	0.82(3)	1.75(3)	2.535(3)	160(3)
O(8)–H(6)...OW10	0.66(3)	1.91(3)	2.551(3)	165(4)
O(10)–H(5)...O(9)#13	0.78(4)	1.77(4)	2.547(2)	179(4)
N(1)–H(1)...OW6#13	0.91(3)	1.91(3)	2.775(3)	157(2)
N(2)–H(2)...OW8	0.85(3)	2.02(3)	2.788(3)	150(3)

Symmetry transformations used to generate equivalent atoms: #1) $-x+2, -y, -z+2$; #2) $-x+2, -y-1, -z+2$; #3) $-x+1, -y, -z+3$; #4) $-x+3, -y, -z+2$; #5) $-x+2, -y, -z+3$; #6) $x, y, z-1$; #7) $x+1, y, z-1$; #8) $-x+2, -y-1, -z+3$; #9) $x, y+1, z$; #10) $x+1, y, z$; #11) $x, y-1, z$; #12) $-x+1, -y-1, z+3$; #13) $x-1, y, z$.

and 934 cm^{-1}. The corresponding stretching (2952–2850 cm^{-1}) and bending (1473–1185 cm^{-1}) vibrations of CH_2 groups have also been detected.

Experimental

Elemental analyses were carried out on a Perkin-Elmer 2400 CHN analyzer instrument. The FT-IR spectra were recorded from KBr pellets in range 4000-400 cm^{-1} on a Mattson Alpha-Centauri spectrometer.

Synthesis of H_8L: H_8L was prepared by a Mannich type reaction according to the procedures previously described.[16] Hexamethylendiamine (0.025mol) was mixed with concentrated hydrochloric acid (10ml), deionized water (10ml), and phosphorous acid (0.10mol). The mixture was allowed to reflux at 125°C for 1 h, then paraformaldehyde (0.20mol) was added in small portions over a period of 1 h, and the mixture was then refluxed for 2 h. Removal of solvent afforded white powder of H_8L.

Synthesis of $[Co(H_2O)_6][Co(H_2O)_4(H_6L)_2]\cdot 12H_2O$ (**1**) : A mixture of $Na_2(H_6L)$ and $Co(NO_3)$ $\cdot 6$ H_2O with a molar ratio of 1:1 in water was stirred at room temperature for 30 min. A couple of days later, pink crystals grew out of the solution by slow evaporation. The crystals were collected by filtration and dried in air. Anal. Calcd. for $[Co(H_2O)_6][Co(H_2O)_4(H_6L)_2]\cdot 12H_2O$: C 16.07, H 6.47, N 3.75. Found: C 16.00, H 6.50, N 3.80%.

Crystal data (**1**): Single-crystal X-ray diffraction data were recorded on a Rigaku RAXIS-RAPID image plate diffractometer using ω scan technique with MoK_α radiation ($\lambda = 0.71073$Å). Absorption corrections were applied using multi-scan technique.[17] The structure was solved with Direct Method of SHELXS-97[18] and refined with full-matrix least-squares techniques using the SHELXL-97 program[19] within WINGX.[20] All non-hydrogen atoms were refined with anisotropic temperature parameters. Crystal size $0.106\times0.329\times0.271 mm^3$, $T = 293(2)$ K, $C_{20}H_{96}Co_2N_4O_{46}P_8$, $Mr = 1494.63$, triclinic, P-1, $a = 7.6729(15)$ Å, $b = 11.701(2)$ Å, $c = 17.485(4)$ Å, $\alpha = 98.92(3)°$, $\beta = 92.95(3)°$, $\gamma = 102.23(3)°$; $V = 1509.9(5)$ $Å^3$, $Z = 1$, 12706 measured reflections, of which 6077 were unique ($R_{int} = 0.0226$); R values ($I > 2\sigma(I)$): $R1 = 0.0265$, $wR2 = 0.0750$, all data: $R1 = 0.0367$, $wR2 = 0.0880$, $-0.432 < \Delta\rho < 0.462$ $eÅ^{-3}$. Crystallographic data for the structure reported in this paper have been deposited with the CCDC (12 Union Road, Cambridge, CB2 1EZ, UK) and are available on request, quoting deposition number CCDC-233532.

Received 3 May 2004; accepted 24 May 2004
Paper 04/2501

References

1 B.Z. Wan, R.G. Anthony and G.Z. Peng, A. Clearfield, *J. Catal.*, 1986, **101**, 19.
2 G. Cao, H. Hong and T.E. Mallouk, *Acct. Chem. Res.*, 1992, **25**, 420.
3 M.E. Thompson, *Chem. Mater*., 1994, **6**, 1168.
4 J.D. Wang, A. Clearfield and G.Z. Peng, *Mater. Chem. Phys.*,1993, **35**, 208.
5 A. Clearfield, *Curr. Opin. Solid State Mater. Sci.*, 1996, **1**, 268.
6 A. Clearfield, Metal phosphonate chemistry. In *Progress in Inorganic Chemistry*, ed K.D. Karlin, John Wiley & Sons, New York, 1998. Vol. **47**, pp. 371.
7 G. Alberti and U. Costantino, In *Comprehensive Supramolecular Chemistry*, ed J.M. Lehn, Pergamon-Elsevier Science Ltd, London, 1996. pp. 151.
8 N. Stock and T. Bein, *Angew. Chem. Int. Ed.*, 2004, **43**, 749.
9 E.V. Bakhmutova, X. Ouyang, D.G. Medvedev and A. Clearfield, *Inorg. Chem*., 2003, **42**, 7046.
10 H. Jankovics, M. Daskalakis, C.P. Raptopoulou, A. Terzis, V. Tangoulis, J. Giapintzakis, T. Kiss and A. Salifoglou, *Inorg. Chem*., 2002, **41**, 3366.
11 L. Kryger and S.E. Rasmussen, *Acta Chem. Scand*., 1972, **26**, 2349.
12 T. Glowiak, W. Sawka-Dobrowolska and B. Jezowska-Trzebiatowska, *Inorg. Chim. Acta*, 1980, **45**, L105.
13 V.S. Sergienko, G.G. Aleksandrov and E.G. Afonin, Zh. Neorg. Khim., 1997, **42**, 1291.
14 A. Clearfield, Metal phosphonate chemistry. In *Progress in Inorganic Chemistry*; Karlin, K.D., Ed.; John Wiley & Sons: New York, 1998; Vol. **47**, pp. 371-510 and references therein.
15 C. Lei, J.-G. Mao, Y.-Q. Sun, H.-Y. Zeng and A. Clearfield, *Inorg. Chem*., 2003, 2003, **42**, 6157.
16 K. Moedritzer and R.R. Irani, *J. Org. Chem.*, 1966, **31**, 1603.
17 T. Higashi, A Program for Absorption Correction, Rigaku Corporation, Tokyo, Japan, 1995.
18 G.M. Sheldrick, SHELXS-97, A Program for Automatic Solution of Crystal Structure, University of Goettingen, Germany, 1997.
19 G.M. Sheldrick, SHELXL-97, A Program for Crystal Structure Refinement, University of Goettingen, Germany, 1997.
20 J. Farrugia, WINGX, A Windows Program for Crystal Structure Analysis, University of Glasgow, Glasgow, UK, 1988.