

## COMMUNICATION

SYNTHESES AND CRYSTAL STRUCTURES OF COBALT(II)  
COMPLEXES WITH PIPERAZINE-1,4-  
DIYLBIS(METHYLENE)BIS(PHOSPHINIC) ACIDIVAN LUKEŠ,\* IVANA ČÍSAŘOVÁ, PAVEL VOJTÍŠEK and  
KONSTANTINOS BAZAKASDepartment of Inorganic Chemistry, Charles University, Albertov 2030, 128 40 Prague 2,  
Czech Republic

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**Abstract**—The synthesis of compounds of piperazine-1,4-diylbis(methylene)bis(phosphinic) acid ( $H_2L$ ) (**1**) with  $Co^{II}$  is described and the X-ray structures of the isolated complexes  $[Co(H_2L)_3](ClO_4)_2 \cdot 2H_2O$  (**2**) and  $[Co(H_2O)_6]L$  (**3**), have been determined. Compound **2** forms a three-dimensional polymeric network of cobalt atoms bridged by **1**, which is monodentately coordinated to cobalt through the phosphinate groups. The nitrogen atoms are protonated and non-coordinated. In **3**, **1** is deprotonated and forms non-coordinated anions and the octahedral coordination sphere of the cobalt atoms consists of water molecules.

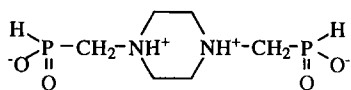
Aminoalkylphosphinic acids are the phosphorus analogues of the better known amino carboxylic acids. Interest in these substances is increasing, similarly to aminoalkylphosphonic acids, because of their biological activity, use in analytical chemistry and in studying their azacycles.<sup>1</sup> Since these applications generally involve complexation with metal ions, the complexing abilities of the  $>NCH_2-P(R)O_2H$  moiety have been studied in solution<sup>2,3</sup> and in the solid state.<sup>4-8</sup>

The structures of the complexes prepared were determined mostly for the complexes with amino-methylene(methylphosphinic) acid. On the basis of the X-ray structural data for complexes with  $H_2NCH_2P(CH_3)O_2^-$ , we found several possibilities

for coordination of **1**. The simplest form, monomers with the phosphinate monodentately coordinated and N atoms protonated, was observed in  $[MnCl_2\{NH_3^+CH_2P(CH_3)O_2^-\}(H_2O)_2]$ .<sup>4</sup> The dimeric form was found for  $[CuCl_2\{NH_3^+CH_2P(CH_3)O_2^-\} \cdot (H_2O)_2]$  with two O—P—O bridges connecting two copper atoms.<sup>5</sup> The analogous complexes  $[ZnCl_2\{NH_3^+CH_2P(CH_3)O_2^-\}]$ <sup>6</sup> and  $[MnBr_2(NH_3^+CH_2P(CH_3)(O)O)_2(H_2O)_2]$ <sup>7</sup> form infinite Zn—O—P—O—Zn or Mn—O—P—O—Mn polymeric chains. Coordination of the amino group was found<sup>8</sup> only in  $[Cu_2Cl_2\{NH_2CH_2P(CH_3)O_2\}_2]$  and phosphinates again formed O—P—O bridges connecting two copper atoms.

The present paper compares potentiometrically

determined species<sup>2</sup> in aqueous solution of **1** and Co<sup>II</sup> with the structure\* of the compounds that were isolated from solution.†



piperazine-1,4-diylbis(methylene)phosphinic acid, **1**

An earlier potentiometric study<sup>2</sup> showed that Co<sup>II</sup> forms diprotonated complexes, with **1** with a metal : ligand molar ratio of 1 : 2 [ $\log \beta_{122} = 15.9(4)$ ] and also complexes with a molar ratio of 1 : 1 [ $\log \beta_{110} = 1.72(4)$ ] in a narrow pH region from 3 to 6.5. The abundance of the 1 : 2 species was highest at a pH of about 4.5 (50%) and of the 1 : 1 species at a pH of about 6.5 (30%). A precipitate formed at about pH 7.

On the basis of these results, we tried to isolate both the compounds from solutions of the appropriate pH values. The product  $[\text{Co}(\text{H}_2\text{L})_3](\text{ClO}_4)_2 \cdot 2\text{H}_2\text{O}$  (**2**) crystallized from a solution of pH 4.2, and a product with the composition  $[\text{Co}(\text{H}_2\text{O})_6]\text{L}$  (**3**), where H<sub>2</sub>L is **1**, was isolated from the solution of pH 6.5.

\* Measurements were made on the Syntex P2<sub>1</sub> (**2**) and CAD4 MACH 3 (**3**) four-circle diffractometers with graphite crystal monochromated Mo-K<sub>α</sub> radiation  $\lambda = 0.71073$ . Crystal data:  $\text{Co}(\text{P}_2\text{N}_2\text{O}_4\text{C}_6\text{H}_{16})_3(\text{ClO}_4)_2 \cdot 2\text{H}_2\text{O}$ , **2**,  $M_r = 1020.3$ , monoclinic space group  $P2_1/c$  (no. 14),  $a = 11.256(3)$ ,  $b = 9.408(2)$ ,  $c = 20.164(6)$  Å,  $\beta = 111.04(3)^\circ$ ,  $U = 1993.0(4)$  Å<sup>3</sup>,  $F(000) = 1058$ ,  $\mu(\text{Mo-K}_\alpha) = 0.893$  mm<sup>-1</sup>,  $Z = 2$ ,  $D_{\text{calc.}} = 1.700$  g cm<sup>-3</sup>. Data were collected in range  $\theta = 0-32^\circ$ . Final  $R = 0.066$ , ( $R_w = 0.074$ ) for 5900 independent reflections with  $I/\sigma(I) > 2$  without correction for absorption.

$\text{Co}(\text{P}_2\text{N}_2\text{O}_4\text{C}_6\text{H}_{14}) \cdot 6\text{H}_2\text{O}$ , **3**,  $M_r = 407.2$ , triclinic space group  $P1$ ,  $a = 6.0404(5)$ ,  $b = 7.4808(3)$ ,  $c = 9.5781(5)$  Å,  $\alpha = 96.645(4)$ ,  $\beta = 107.201(6)$ ,  $\gamma = 99.443(5)^\circ$ ,  $U = 401.60(5)$  Å<sup>3</sup>,  $F(000) = 213$ ,  $\mu(\text{Mo-K}_\alpha) = 1.305$  mm<sup>-1</sup>,  $Z = 1$ ,  $D_{\text{calc.}} = 1.683$  g cm<sup>-3</sup>. Data were collected in the range  $\theta = 0-28^\circ$ . Final  $R = 0.022$ , ( $R_w = 0.036$ ) for 1692 independent reflections with  $I/\sigma(I) > 3$  without correction for absorption.

† Compound **1** was prepared by the procedure described in our previous paper.<sup>2</sup> Complex **2** crystallized from an aqueous solution of 1 g **1** (3.59 mmol) and 0.43 g  $\text{Co}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$  (1.19 mmol) in 10 cm<sup>3</sup> of H<sub>2</sub>O (pH = 4.2) after a few days. The same solution composition was used for the preparation of **3**, only the pH value was shifted to 6.5, by addition of an NaOH solution. Satisfactory elemental analyses were obtained for these compounds.

The crystal structure of **2** is shown in Fig. 1. The coordination sphere of the Co atom is approximately octahedral and is formed by six oxygen atoms of phosphinate groups. Each oxygen atom comes from a different ligand molecule. Nitrogen atoms are protonated and are not coordinated. The distances of Co<sup>II</sup> to the axial oxygen atoms Co—O(21) of 2.128(4) Å are longer than that to the equatorial atoms Co—O(11), Co—O(31) of 2.094(4) and 2.093(4) Å.

The coordination around the phosphorus atom is similar to that found for piperidinomethylphosphinic acid (**4**) (approximately the same bond

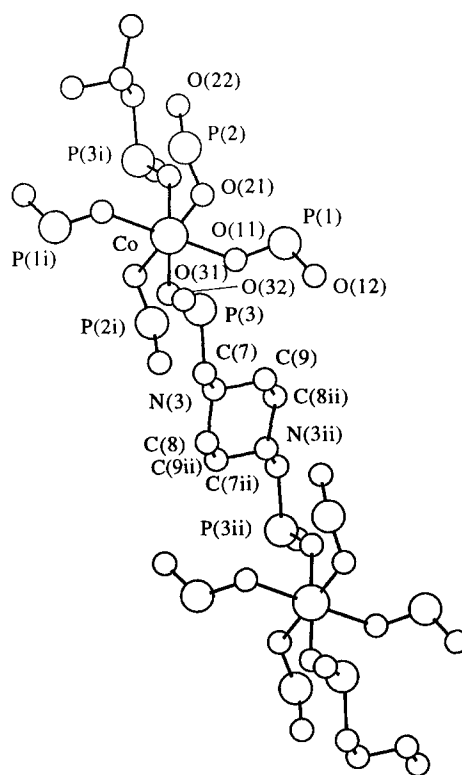


Fig. 1. Molecular structure and labelling scheme for  $[\text{Co}(\text{H}_2\text{L})_3](\text{ClO}_4)_2 \cdot 2\text{H}_2\text{O}$ . Selected bond lengths (Å) and angles ( $^\circ$ ): Co—O(11) 2.094(4), Co—O(21) 2.128(4), Co—O(31) 2.093(4), P(1)—O(11) 1.513(4), P(1)—O(12) 1.503(4), P(2)—O(21) 1.487(4), P(2)—O(22) 1.511(4), P(3)—O(31) 1.497(4), P(3)—O(32) 1.496(4), P(1)—C(1) 1.818(3), P(2)—C(2) 1.838(3), P(3)—C(7) 1.828(3), P(1)—H(1p) 1.24(7), P(2)—H(2p) 1.30(5), P(3)—H(3p) 1.30(7), O(31)—Co—O(11) 89.9(2), O(21)—Co—O(11) 93.1(2), O(31)—Co—O(21) 89.0(2), Co—O(11)—P(1) 127.1(1), Co—O(21)—P(2) 130.4(1), Co—O(31)—P(3) 134.2(2), O(12)—P(1)—O(11) 119.2(2), O(22)—P(2)—O(21) 118.4(2), O(32)—P(3)—O(31) 118.9(2), C(1)—P(1)—O(11) 108.3(1), C(1)—P(1)—O(12) 103.9(1), C(2)—P(2)—O(21) 111.5(1), C(2)—P(2)—O(22) 101.5(1), C(7)—P(3)—O(31) 106.3(1), C(7)—P(3)—O(32) 105.8(1).

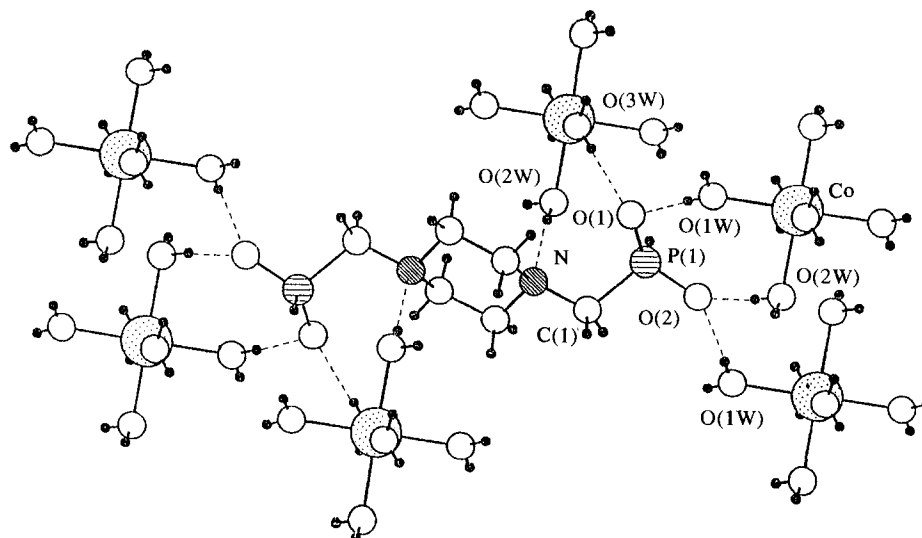


Fig. 2. Molecular structure and labelling scheme for  $[\text{Co}(\text{H}_2\text{O})_6]\text{L}$ . Selected bond lengths ( $\text{\AA}$ ) and angles ( $^\circ$ ): Co—O(1W) 2.035(1), Co—O(2W) 2.113(1), Co—O(3W) 2.145(1), P—O(1) 1.504(1), P—O(2) 1.502(1), P—H(p) 1.22(2), P—C(1) 1.816(2), C(1)—N 1.472(2), O(1W)—Co—O(2W) 90.37(5), O(1W)—Co—O(3W) 92.54, O(1)—P—O(2) 116.7(1), O(1)—P—C(1) 111.9 (1), O(2)—P—C(1) 108.2(1).

angles)<sup>2</sup> and significantly departs from regular tetrahedral. Comparison of the P—O distances for the coordinated and non-coordinated O atoms of the different phosphinates (there are three) in a single molecule shows that the P—O<sub>coor</sub> bonds are longer for phosphinates coordinated in the equatorial positions at a P(1) [P(1)—O(11) distance of 1.513(4)  $\text{\AA}$ ] or comparable at a P(3) [P(3)—O(31) distance of 1.497(4)  $\text{\AA}$ ] with non-coordinated P—O bonds [P(1)—O(12) and P(3)—O(32) distances of 1.503(4) and 1.496(4)  $\text{\AA}$ ]. For the axially coordinated phosphinates, this relation is reversed, and the P(2)—O(21) distance of 1.487(4)  $\text{\AA}$  is shorter than the non-coordinated P(2)—O(22) distance of 1.511(4)  $\text{\AA}$ , pointing to weakness of the Co—O<sub>ax</sub> bond.

The Co atoms are bridged by **1**, two molecules of ligand along the *y* axis and one molecule along the *x* axis (see Fig. 1) and, thus, a polymeric network is formed through the organic part of the ligands. This is in contrast with the previously characterized polymeric complexes of aminoalkyl-phosphinic acids where the bridging occurs through bidentate phosphinate groups.<sup>6,7</sup> This formation of a polymeric structure is similar to the polymeric chain of Cd<sup>II</sup> atoms bridged by phosphonic analogues of **1**.<sup>9</sup> The piperazine ring has a chair conformation and the amine groups are protonated.

The structure is stabilized by the network of hydrogen bonds. Perchlorate anions are not involved in the hydrogen bond network. The anions

are disordered, and therefore, a model involving their rotation around one Cl—O was used.

The molecule structure of **3** is shown in Fig. 2. In spite of the deprotonated phosphinic and amino groups, **1** is not coordinated to cobalt. The approximately octahedral coordination sphere of cobalt is formed by oxygen atoms from six water molecules. The inversion centre at the cobalt atom gives three different Co—O bonds, the Co—O(1W) distance of 2.035(1)  $\text{\AA}$  is considerably shorter than the Co—O(2W) distance of 2.113(1)  $\text{\AA}$  and Co—O(3W) distance of 2.145(1)  $\text{\AA}$ .

The piperazine ring of **3** retains the chair conformation as was found for **2**, and is not protonated. In the piperazine ring, the structure has a second crystallographic inversion centre. Both the phosphinic groups are also not protonated, and the P—O(1) and P—O(2) distances are the same, 1.504(1) and 1.502(1)  $\text{\AA}$ .

As is shown in Fig. 2, phosphinates are connected with the water molecules coordinated via hydrogen bonds with an O $\cdots$ O distance of about 2.71  $\text{\AA}$ . The deprotonated nitrogen atom is connected to the co-ordinated water molecule with an N $\cdots$ O(2W) distance of 2.808(2)  $\text{\AA}$ .

As was mentioned above, the formation constants found indicate that the complexing ability of **1** for cobalt (II) is very low. The values of Jorgensen parameter calculated from the absorption spectra point to the fact that the complexing ability of **1** for cobalt(II), nickel(II) and copper(II) may be very

close to the value of water.<sup>10</sup> Thus, the lattice energy and stabilization by the network of hydrogen bonds and consequently lower solubility determine the crystallization of both the solids from the solutions. Nevertheless, the chelating system of the amine group and the phosphinate close to the  $[\text{Co}(\text{H}_2\text{O})_6]^{2+}$  species is a surprising result of structure **3**.

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