Inorg. Chem. **2002**, *41*, 3366–3374

Inorganic Chemistry
Article

Synthesis and Structural and Spectroscopic Characterization of a Complex between Co(II) and Imino-bis(methylphosphonic acid): Gaining Insight into Biologically Relevant Metal–Ion Phosphonate Interactions or Looking at a New Co(II)–Organophosphonate Material?

H. Jankovics,[†,‡] M. Daskalakis,[†] C. P. Raptopoulou,[§] A. Terzis,[§] V. Tangoulis,[||] J. Giapintzakis,[⊥] T. Kiss,[‡] and A. Salifoglou*[,†]

Department of Chemistry, University of Crete, Heraklion 71409, Greece, Biocoordination Chemistry Research Group of the Hungarian Academy of Sciences, Department of Inorganic and Analytical Chemistry, University of Szeged, Szeged, H-6720, Hungary, Institute of Materials Science, NCSR "Demokritos", Aghia Paraskevi 15310, Attiki, Greece, Department of Materials Science, University of Patras, Patras 26500, Greece, and Institute of Electronic Structure and Laser, Foundation for Research and Technology-Hellas, Heraklion 71110, Greece

Received October 8, 2001

Cobalt is an essential metal ion involved in key biomolecules, regulating processes in human physiology. As a metal ion, Co(II) assumes forms, which are dictated by the nature of organic binders in biological fluids, and the conditions under which metal ion ligand interactions arise. Among the various low molecular mass metal ion binders in biological fluids are amino acids, organic acids, as well as their variably phosphorylated forms. As a representative metal ion binder, the organophosphonate ligand $H_2O_3P–CH_2–NH_2^+–CH_2–PO_3H^-$ was employed in aqueous reactions with Co(II), ultimately leading to the isolation of complex $[Co(C_2H_8O_6NP_2)_2(H_2O)_2]$ (**1**) at pH 2. The complex was characterized analytically, spectroscopically (FTIR, UV–vis, EPR), and magnetically. Compound **1** crystallizes in the monoclinic space group $P2_1/n$, with $a = 7.361(3)$ Å, $b = 8.133(3)$ Å, $c = 14.078(5)$ Å, $\beta = 104.40(1)°$, $V = 816.3(5)$ Å^3, and $Z = 2$. X-ray crystallography reveals that **1** is a compound with a molecular type of lattice. In it, there exist mononuclear octahedral sites of Co(II) surrounded by oxygens, belonging to terminal phosphonates and bound water molecules. Both ends of the ligand zwitterionic form are involved in binding to adjacent Co(II) ions, thus creating tetranuclear 32-membered rings, with cavities extending in two dimensions and holes in the third dimension throughout the lattice of **1**. Similar structural features were observed in other metal organophosphonate lattices of potential catalytic and chemical reactivity. The magnetic and EPR data on **1** support the presence of a high-spin octahedral Co(II) in an oxygen environment, having a ground state with an effective spin $S = {}^1/_2$. The solution UV–vis and EPR data suggest retention of the high-spin octahedral Co(II) ion, consistent with the magnetization measurements on **1**. Collectively, the data reflect the existence of a soluble Co(II)–iminodiphosphonate species not unlike those expected in biological fluids containing the specific ligand or ligands similar to that. Both biologically relevant perspectives and a synthetic outlook into Co(II)–organophosphonate materials are discussed.

Introduction

The significance of cobalt in human physiology has since long been recognized. As a metal cofactor, cobalt enters key biomolecules, such as B_{12} coenzyme and vitamin B_{12}, and establishes the role of a regulator in a number of biological processes.[1–4] Equally significant, cobalt-dependent biomol-

---

* To whom correspondence should be addressed. E-mail: salif@chemistry.uoc.gr. Phone: +30-81-0393-652. Fax: +30-81-0393-601.
[†] University of Crete.
[‡] University of Szeged.
[§] NCSR "Demokritos".
[||] University of Patras.
[⊥] Foundation for Research and Technology-Hellas.

(1) Taylor, D. M.; Williams, D. R. In *Trace Element Medicine and Chelation Therapy*; Royal Society of Chemistry: Cambridge, U.K., 1995.
(2) Balachandran, S.; Vishwakarma, R. A.; Monaghan, S. M.; Prelle, A.; Stamford, N. P. J.; Leeper, F. J.; Battersby, A. R. *J. Chem. Soc., Perkin Trans.* **1994**, *1*, 487–491.
(3) Battersby, A. R. *Acc. Chem. Res.* **1993**, *26*, 15–21.

10.1021/ic011033y CCC: $22.00

ecules involved in bioprocesses include metallohydrolases such as methionine aminopeptidase,[5] nitrile hydratases,[6] ribonucleotide reductase, glutamate mutase, and others.[7] Moreover, absence or deficit of cobalt could be a cause for a number of physiological aberrations, such as pernicious anemia.[8] In fact, in the case of anemia, it was recognized early that cobalt carrying vitamin B_{12} deficiency was the culprit of the symptomatology. In the extreme case of exposure of the human body to large amounts of cobalt, the consequences are dire, resulting in toxic effects manifested in heart disease and excessive formation of red corpuscles.[9,10]

Essential to the participation of cobalt as a metal cofactor in biomolecules is the existence of soluble, bioavailable forms of that metal ion in human fluids. Because both high molecular mass as well as low molecular mass molecules exist with potential binding properties toward metal ions, it is likely that interactions with both types of moieties take place with Co(II).[2,3,6,7] Among the potential Co(II) low molecular mass binders in such fluids are organic acids, amino acids, small peptides, and molecules, like the ones mentioned previously, possessing phosphonate moieties.[11] The latter groups characterize biological sites in small molecules and proteins or enzymes with key roles in signal transduction, enzyme inhibition, neuroactivity, plant growth regulation, antibiotic, and herbicidal activity.[11,12] A wide class of molecules containing such phosphonate moieties includes organophosphonates.

Furthermore, genuine interest in organophosphonates has been developed over the years, primarily because of their versatile coordination chemistry with various metal ions.[13] Variable nuclearity[14] and linear one-dimensional compounds[15] as well as layered metal organophosphonates[16] have been synthesized. These materials have been found to exhibit interesting reactivity properties, which could render them useful for practical applications in catalysis, ion exchange, intercalation chemistry, film preparation with optical properties, and others.[17,18]

Despite the research activity in the field of metal organophosphonate chemistry, significant aspects of the relevant chemistry (including that of Co(II))[19] have yet to be discovered. Being cognizant of the significance of the nature of X, in $H_2O_3P-X-PO_3H_2$, in dictating the structural properties of the final structure and hence its potential chemical (intercalation, catalytic, etc.) and biological properties, we launched research efforts targeting the reactivity of one such class of diphosphonic ligands containing $X = NR'$ ($R' = H$) toward cobalt(II). Concurrently, use of $H_2O_3P-CH_2-NH_2^+-CH_2-PO_3H^-$ exemplifies quite well structural attributes of phosphonic analogues of amino acids, for which structurally characterized complexes with Co(II) in aqueous media are limited. Toward this end, we report herein the synthesis, isolation, and spectroscopic and structural characterization as well as magnetic and EPR studies of a new species between cobalt(II) and the diphosphonate ligand imino-bis(methylphosphonic acid).

Experimental Section

Materials and Methods. All experiments were carried out in the open air, at room temperature. Nanopure quality water was used for all reactions. $Co(NO_3)_2 \cdot 6H_2O$, and imino-bis(methylphosphonic acid) (H_4IDA2P), were purchased from Aldrich. KOH, NaOH, and ammonia were supplied by Fluka.

Physical Measurements. FTIR measurements were taken on a Perkin-Elmer 1760X FTIR spectrometer. UV−vis spectra were recorded on a Hitachi U-2001 spectrophotometer in the 200−1000 nm range. The EPR spectra of complex **1** in the solid state and in aqueous solutions were recorded on a Bruker ER 200D-SRC X-band spectrometer, equipped with an Oxford ESR 9 cryostat at 9.174 GHz, 10dB, and at 4 K. Magnetic susceptibility data were collected on powdered samples of **1** with a Quantum Design SQUID susceptometer in the 1.7−260 K temperature range, under various applied magnetic fields. Magnetization measurements were carried out at three different temperatures in the field range 0−7 T. Elemental analyses were performed by Quantitative Technologies, Inc.

---

(4) Debussche, L.; Couder, M.; Thibaut, D.; Cameron, B.; Crouzet, J.; Blanche, F. *J. Bacteriol.* **1992**, *22*, 7445−7451.

(5) (a) Roderick, S. L.; Matthews, B. W. *Biochemistry* **1993**, *32*, 3907−3912. (b) Ben-Bassat, A.; Bauer, K.; Chang, S.-Y.; Myambo, K.; Boosman, A.; Chang, S. *J. Bacteriol.* **1987**, *169*, 751−757.

(6) Payne, M. S.; Wu, S.; Fallon, R. D.; Tudor, G.; Stieglitz, B.; Turner, I. M., Jr.; Nelson, M. J. *Biochemistry* **1997**, *36*, 5447−5454.

(7) Lippard, S. J.; Berg, J. M. In *Principles of Bioinorganic Chemistry*; University Science Books: Mill Valley, CA, 1994; Chapter 11, pp 336−347.

(8) Hamilton, E. M. N.; Gropper, S. A. S. In *The Biochemistry of Human Nutrition*; West Publishing Company: New York, 1987; pp 298−301.

(9) Helis, H. M.; de Meester, P.; Hodgson, D. J. *J. Am. Chem. Soc.* **1977**, *99*, 3309−3312.

(10) Waldbott, G. L. In *Health Effects of Environmental Pollutants*; Mosby, Inc.: St. Louis, MO, 1973.

(11) (a) Kiss, T. In *Biocoordination Chemistry*; Burger, K., Ed.; Ellis Horwood: Chichester, U.K., 1990; p 56. (b) Martin, R. B. *J. Inorg. Biochem.* **1986**, *28*, 181−187. (c) May, P. M.; Linder, P. W.; Williams, D. R. *J. Chem. Soc. Dalton Trans.* **1977**, 588−595. (d) Perrin, D. D.; Agarwal, R. P. In *Metal Ions in Biological Systems*; Sigel, H., Ed.; Marcel Dekker: New York, 1973; Vol. 2, p 168. (e) Perrin, D. D. *Nature* **1965**, *206*, 170.

(12) (a) Sanna, D.; Bodi, I.; Bouhsina, S.; Micera, G.; Kiss, T. *J. Chem. Soc., Dalton Trans.* **1999**, 3275−3282. (b) Kafarski, P.; Mastalerz, P. *Beitr. Wirkstofforsch.* **1984**, *21*, 1.

(13) (a) Zubieta, J. *Comments Inorg. Chem.* **1994**, *16*, 153−183. (b) Bhardwaj, C.; Hu, H.; Clearfield, A. *Inorg. Chem.* **1993**, *32*, 4294−4299. (c) Clearfield, A. *Comments Inorg. Chem.* **1990**, *10*, 89−128.

(14) (a) Chen, Q.; Salta, J.; Zubieta, J. *Inorg. Chem.* **1993**, *32*, 4485−4486. (b) Clarke, E. T.; Rudolph, P. R.; Martell, A. E.; Clearfield, A. *Inorg. Chim. Acta* **1989**, *164*, 59−63. (c) Rudolph, P. R.; Clarke, E. T.; Martell, A. E.; Clearfield, A. *J. Coord. Chem.* **1985**, *14*, 139−149.

(15) Bujoli, B.; Palvadeau, P.; Rouxel, J. *Chem. Mater.* **1990**, *2*, 582−589.

(16) (a) Zhang, Y.; Clearfield, A. *Inorg. Chem.* **1992**, *31*, 2821−2826. (b) Huan, G. H.; Jacobson, A. J.; Johnson, J. W.; Corcoran, E. W., Jr. *Chem. Mater.* **1990**, *2*, 91−93. (c) Cao, G.; Lee, H.; Lynch, V.; Mallouk, T. E. *Inorg. Chem.* **1988**, *27*, 2781−2785.

(17) (a) Burwell, D. A.; Valentine, K. G.; Timmermans, J. H.; Thompson, M. E. *J. Am. Chem. Soc.* **1992**, *114*, 4144−4150. (b) Rosenthal, G. L.; Caruso, J. *Inorg. Chem.* **1992**, *31*, 3104−3106. (c) Dines, M. B.; Griffith, P. C. *Inorg. Chem.* **1983**, *22*, 567−569. (d) Dines, M. B.; DiGiacomo, P. M. *Inorg. Chem.* **1981**, *20*, 92−97.

(18) (a) Byrd, H.; Pike, J. K.; Talham, D. R. *J. Am. Chem. Soc.* **1994**, *116*, 7903−7904. (b) Katz, H. E.; Wilson, W. L.; Scheller, G. *J. Am. Chem. Soc.* **1994**, *116*, 6636−6640. (c) Ungashe, S. B.; Wilson, W. L.; Katz, H. E.; Scheller, G. R.; Putrinski, T. M. *J. Am. Chem. Soc.* **1992**, *114*, 8717−8719. (d) Wang, R.-C.; Zhang, Y.; Hu, H.; Frausto, R. R.; Clearfield, A. *Chem. Mater.* **1992**, *4*, 864−871. (e) Rosenthal, G. L.; Caruso, J. *Inorg. Chem.* **1992**, *31*, 144−145.

(19) (a) Cao, G.; Mallouk, T. E. *Inorg. Chem.* **1991**, *30*, 1434−1438. (b) Frink, K. J., Wang, R.-C.; Colon, J. L.; Clearfield, A. *Inorg. Chem.* **1991**, *30*, 1438−1441.

Table 1. Summary of Crystal, Intensity Collection and Refinement Data for $[Co(C_2H_8O_6NP_2)_2(H_2O)_2]$ (**1**)

	1
empirical formula	$C_4H_{20}N_2O_{14}P_4Co$
fw	503.03
T, °C	25
wavelength, λ (Å)	Mo Kα 0.71073
space group	$P2_1/n$
a (Å)	7.361(3)
b (Å)	8.133(3)
c (Å)	14.078(5)
α, deg	
β, deg	104.40(1)
γ, deg	
V, (Å^3)	816.3(5)
Z	2
ρ_{calcd}/ρ_{obsd} (g/cm^3)	2.047/2.040
abs coeff (μ), mm^{-1}	1.520
R^a	0.0303^b
$R_w{}^a$	0.0821^b

[a] R values are based on F values, R_w values are based on F^2; $R = [\sum||F_o| - |F_c||]/\sum(|F_o|)$, $Rw = (\sum[w(F_o^2 - F_c^2)^2]/\sum[w(F_o^2)^2])^{1/2}$. [b] For 1297 reflections with $I > 2\sigma(I)$.

Preparation of Complex. (a) $[Co(C_2H_8O_6NP_2)_2(H_2O)_2]$ (1). A sample of 0.23 g (0.79 mmol) of $Co(NO_3)_2{\cdot}6H_2O$ and 0.16 g (0.79 mmol) of imino-bis(methylphosphonic acid) were dissolved in nanopure water. The pH of the resulting solution was carefully raised to ~2 with 0.1 M KOH. The derived reaction mixture was stirred at room temperature overnight. On the following day, the solution was clear, and its color was pink. The volume of the reaction mixture was reduced by 50% through a rotary evaporation. The solution was filtered and allowed to stand at room temperature. A couple of days later, pink prismatic crystals grew out of the solution by slow evaporation. The crystalline material was collected by filtration and was dried under vacuum. Yield based on H_4IDA2P: 0.13 g (65.7%). Anal. Calcd for **1**, $[Co(C_2H_8O_6NP_2)_2(H_2O)_2]$ ($C_4H_{20}O_{14}N_2P_4Co$, MW = 503.03): C, 9.54; H, 3.98; N, 5.57. Found: C, 9.68; H, 4.03; N, 5.64.

(b) The same reaction was run in the presence of NaOH or ammonia solution, yielding morphologically identical pink prismatic crystals. The yields in these cases were 45.0% (NaOH) and 55.5% (ammonia). The FTIR of the crystals in conjunction with the X-ray unit cell determination of one of the single crystals isolated identified the material as complex **1**.

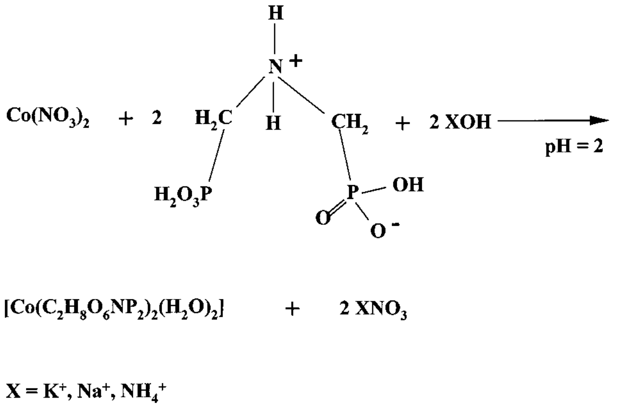
(c) The reaction outlined in (a) was also run with a metal to ligand stoichiometry of 1:2. In the presence of various alkali solutions and under identical conditions the reaction afforded, in comparative yields, pink prismatic crystals identical to those originally identified as complex **1**. The yields in these cases were 56.5% (KOH), 60.0% (NaOH), and 51.0% (ammonia). Positive identification was provided by FTIR spectroscopy in combination with X-ray crystallography.

X-ray Crystallography. Crystal Structure Cetermination. X-ray quality crystals of compound **1** were grown from aqueous solutions. A single crystal, with dimensions 0.10 × 0.15 × 0.40 mm^3 (**1**), was mounted on a Crystal Logic dual-goniometer diffractometer, using graphite monochromated Mo Kα radiation. Unit cell dimensions for **1** were determined and refined by using the angular settings of 25 automatically centered reflections in the range $11° < 2\theta < 23°$. Crystallographic details are given in Table 1. Intensity data were measured by using $\theta-2\theta$ scans. Throughout data collection, three standard reflections were monitored every 97 reflections and showed less than 2% variation and no decay. Lorentz, polarization, and ψ-scan absorption corrections were applied by using Crystal Logic software. Further experimental crystallographic details for **1**: $2\theta_{max} = 50°$; scan speed 4.0°/min; scan range $2.3 + \alpha_1\alpha_2$ separation; number of reflections collected/unique/used, 1497/1438 ($R_{int} = 0.0575$)/1438; 155 parameters refined; $F(000) = 514$; $(\Delta/\sigma)_{max} = 0.018$; $(\Delta\rho)_{max}/(\Delta\rho)_{min} = 0.731/-0.410$ e/Å^3; GOF = 1.042; R1/wR2 (for all data), 0.0342/0.0850.

The structure of complex **1** was solved by direct methods using SHELXS-86[20] and refined by full-matrix least-squares techniques on F^2 with SHELXL-97.[21] All non-H atoms in the structure of **1** were refined anisotropically. All H-atoms in the structure of **1** were located by difference maps and were refined isotropically.

Results

Synthesis. The synthesis of complex **1** was expediently carried out in the presence of simple reagents of Co(II) and imino-bis(methylphosphonic acid). The overall reaction leading to compound **1** is depicted schematically.



In all cases, the reaction was run in water. The initial metal to ligand stoichiometry employed was 1:1. The pH of the solution was critical for the outcome of the reactions run, following overnight stirring of the initial reaction mixture. Specifically, the pH was optimally adjusted to ~2 to avoid precipitation of powdery products. These observed precipitates redissolve only at higher pH values, around 6.5. Slow evaporation of the well-stirred reaction mixture overnight led to the precipitation of well-formed pink prismatic crystals. Elemental analysis on the crystalline material was consistent with the formulation $Co(C_2H_8O_6NP_2)_2(H_2O)_2$ for complex **1**.

All three alkalis used to adjust the pH (KOH, NaOH, and ammonia) were equally effective in providing the conditions, under which a pure crystalline product was isolated. The yields of all these reactions were in the range from 45% to 65%. Therefore, as it was later shown by X-ray crystallography, the role of the base was none other than adjusting the pH of the reaction mixture. No participation in the crystal lattice of the derived compound was found for the cation(s) of the different bases used. Further proof on that contention was provided by elemental analysis as well.

---

(20) Sheldrick, G. M. *SHELXS-86: Structure Solving Program*; University of Göttingen: Germany, 1986.

(21) Sheldrick, G. M. *SHELXL-97: Structure Refinement Program*; University of Göttingen: Germany, 1997.

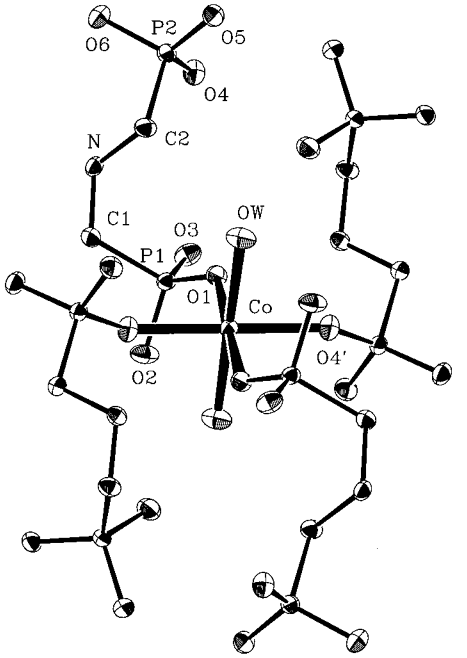


Figure 1. ORTEP structure of $[Co(C_2H_8O_6NP_2)_2(H_2O)_2]$ in **1**, along with the atom-labeling scheme. Thermal ellipsoids were drawn by ORTEP and represent 50% probability surfaces.

In an effort to investigate the reactivity of the Co(II)−H_4IDA2P system in aqueous solutions, reactions were also carried out employing metal to ligand stoichiometries of 1:2. Under identical experimental conditions, and in the presence of various alkalis (as in the case of the synthesis of complex **1**), a pink crystalline material was isolated. The yields of all these reactions were in the range from 51% to 60%. The crystalline product was shown by FTIR spectroscopy and X-ray crystallography to be identical to the one obtained from the reaction of Co(II) with H_4IDA2P, with a metal to ligand stoichiometry of 1:1. This result was a strong indication of the high stability of complex **1** present in the equilibria arising in the Co(II)−H_4IDA2P aqueous systems, and under different metal to ligand stoichiometries.

The isolated crystalline material **1** appears to be stable in the solid state for long periods of time, with no visible deterioration. Complex **1** is soluble in water and insoluble in alcohols (CH_3OH, *i*-PrOH), acetonitrile, and dimethyl sulfoxide (DMSO). Recrystallization of complex **1** from water proceeds easily and affords highly pure (by FTIR and X-ray unit cell determination) single crystalline material.

X-ray Crystallographic Structure. (a) $[Co(C_2H_8O_6NP_2)_2(H_2O)_2]$ (1). The X-ray crystal structure of **1** reveals the presence of a molecular lattice. The compound crystallizes in the monoclinic system $P2_1/n$. The ORTEP diagram of **1** is shown in Figure 1. Selected interatomic distances and bond angles for **1** are listed in Table 2. The structure consists of a mononuclear core unit composed of an octahedral Co(II) ion, sitting on a center of inversion. The coordination sphere of Co(II) is an all-oxygen donor atom sphere, created by two different types of ligands, namely, imino-bis(methylphosphonate) ($^-HO_3P-CH_2-NH_2^+-CH_2-PO_3H^- = H_3$-IDA2P$^-$) and water. Specifically, two H_3IDA2P^- ligands each employ one phosphonate group to coordinate to the metal ion through one of its deprotonated hydroxides, with the remaining hydroxide staying in the protonated form. In addition, two water molecules are coordinated to the Co(II) ion, and, with the previous two terminal H_3IDA2P^- ligands, complete the equatorial plane coordination requirements of the octahedral metal ion. Two more H_3IDA2P^- molecules bind to Co(II) through their deprotonated hydroxide oxygen donor atoms, which occupy the axial positions in the octahedron. In view of this description, the mononuclear Co(II) ion resides in a distorted octahedron.

Table 2. Selected Bond Distances [Å] and Angles [deg] for $[Co(C_2H_8O_6NP_2)_2(H_2O)_2]$ (**1**)[a]

Co−O(4)′	2.067(2)	O(4)′−Co−O(4)″	180.0
Co−OW	2.094(2)	O(4)′−Co−OW‴	87.2(1)
Co−O(1)	2.132(2)	O(4)′−Co−OW	92.8(1)
P(1)−O(1)	1.499(2)	OW‴−Co−OW	180.0
P(1)−O(3)	1.501(2)	O(4)′−Co−O(1)	91.70(8)
P(1)−O(2)	1.559(2)	O(4)″−Co−O(1)	88.30(8)
P(1)−C(1)	1.822(3)	OW‴−Co−O(1)	93.09(9)
P(2)−O(4)	1.490(2)	OW−Co−O(1)	86.91(9)
P(2)−O(5)	1.507(2)	O(1)−Co−O(1)‴	180.0
P(2)−O(6)	1.560(2)	P(1)−O(1)−Co	131.6(1)
P(2)−C(2)	1.818(3)	P(2)−O(4)-Co⁗	140.9(1)
N−C(1)	1.499(3)	C(1)−N−C(2)	114.3(2)
N−C(2)	1.503(3)	HNA−N−C(1)	110.9(2)
		HNA−N−C(2)	104.3(2)
		HNB−N−C(1)	108.1(2)
		HNB−N−C(2)	107.2(2)
		HNA−N−HNB	112.1(2)

[a] Symmetry transformations used to generate equivalent atoms: ′ $x - {}^1/_2, -y - {}^1/_2, z - {}^1/_2$; ″ $-x + {}^1/_2, y + {}^1/_2, -z + {}^1/_2$; ‴ $-x, -y, -z$; ⁗ $-x + {}^1/_2, y - {}^1/_2, -z + {}^1/_2$.

The Co−O distances in **1** are similar to those observed in other mononuclear octahedral Co(II) sites, among which are those in $(NH_4)_4[Co(C_6H_5O_7)]_2$ (2.051(2)−2.157(2) Å) (**2**),[22] $[Co\{COOCH_2CH(OH)COO\}]\cdot 3H_2O$ (2.067(3)−2.136(3) Å) (**3**),[23] the phosphonate derivatives $[Co(NH_3CH_2PO_3)_2(H_2O)_2]_n\cdot nH_2O$ (2.104(4)−2.121(4) Å) (**4**),[24] $[Co(HO_3PC(CH_3)(OH)PO_3H)_2(H_2O)_2][NH_2(C_2H_5)_2]_2$ (2.064(2)−2.179(2) Å) (**5**),[25] and $[Co(OPMe_3)_3(H_2O)_2]I_2\cdot[Co(OPMe_3)_3(H_2O)_3]I_2$ (1.87(6)−2.18(4) Å for the octahedral site).[26]

The Co−O distances in the equatorial plane of the octahedron are of similar length, despite the variable nature of the ligands, which utilize their oxygens as terminal anchors to Co(II). In contrast, the corresponding axial Co−O bond lengths are longer than the equatorial ones by 0.04−0.07 Å. It is not unlikely that such bond distance variations might be due to Jahn−Teller distortions, usually encountered in high-spin Co(II) octahedral complexes.

The angles within the equatorial plane defined by O(4)′, O(4)″, Ow, and Ow‴ are in the range 87.2(1)°−92.8(1)°, and hence fairly close to the ideal octahedral angle of 90°. Similar is the angle variation observed between the axial

---

(22) Matzapetakis, M.; Dakanali, M.; Raptopoulou, C. P.; Tangoulis, V.; Terzis, A.; Moon, N.; Giapintzakis, J.; Salifoglou, A. *J. Biol. Inorg. Chem.* **2000**, *5*, 469−474.

(23) Kryger, L.; Rasmussen, S. E. *Acta Chem. Scand.* **1972**, *26*, 2349−2359.

(24) Glowiak, T.; Sawka-Dobrowolska, W.; Jezowska-Trzebiatowska, B. *Inorg. Chim. Acta* **1980**, *45*, L105−L106.

(25) Sergienko, V. S.; Aleksandrov, G. G.; Afonin, E. G. *Zh. Neorg. Khim.* **1997**, *42*, 1291−1296.

(26) Godfrey, S. M.; Kelly, D. G.; McAuliffe, C. A.; Pritchard, R. G. *J. Chem. Soc., Dalton Trans.* **1995**, 1095−1101.

Table 3. Hydrogen Bonds in $[Co(C_2H_8O_6NP_2)_2(H_2O)_2]$ (**1**)

interaction	D···A (Å)	H···A (Å)	D−H···A (deg)	symmetry operation
N−HNA···O5	2.820	2.018	171.3	$1.5 - x, -0.5 + y, 0.5 - z$
N−HNB···O1	2.834	2.009	153.3	$0.5 - x, -0.5 + y, 0.5 - z$
O2−HO2···O5	2.534	1.862	170.7	$0.5 - x, -0.5 + y, 0.5 - z$
O6−HO6···O3	2.570	1.808	168.0	$1 + x, y, z$
OW−HWA···O3	2.859	2.141	170.8	$0.5 - x, 0.5 + y, 0.5 - z$
OW−HWB···O6	3.093	2.485	133.2	$-0.5 + x, -0.5 - y, -0.5 + z$

donor atoms and those in the equatorial plane (range: 86.91(9)°−93.09(9)°). The aforementioned sets of angles are similar to those observed in **2**−**6** and in complexes $[Cu(HO_3PC(CH_3)(OH)PO_3H)_2(H_2O)_2]^{2-}$ (84.7(2)°−95.3(2)° and 87.8(2)−92.2(2)°, respectively)[25] and $[Zn(HO_3PC(CH_3)(OH)PO_3H)_2(H_2O)_2]^{2-}$ (84.98(6)°−95.02(6)° and 88.65(6)°−91.37(6)°, respectively).[27]

The bidentate mode of coordination of the H_3IDA2P^- ligand to the metal ion is exemplified through the binding of the two phosphonate anchors to two different Co(II) ions. Moreover, the four H_3IDA2P^- molecules, surrounding the central metal ion Co(II), are also coordinated to four other Co(II) ions as a consequence of the presence of the second phosphonate group in each molecule. In this sense, occupancy of the coordination sites in contiguous octahedral Co(II) ions extends to infinity, thus affording the molecular lattice in **1**.

An interesting attribute of the H_3IDA2P^- participation in the coordination sphere of Co(II) is the presence of a protonated central imino moiety, thus revealing the tetrahedral nature of the imino nitrogen and the zwitterionic form of the ligand. Overall, the charge of the ligand H_3IDA2P^- coordinated to Co(II) is 1−. Two of these ligands coordinated to Co(II) yield an overall charge of zero for the complex. The extra two H_3IDA2P^- ligands attached to Co(II) do not contribute to the charge of the mononuclear site as they originate in an adjacent mononuclear Co(II) site, for which the negative charge has been assigned to and accounted for.

Hydrogen bonding interactions are present in the crystal structure of **1** (Table 3). These interactions involve the coordinated water molecules, the imino nitrogen, and the phosphonate oxygen and hydroxyl moieties on the H_3IDA2P^- ligands. Collectively, the hydrogen bonds generate an extensive network, which likely contributes to the overall stability of the crystal lattice in **1**.

Electronic Spectroscopy. The UV−vis spectrum of **1** was recorded in water. The spectrum exhibits a major peak at $\lambda_{max} = 511$ nm ($\epsilon = 5.3$), subtly discernible shoulders around 479 ($\epsilon \sim 4$) and 462 ($\epsilon \sim 3.5$), and a distant shoulder around 280 nm ($\epsilon \sim 2.5$). The absorption features are most likely d−d transitions in origin, typical for a Co(II) d^7 octahedral species.[28] The band at 511 nm could be tentatively attributed to the $^4T_{1g} \rightarrow {}^4T_{1g}(P)$ transition. The observed multiple structure is in line with literature reports invoking (a) admixture of spin forbidden transitions to doublet states derived from ^2G and ^2H, (b) spin−orbit coupling, and (c) vibrational or low symmetry components, to account for the complexity of the spectrum.[29] In the absence of detailed studies, no further assignments could be proposed. The spectrum of **1** is distinct and different from that of $Co(II)_{aq}$,[30] indicating that in solution the coordination sphere of Co(II) in **1** remains octahedral and retains H_4IDA2P ligands and water molecules.

FTIR Spectroscopy. The FTIR spectrum of the title compound, in KBr, exhibits strong absorptions for the various vibrationally active groups. Specifically, absorptions for the PO_3 groups are observed for the antisymmetric stretching vibrations $\nu_{as}(PO_3)$ between 1090 and 980 cm^{-1}. A symmetric stretching vibration $\nu_s(PO_3)$ is observed in the range 970−920 cm^{-1}. The frequencies for the aforementioned stretches appear to be shifted to lower values compared to those of free H_4IDA2P acid, indicating changes in the vibrational status of the ligand upon coordination to the Co(II) ion.[31,32] The vibrations $\delta(NH_2)^+$ are located in the range 1560−1600 cm^{-1}. The aforementioned tentative assignments are, also, in consonance with previous results reported for iminophosphonate containing complexes of various metals.[33]

Magnetic Susceptibility Studies. Magnetic susceptibility measurements were carried out at different magnetic fields and in the temperature range 1.7−260 K. Figure 2 shows the $\chi_M T$ versus T susceptibility data at 0.6 T, with the dotted and solid lines representing the two different fits according to the following general Hamiltonian:

$$H = D\left[S_z^{\,2} - \frac{1}{3}S(S+1)\right] + E(S_x^{\,2} - S_y^{\,2}) + g\beta \mathrm{H}\cdot \mathrm{S}$$

where all the parameters have their usual definitions, and $S = {}^3/_2$.

The $\chi_M T$ values decrease smoothly from 2.55 emu·mol^{-1}·K at 270 K to 1.91 emu·mol^{-1}·K at 11 K and then more abruptly to the value of 1.41 emu·mol^{-1}·K at 1.7 K. The

---

(27) Sergienko, V. S.; Afonin, E. G.; Aleksandrov, G. G. *Zh. Neorg. Khim.* **1998**, *43*, 1002−1007.

(28) Drago, R. S. In *Physical Methods in Chemistry*; W. B. Saunders Company: Philadelphia, 1977; pp 359−410.

(29) Lever, A. B. P. In *Inorganic Electronic Spectroscopy*, 2nd ed.; Elsevier: Amsterdam, 1984; pp 480−490.

(30) (a) Figgis, B. N. In *Introduction to Ligand Fields*; Interscience Publishers: New York, 1966. (b) Jorgensen, C. K. *Adv. Chem. Phys.* **1963**, *5*, 33−146. (c) Ballhausen, C. J. In *Introduction to Ligand Field Theory*; McGraw-Hill Book Co.: New York, 1962.

(31) (a) Corbridge D. E. C. *J. Appl. Chem.* **1956**, *6*, 456−465. (b) Gore, R. C. *Discuss. Faraday Soc.* **1950**, *9*, 138−143. (c) Bell, J. V.; Heisler, J.; Tannenbaum, H.; Goldenson, J. *J. Am. Chem. Soc.* **1954**, *76*, 5185−5189. (d) Thomas, L. C.; Chittenden, R. A. *Spectrochim. Acta* **1964**, *20*, 467−487.

(32) (a) McIvor, R. A.; Hubley, C. E. *Can. J. Chem.* **1959**, *37*, 869−876. (b) Thomas, L. C.; Chittenden, R. A. *Chem. Ind. (London)* **1961**, 1913.

(33) (a) Sagatys, D. S.; Dahlgren, C.; Smith, G.; Bott, R. C.; Willis, A. C. *Aust. J. Chem.* **2000**, *53*, 77−81. (b) Shoval, S.; Yariv, S. *Agrochimica* **1981**, *25*, 377−386. (c) Subramanian, V.; Hoggard, P. E. *J. Agric. Food Chem.* **1988**, *36*, 1326−1329.

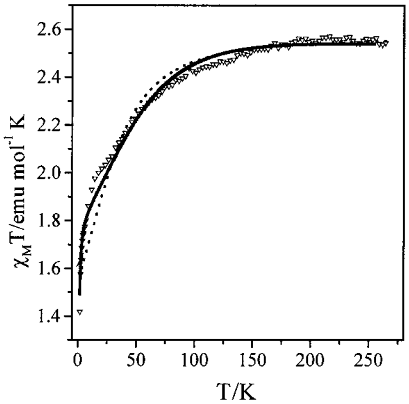


Figure 2. Temperature dependence of the magnetic susceptibility of compound **1**, in the form of $\chi_M T$ vs T, at 0.6 T and in the temperature range 1.7−260 K. The solid and dotted lines represent the theoretical fitting results (see text).

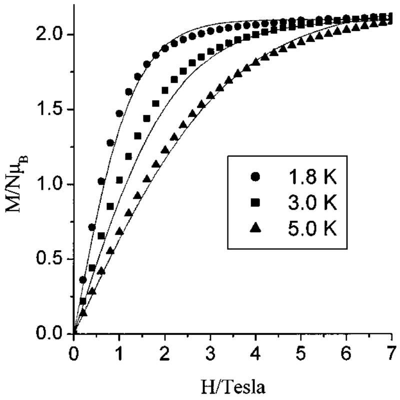


Figure 3. Magnetization, in the form of $M/N\mu_B$ vs H/T, at three different temperatures and in the field range 0−7 T, for compound **1**. The solid lines represent the best theoretical fit according to the theoretical Brillouin function for a system with spin $S = {}^1/_2$ and an effective $g = 4.2$.

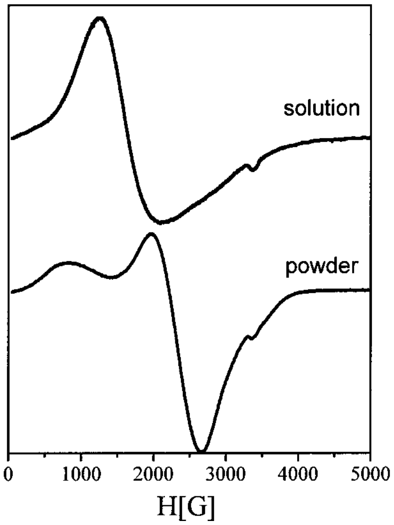


Figure 4. X-Band powder and solution EPR spectra of compound **1** in water recorded at 4 K.

high-temperature value of $\chi_M T$ is higher than 1.875 emu·mol^{-1}·K, the value that would be expected for a Co(II) system with an $S = {}^3/_2$. This behavior is consistent with the presence of a significant orbital contribution to the anisotropic nature of the Co(II) system investigated.

Two fitting models were considered. The first fitting model takes into account only the axial part of distortion of the crystal field D, and an isotropic g-value, while the fitting results provide the following parameters: $D = 40$ cm^{-1} and $g = 2.33$. The theoretical curve is shown in the same figure as a dotted line. It must be pointed out that from powder magnetic measurements the sign of the D parameter is not resolved. The large value of the D parameter is in accordance with an octahedral Co(II), where the ground state doublet is well-isolated from the excited ones.[34] The employed fit, however, fails to explain the low-temperature behavior of the system. Therefore, a different fit was employed, this time using both kinds of crystal field distortion (D, $E \neq 0$) and two parameters for the g value ($g_{\parallel}$, $g_{\perp}$). The values derived from the fitting process were $D = 52$ cm^{-1}, $E/D = 0.33$, $g_{\parallel} = 1.70$, and $g_{\perp} = 2.53$. The theoretical curve is also shown in Figure 2 (solid line). Taking into consideration the second model, which takes into account rhombic distortions of the crystal field, the low-temperature behavior of the system is better resolved.

The magnetization data for **1** in the form of $M/N\mu_B$ versus H/Tesla are shown in Figure 3, for three different temperatures and in the field range 0−7 T. The solid lines represent the theoretical magnetization curves for a system having a ground state with an effective spin $S = {}^1/_2$ and effective g value equal to 4.2. The ground state of the free high-spin Co(II) ion in an octahedral environment is ^{4}F, but the orbital degeneracy is removed in an octahedral crystal field yielding one ^{4}A and two ^{4}T levels with the lowest-lying state being a $^4T_{1g}$. The degeneracy of the $^4T_{1g}$ level is removed by the action of axial and rhombic distortions of the crystal field, as well as by spin−orbit coupling. The overall effect of low-symmetry crystal-field components and spin−orbit coupling produces six Kramers doublets and results in a doublet ground state. Because the same doublet energy level remains lowest in energy for all values of the applied field strength, and because the energy difference between the two lowest-lying doublets is relatively large with respect to thermal energy present at low temperatures (<30 K), the cobalt(II) system may be described as one having a ground state with an effective spin of $S = {}^1/_2$.

EPR Spectroscopy. X-Band EPR measurements were carried out in powder samples of **1** as well as in solutions of it in water and are shown in Figure 4. As a consequence of the fast spin−lattice relaxation time of high-spin Co(II), signals were observed only below 40 K. The g-values of the powder sample are $g_{\parallel} = 6.4$, $g_{\perp} = 2.93$. The data are in line with the presence of an octahedral Co(II) species and give an effective g-value of 4.1.[35] The latter value is very close to the value derived from the aforementioned magnetization measurements. In solution, the g_{eff} value of Co(II) is isotropic and equal to the value of 4.1, again in accordance with the magnetization measurements.

---

(34) Kahn, O. In *Molecular Magnetism*; Wiley-VCH Inc.: New York, 1993.

(35) Abragam, A.; Bleaney, B. In *Electron Paramagnetic Resonance of Transition Ions*; Clarendon Press: Oxford, 1970.

Discussion

The Chemistry and Its Relevance to Aqueous Co(II)−Phosphonate Species. The employment of simple reagents reacting in water, under specific pH conditions, was the basic premise behind the synthetic initiative of the reported work. In this context, through a facile reaction in an aqueous medium, $Co(NO_3)_2$ and $H_2O_3P-CH_2-NH_2^+-CH_2-PO_3H^-$ reacted, and complex **1** was crystallized and isolated. Two factors appeared to play a role in the isolation of the final product: (a) The pH of the aqueous solution, in which the reaction was run, which was acidic enough (pH ∼ 2) to allow for product formation and subsequent isolation of **1**. Raising the pH beyond this value consistently resulted in precipitates of noncrystalline nature. These precipitates redissolved only at higher pH values around 6.5. (b) The employment of alkalis in the adjustment of the pH was a factor. Regardless of the base used to set the pH of the reaction medium, the isolated product was the same and did not contain a cation originating in the base used. Thus, the bases were merely there to facilitate precipitation of the crystalline product out of solution. Furthermore, the employment of different Co(II)/ligand molar ratios in the reaction examined led to the factual conclusion that the only product isolated was complex **1**. Thus, the stability of the specific lattice achieved under the experimental conditions was high enough only for complex **1** to be isolated in a crystalline form. The nature of **1** was that of a compound in a molecular type of lattice, comprised of octahedral Co(II) ions linked via the betainic diphosphonate ligand throughout the assembled lattice. The possibility of other species being present in solution that presently elude isolation and characterization cannot be discounted.

The iminodiphosphonate ligand anchored onto the octahedral Co(II) sites revealed a coordination mode typical of a singly negatively charged phosphonate terminal group on either side of the central imino group. Variable modes of phosphonate coordination were previously observed in a plethora of metal organophosphonate complexes containing the phosphonate ligand terminals in varying deprotonation states.[36]

The magnetic susceptibility and magnetization measurements on **1** suggested the presence of a high-spin octahedral Co(II) species having a ground state with an effective spin of $S = {}^{1}/_{2}$. EPR measurements in the solid state and in aqueous solution corroborated the magnetization data, projecting the existence of a high spin Co(II) complex in solution with $g_{\mathrm{eff}} = 4.1$. Such a complex in solution would very likely include an oxygen ligand octahedral environment comprised of iminodiphosphonate ligands and water molecules.[37] To this end, on the basis of UV−vis and EPR data, it would not be unreasonable to envision that the environment around Co(II) reflects a formulation for an octahedral complex species not unlike $[Co(C_2H_8O_6NP_2)_2(H_2O)_4]^0$.

The solution properties of **1** projected one out of a number of species in the Co(II) and H_4IDA2P speciation. H_4IDA2P is a ligand, which can be viewed as a derivative of the iminodiacetic acid ligand H_2IDA, with the two terminal carboxylates replaced by phosphonates. Both solution and synthetic studies have been carried out for this dicarboxylic acid,[38,39] aminoalkylphosphonates, and IDA derivative phosphonate ligands, like *N*-(phosphonomethyl) glycine,[40] in the presence of various metal ions.[41,42] The studies suggest that these ligands react expediently with metal ions, including Co(II), forming soluble metal chelate complexes.[12a] Despite the fact that analogous studies with $H_2O_3P-CH_2-NH_2^+-CH_2-PO_3H^-$ and Co(II) have not been carried out, it would not be unreasonable to suggest that similar chemistry may be unfolding in this system too. Pertinent investigations, in this regard, would be exceedingly helpful in delineating the nature of interaction as well as the properties of the species arising in the pH useful range (excluding the window from pH 2 to 6.5).

Furthermore, albeit speculative at this juncture, it logically ensues that the potential biological significance of soluble Co(II)−aminophosphonate species, akin to those discussed previously, may arise from their ability to influence proteins and enzymes involved in requisite biological pathways. Concomitantly, the ability of such species to elicit interactions from molecular biological targets is crucial and may be intimately linked to their bioavailability. To our knowledge, however, such studies have not been conducted and could reveal aspects of the biological chemistry of Co(II) that are still unknown.

Relevance to Metal Organophosphonate Materials. Metal organophosphonates have drawn considerable attention in research over the past decades. Numerous such materials sprung out of synthetic approaches and methodologies targeting structure specific compounds with a wide spectrum of potential practical applications, spanning from catalysis

---

(36) (a) Sergienko, V. S.; Aleksandrov, G. G.; Afonin, E. G. *Kristallografiya* **2000**, *45*, 262−265. (b) Smith, P. H.; Raymond, K. N. *Inorg. Chem.* **1988**, *27*, 1056−1061. (c) Glowiak, T.; Sawka-Dobrowolska, W.; Jezowska-Trzebiatowska, B.; Antonow, A. *J. Cryst. Mol. Struct.* **1980**, *10*, 1−10. (d) Fenot, P., Darriet, J.; Garrigou-Lagrange, C. *J. Mol. Struct.* **1978**, *43*, 49−60.

(37) (a) The related case of the dinuclear complex $(Cat)_2[Co_2(C_6H_5O_7)_2(H_2O)_4]$ (Cat = K^+, Na^+; Co⋯Co 5.247(1) Å (K^+) and 5.361(1) Å (Na^+)) and its nature in the solid state and in aqueous solution was studied in our lab. Magnetization measurements in combination with EPR data, in the solid state and in aqueous solution, for the dinuclear complex suggested its dissociation into octahedral monomers, formulated as $[Co(C_6H_5O_7)(H_2O)_3]^-$ (see ref 37b). (b) Kotsakis, N.; Raptopoulou, C. P.; Tangoulis, V.; Terzis, A.; Giapintzakis, J.; Jakusch, T.; Kiss, T.; Salifoglou, A. *Inorg. Chem.*, submitted.

(38) (a) Petrosyants, S. P.; Malyarik, M. A.; Ilyukhin, A. B. *Zh. Neorg. Khim.* **1995**, *40*, 769−775. (b) Smith, B. B.; Sawyer, D. T. *Inorg. Chem.* **1968**, *7*, 922−928.

(39) (a) Mootz, D.; Wunderlich, H. *Acta Crystallogr.* **1980**, *B36*, 445−447. (b) Mammano, N. J.; Templeton, D. H.; Zalkin, A. *Acta Crystallogr.* **1977**, *B33*, 1251−1254. (c) Corradi, A. B.; Palmieri, C. G.; Nardelli, M.; Pellinghelli, M. A.; Tani, M. E. V. *J. Chem. Soc., Dalton Trans.* **1973**, 655−658.

(40) (a) Motekaitis, R. J.; Martell, A. E. *J. Coord. Chem.* **1985**, *14*, 139−149. (b) Lundager Madsen, H. E.; Christensen, H. H.; Gottlieb-Petersen, C. *Acta Chem. Scand., Ser. A* **1978**, *32*, 79−83.

(41) (a) Wozniak, M.; Nowogrocki, G. *Talanta* **1979**, *26*, 1135−1141. (b) Wozniak, M.; Nowogrocki, G. *Talanta* **1979**, *26*, 381−388. (c) Kiss, T.; Balla, G.; Nagy, G.; Kozlowski, H.; Kowalik, J. *Inorg. Chim. Acta* **1987**, *138*, 25−30. (d) Radomska, B.; Matczak-Jon, E.; Woiciechowski, W. *Inorg. Chim. Acta* **1986**, *124*, 83−85. (e) Ignat'eva, T. I.; Bovin, A. N.; Yarkov, A. V.; Chekhlov, A. N.; Tsvetkov, E. N.; Raevskii, O. A. *Koord. Khim.* **1989**, *15*, 1179−1185.

(42) (a) Appleton, T.; Hall, J. R.; McMahon, I. J. *Inorg. Chem.* **1986**, *25*, 726−734. (b) Motekaitis. R. J.; Murase, I.; Martell, A. E. *Inorg. Chem.* **1976**, *15*, 2303−2306.

to electronics. Among the various classes of metal phosphonates synthesized to date are those containing simple phosphate groups,[43] monophosphonate ligands,[44] like $H_2O_3P-CH_2-CH_2-COOH$, or diphosphonic acids,[45] like $H_2O_3P-R-PO_3H_2$, where the nature of $R = (CH_2)_n$, and specifically the length of the tether R adjoining the phosphonate group termini, plays a role in the attained dimensionality of the material.[46] The emerging chemistry of small molecules in such structural networks is dependent upon a number of host attributes, including shape, size, and selectivity dependent intercalation, interlayer distance, coordination site availability, and others. Among the outstanding properties possessed by these structures is their ability to retain water molecules or readily dehydrate with retention of their layered structure, concomitantly becoming prone to acting as hosts to other organic molecules such as amines, alcohols, and others. On the basis of the features seen in **1**, it would not be unreasonable to explore the potential of this compound to exhibit similar properties.

The extended structure of **1** relies on a basic scaffolding unit of four mononuclear Co(II) octahedral sites. The iminodiphosphonate groups act as intervening linkers bringing the four Co(II) sites in proximity to each other. Further interconnection of similar units through iminodiphosphonate terminals creates the two-dimensional arrangement in the plane defined by the *ac* diagonal in the lattice of **1**. Formation of the aforementioned closed unit of four Co(II) sites results in 32-membered rings, which define the periphery of large elliptical cavities (Figure 5A). The conformational state of the organophosphonate ligand appears to play a crucial role in shaping the assembled tetranuclear ellipses. The approximate dimensions of the assembled elliptical cavities are 8.133 Å (*b* axis length) and 17.43 (*ac* diagonal length) Å. The associated surface area of the cavity approaches 111.4 $Å^2$.

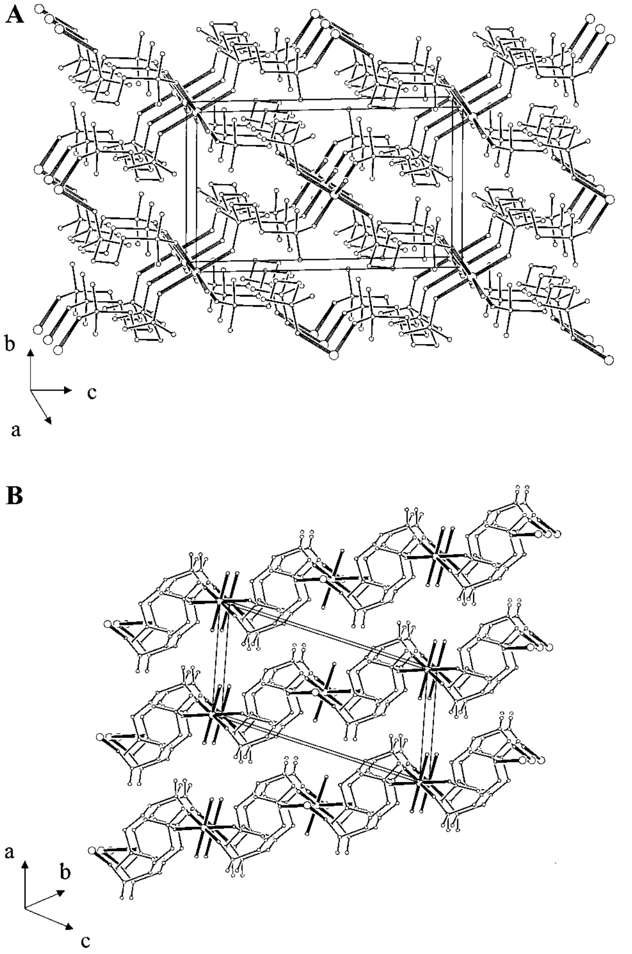


Figure 5. A. Packing diagram of compound **1**. The view of the structure is down the crystallographic *a* axis, showing the created elliptical 32-membered ring cavities. B. Packing diagram of compound **1**. The view of the structure is down the crystallographic *b* axis, showing the interlayer spacing between contiguous sheets of **1**. Co(II) locations are large open circles occupying octahedral sites.

The formulated sheets of elliptical units of Co(II)−organophosphonate sites are stacked, thus creating horizontal interlayer voids between consecutive sheets. The height of the void created between the two-dimensional sheets is 5.76 Å (Figure 5B), raising the volume of each cavity to 641.9 $Å^3$. Hence, two types of cavities are created in the three-dimensional lattice of **1**: (a) horizontal interlayer voids separating the layers and (b) adjacently located elliptical holes, in the plane defined by the *ac* diagonal, running vertical to the aforementioned voids throughout the lattice. It is worth mentioning that the two bound water molecules in each Co(II) octahedral site project above and below each layer, well into the interlamellar space. The same is true for the hydrogens on the protonated imino group of the diphosphonate ligand as well as the protonated hydroxides of the phosphonate termini.

Diphosphonate group-containing pillared layered structures have been obtained for vanadium,[46,47a] while three-dimensional phases were isolated with manganese and cobalt.[47b] Some of the aforementioned solids included $[(VO)(H_2O)\{O_3PCH_2NH(C_2H_4)_2NH\ CH_2PO_3\}]$[47a] and $[M\{O_3PCH_2NH(C_2H_4)_2NHCH_2PO_3\}]\cdot H_2O$ (M = Mn(II), Co(II)).[47b] The structural features observed in these structures resemble those encountered in **1**, with that of the Co(II) analogue exhibiting elliptical cavities composed of 44-membered rings and dimensions of 4.7 by 18.0 Å, and an associated surface area of 66.4 $Å^2$.

Finally, the collective data on complex **1** formulate the profile of a cavity specific size and shape material. These structural attributes in combination with its facile recrystallizability from aqueous media may hint for a potential candidate material in processing applications.

---

(43) Choudhury, A.; Natarajan, S. *Solid State Sciences* **2000**, *2*, 365−372.

(44) (a) Cao, G.; Lynch, V. M.; Swinnea, J. S.; Mallouk, T. E. *Inorg. Chem.* **1990**, *29*, 2112−2117. (b) Hix, G. B.; Carter, V. J.; Wragg, D. S.; Morris, R. E.; Wright, P. A. *J. Mater. Chem.* **1999**, *9*, 179−185.

(45) (a) Drumel, S.; Janvier, P.; Barboux, P.; Bujoli-Doeuff, M.; Bujoli, B. *Inorg. Chem.* **1995**, *34*, 148−156. (b) Drumel, S.; Janvier, P.; Barboux, P.; Bujoli-Doeuff, M.; Bujoli, B. *New J. Chem.* **1995**, *19*, 239−242.

(46) Soghomonian, V.; Chen, Q.; Haushalter, R. C.; Zubieta, J. *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 223−226.

(47) (a) Soghomonian, V.; Diaz, R.; Haushalter, R. C.; O'Connor, C. J.; Zubieta, J. *Inorg. Chem.* **1995**, *34*, 4460−4466. (b) LaDuca, R.; Rose, D.; DeBord, J. R. D.; Haushalter, R. C.; O'Connor, C. J.; Zubieta, J. *J. Solid State Chem.* **1996**, *123*, 408−412.

Conclusions

A Co(II)−imino-bis(methylphosphonate) complex **1** was synthesized, with solid-state properties similar to those observed in metal organophosphonate materials and reminiscent of basic structural attributes of aqueous mononuclear Co(II) sites in low molecular mass species of potential biological relevance. In solution, the retention of the octahedral coordination environment in what has been suggested by the collective spectroscopic data as $[Co(C_2H_8O_6NP_2)_2(H_2O)_4]^0$, attributable to high-spin Co(II), substantiates the contention that the particular metal ion could interact with phosphonate containing ligands in an aqueous medium. In view of the fact that Co(II) interactions with simple phosphonate ligands have been probed in aqueous solutions,[40] it is not unreasonable to envision similar species arising from a system composed of Co(II) and iminodiphosphonic acid. The proposed soluble complex arising from **1**, albeit at low pH, denotes the distinct possibility of other species being present in solution and necessitates the perusal of the Co(II)−H_4IDA2P system speciation in the physiological pH range. It remains to be seen whether species of the herein proposed nature or similar to it represent bioavailable forms of Co(II), which can elicit interactions at the cellular level not unlike the ones involved in biological processes. To this end, continuing efforts to synthesize and characterize other soluble forms of Co(II)-phosphonates, bearing variable metal to ligand stoichiometries at physiological pH values, are under way in our labs.

Acknowledgment. This work was supported with funds provided by the Department of Chemistry, University of Crete, Greece.

Supporting Information Available: X-ray crystal crystallographic files, in CIF format, and listings of positional and thermal parameters and H-bond distances and angles for **1**. The material is available free of charge via Internet at http://pubs.acs.org.

IC011033Y