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Structural speciation of the binary Co(II)- phosphonate system

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Abstract

A new Co(II)-(H_5NTA_2P) complex was synthesized in aqueous solutions under pH-specific conditions. The new species was isolated in pure crystalline form and characterized by elemental analysis, spectroscopic techniques, and magnetic studies. In addition, aqueous speciation studies of the binary system Co(II)-(H_5NTA_2P) were carried out. The collective physicochemical properties of the derived species project fundamental chemical and structural properties of Co(II)- organophosphonate interactions akin to biochemical processes and/or the chemistry of advanced materials.

Keywords: Cobalt(II), organophosphonate substrates

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1. Introduction

Cobalt is a metalloelement known to be present as an essential element in biological systems. Its involvement in biomolecular activity is intimately linked to its: a) presence in molecular targets such as B_{12} coenzyme and vitamin B_{12}, and b) potential as an inorganic cofactor to influence biological processes.[1,2,3,4] Moreover, cobalt has been found in metalloenzyme systems, such as metallohydrolases, methionine aminopeptidase,[5] nitrile hydratases,6 ribonucleotide reductase, glutamate mutase, and others.[7]

In order to understand the role of cobalt in those biological systems entails deep understanding of its biochemical interactions with low as well as high molecular mass biomolecules in the requisite biological fluids. Low molecular mass target molecules include organic acids, amino acids, small peptides, and molecules possessing variable structural features prominent among which stand the carboxylic and phosphonic moieties.[8] Phosphonate groups have been known to participate in phosphorylation events on small as well as large molecules influencing enzyme inhibition, neuroactivity, plant growth regulation, antibiotic, and herbicidal activity.[9]

In an effort to delineate Co(II) interactions with biologically significant targets, we have explored the relevant synthetic aqueous chemistry arising between Co(II) and the organophosphonate binder (H_2O_3P-$CH_2)_2N$-CH_2-COOH (H_5NTA_2P). To this end, we studied the synthesis, isolation, spectroscopic and structural properties of a new species between Co(II) and the carboxy-diphosphonate ligand N,Nbis (phosphonomethyl) glycine (H_5NTA_2P).

2. Materials and Method

We investigated the aqueous chemistry of the binary system $Co(NO_3)_2 .6H_2O$-N,N-bis(phosphonomethyl) glycine (H_5NTA_2P), whereby under specific stoichiometric and pH conditions, reactions led to the isolation of a new Co(II)- H_5NTA_2P species **(1)**.

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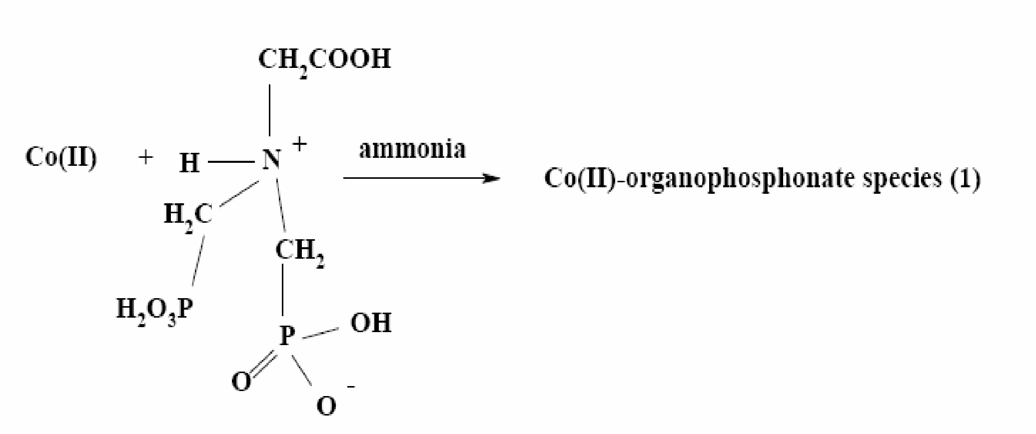
Addition of ammonia for the adjustment of pH, was crucial in the isolation of the new Co(II)-organophosphonate species. The resulting reaction mixture was placed in the refrigerator at 4°C. Following several months of standing under those conditions, the reaction afforded pink crystals, which were collected by filtration. The crystalline solid has proven to be stable in the air for long periods of time. The isolated species **(1)** is soluble in water, but insoluble in methanol, ethanol, DMF, DMSO and CH_3CN.

Elemental analysis of the isolated Co(II)-H_5NTA_2P species found: (%) C, 10.28; H, 5.57; N, 8.06. Species **(1)** was further characterized by FT-IR spectroscopy and UV-Visible spectroscopy in water.

The FT-IR spectrum of the Co(II)-organophosphonate species is presented in Figure 1. The FT-IR spectrum was recorded in KBr and reflected the presence of vibrationally active carboxylate as well as as phosphonate groups. The antisymmetric stretching vibrations for (**1**) νas(COO-) appear at 1590 cm-1, whereas the symmetric stretches νs(COO-) appear in the range from 1450 up to 1380 cm-1. The antisymmetric stretching vibrations for the phosphonate groups νas(PO3) appear in the range from 1115 up to 1050 cm-1, whereas the symmetric stretches νs(PO3) appear in the range from 976 up to 938 cm-1. The frequencies for all bands are shifted to lower values in comparison to those of free N,N- bis(phosphonomethyl) glycine (H5NTA2P). From that point of view, the change in the vibrational status of the employed organophosphonate anion is due to its coordination to the metal ion. The difference, Δ(νas(COO-)-νs(COO-)), is greater than 200 cm-1, indicating the presence of deprotonated carboxylate groups free or coordinated to the metal ion in a monodentate fashion.

Furthermore, the UV/Visible spectrum in the range 200 to 800 nm of (**1**) was taken in water (Figure 2). The spectrum shows a band around λmax 540 nm (ε ~ 15 M-1 cm-1) nm and a band around λ 476 nm (ε~12 M-1 cm-1). Moreover, a distant band rising into the UV region appeared around 220 nm (ε 700 M-1 cm-1). The absorption features in the low energy region are likely due to d-d transitions, which are typical for a Co(II) d7 octahedral species.

Moreover, magnetic susceptibility studies and EPR studies on (**1**) in the solid state and in solution were carried out to provide valuable information on the nature of the isolated species. At this end, aqueous speciation studies of the binary system Co(II)-H5NTA2P were carried out to shed light onto the different chemical aspects arising from varying Co(II)-substrate stoichiometries and pH values. The reaction is shown schematically below:



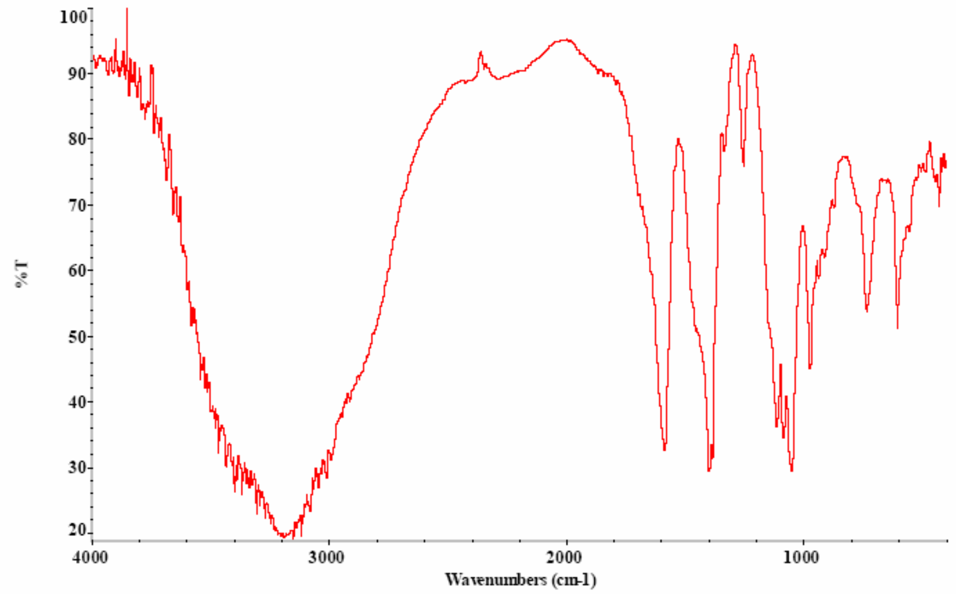


Figure 1: The FT-IR spectrum of species (**1**)

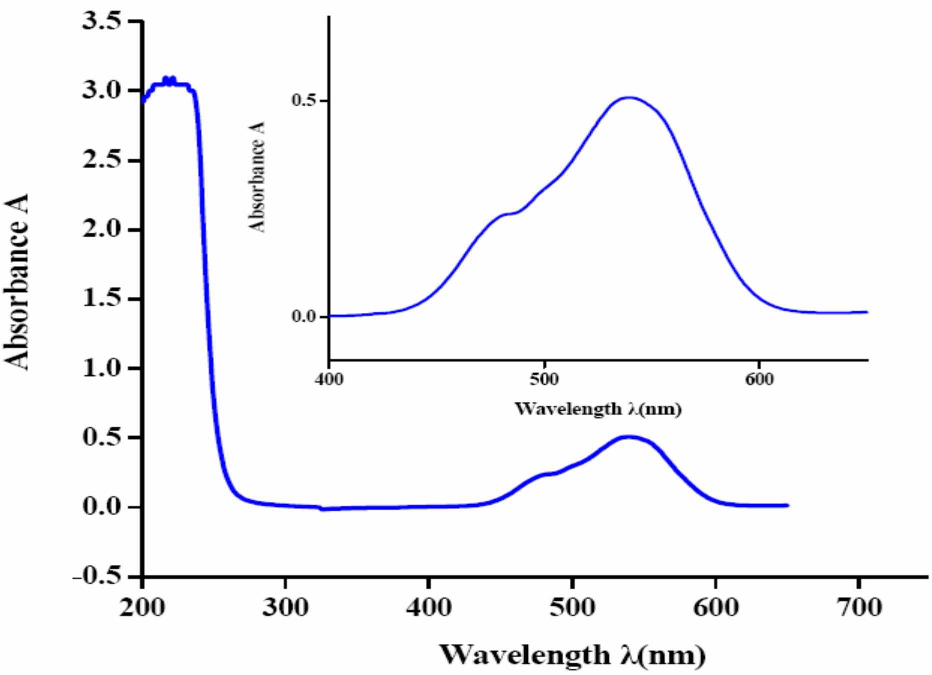


Figure 2: The UV-Vis spectrum of species (**1**)

The syntheses and the detailed characterization of species (**1**) provide a clear case of an interaction of the organophosphonate binder H5NTA2P with Co(II), leading to a new material. The physicochemical properties of the aforementioned species, suggest that the structural and chemical reactivity characteristics are associated with the aqueous speciation distributions.

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References

1. Taylor, D. M.; Williams, D. R. In: *Trace Element Medicine and Chelation Therapy*; Royal Society of Chemistry: Cambridge, **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.
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*; U. Science Books: M. Valley, CA, **1994**.
8. (a) Kiss, T. In: *Bioinorganic Chemistry*; Burger, K, Ed.; Ellis Horwood: Chichester, **1990**. (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, Inc.: New York, **1973**. (e) Perrin, D. D. *Nature* **1965**, *206*, 170.
9. (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. Wirkst. Forsch.***1984**, *21*, 1.