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Structural speciation of binary Ni(II)-phosphonate systems

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Abstract

Ni(II)-organophosphonate species were synthesized and isolated in aqueous media under pH-specific conditions. Ni(II) interacted with various mixed organophosphonate ligands: a) imino bis(methylphosphonic acid), b) N-(phosphonomethyl) glycine, and c) N-(phosphonomethyl) iminodiacetic acid. The pH in each examined binary system was adjusted with several bases (ammonia, KOH, NaOH). Crystalline material was isolated from each binary system and was further characterized by elemental analysis, spectroscopic techniques (FT-IR, UV-Visible), and X-ray crystallography. Magnetic susceptibility studies on each new material support the presence of high-spin octahedral Ni(II), consistent with X-ray crystallography. Therefore, distinct species with variable structural features arise that can be studied for their potential applications either from the biological or materials chemistry point of view. The results of the solid state and solution studies provide a clear picture of the binary interactions involved as well as the physicochemical properties of emerging species from such binary systems.

Keywords: Nickel(II), organophosphonates, X-ray crystallography, magnetic susceptibility

1. Introduction

Nickel is an abundant natural element, which is recognized as an essential trace element for most of the living organisms, such as bacteria, plants, animals and humans [1].Moreover, nickel is encountered in a wide range of biological systems and in all types of soils. In biological systems, nickel exists as an inorganic cofactor, in addition to iron-sulfur clusters [2]. As an example, urease contains nickel. Moreover, nickel enzymes such as CODH and ACS have proven to play an important role in carbon cycling [3].Finally, nickel plays various roles in the formation of a) alloys, b) stainless steel, and c) coins with various metals (e.g. iron and copper).

Over the last decades, great attention has been paid to the study of the interaction of various metal ions (especially transition metal ions) with organophosphonate ligands. In this regard, mixed (carboxy) phosphonate ligands have attracted considerable interest from all scientists all over the world.

Three such representative mixed organophosphonate ligands are: a) imino bis(methylphosphonic acid), b) N-(phosphonomethyl) glycine, and c) N-(phosphono methyl) iminodiacetic acid. N-(phosphonomethyl) glycine (glyphosate) is a non-selective systemic herbicide, which can be absorbed through the leaves, injected into the bole or applied to the stump of a tree [4]. Its crystal structure shows that it exists in a zwitterionic form. A similar representative organophosphonate ligand is imino bis(methyl phosphonic acid), $H_2O_3P\text{-}CH_2\text{-}NH_2^+\text{-}CH_2\text{-}PO_3H^-$ (IDA2P) [5]. Nickel is also used to kill weeds, especially perennials or used in the cut-stump treatment as a forestry herbicide, although some crops have been found to be resistant to it. Therefore, the binary interaction in these metal-organic systems emerges quite significant. All (carboxy)phosphonate binders, due to the three internal donor sites, are capable of interacting with metal ions such as nickel, cobalt, and manganese, leading to complexes with distinct physicochemical properties.

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Key reacting moieties in these ligands include: a) a phosphate group, b) a carboxylate group, and c) an amino moiety. In that sense, a genuine interest in organophosphonates developed over the years, is primarily due to their versatile metal coordination chemistry [6]. On the other hand, variable nuclearity and linear one-dimensional compounds as well layered metal organophosphonates have been synthesized and characterized. Such materials have been found to exhibit interesting reactivity properties, which could further be used in the promotion of practical applications spanning from catalysis, ion exchange, intercalation chemistry, to film preparation with optical properties [7].

2. Materials and methods

All experiments were carried out in aqueous media under aerobic conditions. Nanopure quality water was used for all reactions. $Ni(NO_3)_2 \cdot 6H_2O$ was purchased from Carlo Erba, and imino bis(methylphosphonic acid) from Fluka. Ammonia, KOH and NaOH were also supplied by Fluka. N-(phosphonomethyl) glycine and N-(phosphonomethyl) iminodiacetic acid were purchased from Aldrich.

3. Results and Discussion

The aqueous synthetic chemistry of three binary systems with Ni(II)-organophosphonate ligands was investigated. Therefore, under specific pH-conditions, the arisen reactivity in the binary Ni(II)-N-(phosphonomethyl) glycine led to the isolation of the new species: $[Ni(OOC\text{-}CH_2\text{-}NH\text{-}CH_2\text{-}PO_3H)_2]\cdot[Ni(H_2O)_6]\cdot 3.3H_2O$ (**1**). In the same respect, the aqueous synthetic chemistry of the binary Ni(II)-imino bis(methylphosphonic acid) system led to the isolation of the inorganic-organic hybrid: $[Ni(C_2H_8O_6NP_2)_2(H_2O)_2]$ (**2**). Finally, the aqueous synthetic chemistry of the binary Ni(II)-N-(phosphonomethyl) iminodiacetic acid led to the isolation of a mononuclear species.

The pH-dependent synthesis in each binary system was carried out in aqueous media. The pH was adjusted to 4 with ammonia for complex **1**, and 3 for complex **2**, using various bases. The resulting reaction mixtures were allowed to stand in the open air for several months. Both compounds were isolated in pure crystalline form.

The FT-IR spectrum of **1** in KBr exhibits strong absorption for the various vibrationally active groups: the carbonyl moiety of the carboxylate group and the PO_3 group in the antisymmetric and symmetric vibration regions. The antisymmetric stretching vibrations $\nu_{as}(COO^-)$ appear in the range from 1600 to 1550 cm^{-1}, whereas the corresponding symmetric stretches $\nu_s(COO^-)$ appear in the range from 1475 to 1385 cm^{-1}. Moreover, the antisymmetric stretching vibrations $\nu_{as}(PO_3)$ appear in the range from 1209 to 1140 cm^{-1}, whereas the symmetric stretching vibration $\nu_s(PO_3)$ appear in the range from 1074 to 993 cm^{-1}. The frequencies of the various stretches are shifted to lower values compared to those of free binder, due to the coordination of the ligand to the Ni(II) ion.

The FT-IR spectrum of **2** was recorded in KBr. The spectrum exhibits strong absorptions for the PO_3 groups observed in both the antisymmetric $\nu_{as}(PO_3)$ and symmetric $\nu_s(PO_3)$ vibration regions. The antisymmetric stretching vibrations appear in the range between 1090 and 980 cm^{-1}, whereas the symmetric stretching vibrations appear 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 ligand, indicating changes in the vibrational status of the ligand due to coordination to the Ni(II) ion.

The FT-infrared spectrum of **3**, exhibits strong absorptions for the vibrationally active groups: the carbonyl moiety of the carboxylate group and the PO_3 group in the antisymmetric and symmetric vibration regions. Finally, the frequencies for the stretches appear to be shifted to lower values compared to those of free mixed (carboxy)phosphonate ligand, indicating changes in the vibrational status of the ligand due to the coordination to the Ni(II) ion.

X-Ray crystallography was instrumental in revealing the three dimensional structure of all investigated molecules. Complex **1** consists of two different monomeric units. In the first unit, Ni(II) ion is coordinated to two different glyphosate ligands, with each glyphosate ligand bearing a 2- charge. Formation of two five-membered metallacyclic rings is most likely a source for stability in the arising complex. The negative charge on the first anionic unit $[Ni(OOC\text{-}CH_2\text{-}NH\text{-}CH_2\text{-}PO_3H)_2]^{2-}$ is counteracted by the second mononuclear $[Ni(H_2O)_6]^{2+}$ unit.

Compound **2** consists of a mononuclear core unit composed of an octahedral Ni(II) ion sitting on a center of inversion. The coordination sphere of Ni(II) is an all-oxygen donor atom sphere, created by two ligands, the organophosphonate binder and water. The mode of coordination of the ligand to the metal ion is monodentate.

Finally, compound **3** consists of a mononuclear core unit composed of an octahedral Ni(II) ion in an N,O-environment. The organophosphonate ligand N-(phosphonomethyl) iminodiacetic acid proved to be an excellent chelator.

4. Conclusion

The synthesis of **1**, **2** and **3**, their isolation, and their characterization provide a clear picture of the structural and chemical interaction of each organophosphonate binder with nickel ions. All three crystal structures project the diversity of possible species arising from the interaction of Ni(II) with polyfunctional binders such as mixed (carboxy)organophosphonate substrates. The emerging information from this work leads to well-defined species shedding light onto the speciation distribution of Ni(II) with low molecular mass ligands. The importance of such information is exemplified through a) the nature of further developing binary and ternary interactions with Ni(II), and b) any potential activity relating to the physiology or toxic effects in fundamental cell structures or even to the characterization of new materials.

The carboxylate groups, the phosphonate groups and the nitrogen functionalities of all examined ligands have proven to be capable of promoting metal ion binding chemistries. Collectively, the herein chemical reactivity and structural identity may indicate analogous chemical reactivity at the biological level in essential biosynthetic pathways, which may influence cellular integrity (e.g. in plants).

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