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Aqueous Ni(II)-phosphonate chemistry of biological relevance

Melita Menelaou[a] Marianna Dakanali[b] A. Salifoglou[a]

[a]Department of Chemical Engineering, Aristotle University of Thessaloniki, Thessaloniki 54124, Greece
[b]Department of Chemistry, University of Crete, Heraklion 71409, Greece

Abstract

New Ni(II)-organophosphonate species were synthesized in aqueous solution under specific conditions. Glyphosate, N-(phosphonomethyl) glycine and imino bis(methylphosphonic acid), H2O3P-CH2-NH2+-CH2-PO3H-, interacted with Ni(II) and the pH was adjusted with addition of ammonia and other bases. Each isolated crystalline product was isolated and was characterized by elemental analysis, spectroscopic techniques (FT-IR), and X-ray crystallography.

Keywords: Nickel(II), Organophosphonates

1. Introduction

Nickel is an abundant natural element and is recognized as an essential trace element in bacteria, plants, animals and humans (Halcrow, M.A. et. al). Nickel plays various roles in the formation of alloys, stainless steel and coins with other metals (such as iron and copper). Moreover, nickel is encountered in a wide range of biological systems as well as in all types of soil. In biological systems, nickel exists as an inorganic cofactor, in addition to iron-sulfur clusters (Bbouwman, E. et. al.). In fact, urease contains nickel. Also, nickel enzymes like CODH and ACS play an important role in carbon cycling (Evans, D. J.).

Glyphosate, N-(phosphonomethyl) glycine, 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 (Wang, Y-J. et. al.). Mostly, nickel is 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. Its crystal structure shows that it exists in a zwitterionic form.

A similar representative organophosphonate ligand is imino bis(methylphosphonic acid), $H_2O_3P\text{-}CH_2\text{-}NH_2^+\text{-}CH_2\text{-}PO_3H^-$ (IDA2P) (Kelley, C. J. et. al.).

Both binders, glyphosate and IDA2P, can interact with metal ions like nickel, cobalt, copper to form complexes with distinct physicochemical properties, due to its three internal donor sites: a) phosphate, b) carboxylate, and c) amino moiety. Furthermore, genuine interest in organophosphonates has been developed over the years, primarily due to their versatile coordination chemistry with various metal ions (Zubieta, J.). Variable nuclearity and linear one-dimensional compounds as well as layered metal organophosphonates have been synthesized and characterized. These materials have been found to exhibit interesting reactivity properties, which could be used in the promotion of practical applications in catalysis, ion exchange, intercalation chemistry, film preparation with optical properties, and others (Burwell, D. A.).

Corresponding author: *e-mail address*: salif@chemistry.uch.gr

2. Experimental Section

The aqueous synthetic chemistry of the binary system $Ni(NO_3)_2$-glyphosate was investigated. Under specific pH-conditions, the arisen reactivity led to the isolation of the new species: $[Ni(OOC\text{-}CH_2\text{-}NH\text{-}CH_2\text{-}O_3H)_2].[Ni(H_2O)_6]$ $.3.3H_2O$ (1).

Under similar conditions, the aqueous synthetic chemistry of the binary system $Ni(NO_3)_2$-IDA_2P led to the isolation of the new species: $[Ni(C_2H_8O_6NP_2)_2(H_2O)_2]$ (2).

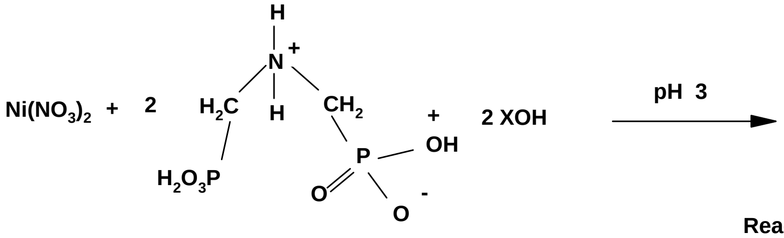
The pH-dependent synthesis of complexes **1** and **2** was carried out in aqueous media. The pH was adjusted to 5 with ammonia for complex **1** and 3 for complex **2**, using various bases. The resulting reaction mixtures were allowed to stand in the open air for several months. Both compounds were isolated in pure crystalline form. The stoichiometric reaction for the synthesis of the new complex of Ni(II) with glyphosate is given below:

$$2\ Ni(NO_3)_2 \cdot 6\,H_2O + 2\ C_3H_8NO_5P + 4\ NH_3 + 0.6\ H_2O \xrightarrow{\text{pH 5}}$$

Reaction 1

$$[Ni(C_3H_6NO_5P)_2] \cdot [Ni(H_2O)_6] \cdot 3.3\,H_2O + 4\ NH_4NO_3 + 3.3\ H_2O$$

The stoichiometric reaction for the synthesis of complex **2** of Ni(II) with IDA2P is given below:



Reaction 2

$[Ni(C_2H_8O_6NP_2)_2(H_2O)_2]$ + 2 XNO_3

X = K^+, Na^+, NH_4^+

The FT-IR spectrum of **1** exhibits strong absorptions for the carbonyls of the carboxylate groups in both the antisymmetric and symmetric vibration regions. The antisymmetric stretching vibrations $\nu_{as}(COO^-)$ appear in the range 1680-1585 cm^{-1}, whereas the symmetric stretches $\nu_s(COO^-)$ appear in the range 1474-1380 cm^{-1}. The frequencies for the carbonyl stretches in **1** are shifted to lower values compared to those of the free glyphosate. Absorptions for the PO_3 groups are observed for the antisymmetric stretching vibrations $\nu_{as}(PO_3)$ between 1090 and 980 cm^{-1}.

The FT-infrared spectrum of **2**, exhibits strong absorptions for the vibrationally active groups. A symmetric stretching vibration $\nu_s(PO_3)$ is observed in the range 970 - 920 cm^{-1}. The frequencies for the stretches appear to be shifted to lower values compared to those of free IDA2P acid, 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 the investigated molecules. Complex **1** consists of two different monomeric units. In the first unit, Ni(II) ion is coordinated by two different glyphosate ligands where each glyphosate ligand bears 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 monomeric unit.

Complex **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, IDA2P and water. The mode of coordination of the $IDA2P^-$ ligand to the metal ion is monodentate.

3. Conclusions

The synthesis of **1** and **2**, their isolation, and the spectroscopic characterization provide a clear picture of the structural and chemical interaction of the organophosphonate binders with nickel. Also, both crystal structures project the diversity of possible species arising from the interaction of Ni(II) with polyfunctional binders such as glyphosate and IDA2P. The emerging information from this work leads to well-defined species shedding light onto the distribution of Ni(II) with low molecular mass ligands. The importance of such information is exemplified through a) the nature of developing further 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 phosphonate groups as well as the nitrogen functionalities of both ligands are capable of promoting metal ion binding chemistries, where the herein observed chemical reactivity and structural identity, may indicate analogous chemical reactivity at the biological level. There, natural organic ligands such as glyphosate are key molecular targets, participating in essential biosynthetic pathways which may influence cellular integrity or/and survival in plants

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