

Investigation of the aqueous chemistry of Pb(II) with O- and N- substrates

Catherine Gabriel, A. Salifoglou*

^a Department of Chemical Engineering, Aristotle University of Thessaloniki,
Thessaloniki 54124, Greece

Abstract

Contamination of soils by heavy metals is of widespread occurrence as a result of human, agriculture and industrial activities. Among heavy metals, Pb is an environmental pollutant, which readily accumulates in soils and sediments. Lead (Pb) is one of the major heavy metals of antiquity and has gained considerable importance as a potent environmental pollutant. Apart from the natural weathering processes, Pb(II) contamination of the environment has resulted from mining and smelting activities, Pb(II)-containing paints, gasoline and explosives as well as from the disposal of municipal sewage sludge enriched in Pb(II). In this research work, we investigated the aqueous chemistry of Pb(II) with O- and N-containing substrates as 2-hydroxyethyl-iminodiacetic acid (HEIDA) and 1,3-diamino-2-propanol-N,N,N,N-tetraacetic acid. Through the hydrothermal method two new species were isolated. Complexes **1** and **2** were further characterized by FT-IR spectroscopy, Solid State NMR spectroscopy and X-Ray crystallography.

Keywords: Lead, N-substrates, plant toxicity

1. Introduction

Lead (Pb) is one of the major heavy metals of antiquity and has gained considerable importance as a potent environmental pollutant. Apart from the natural weathering processes, Pb(II) contamination of the environment has resulted from mining and smelting activities, Pb(II)-containing paints, gasoline and explosives as well as from the disposal of municipal sewage sludge enriched in Pb(II).¹ As many of the Pb(II) pollutants are indispensable for modern human life, soil contamination with Pb(II) is not likely to decrease in the near future.² Significant increases in the Pb(II) content of cultivated soils has been observed near industrial areas. Pb(II) tends to accumulate on the surface ground layer and its concentration decreases with soil depth.³ It is easily taken up by plants from the soil and is accumulated in different organs. Pb(II) is considered to be a general protoplasmic poison, which is cumulative, slow-acting and subtle. Soils contaminated

with Pb(II) cause a decrease in crop productivity, thereby posing a serious problem for agriculture.⁴

On the other hand, Pb(II) is very harmful to human health. Lead is a very strong poison. When a person swallows a lead object or inhales lead dust, some of the poison can stay in the body and cause serious health problems. A single high, toxic dose of lead can cause severe emergency symptoms. However, it is more common for lead to build up slowly over time. This occurs as a result of chronic exposure to small amounts of lead. In this case, there may not be any obvious symptoms, but lead can still cause serious health problems over time, such as difficulty in sleeping or lowered IQ in children. Lead is much more harmful to children than adults because it can affect children's developing nerves and brains. The younger the child, the more harmful lead can be. Unborn children are the most vulnerable. Children get lead in their bodies when they put lead objects in their mouth,

* Corresponding author: *e-mail address:* salif@chemistry.ucl.ac.uk

especially if they swallow a lead object. They can even get lead poison on their fingers by touching a dusty or peeling a lead object, and then putting their fingers in their mouth or eating food afterward. Tiny amounts of lead can also be inhaled.^{5,6}

The lack of knowledge of the chemistry arising through the interaction between Pb(II) and O- and N-containing substrates, and the absence of crystallographically characterized Pb(II)-dicarboxylates species prompted us to pursue the relevant synthetic chemistry in aqueous solutions. In this work, we report on the synthesis, spectroscopic and structural characterization of some new compounds isolated from aqueous solutions.

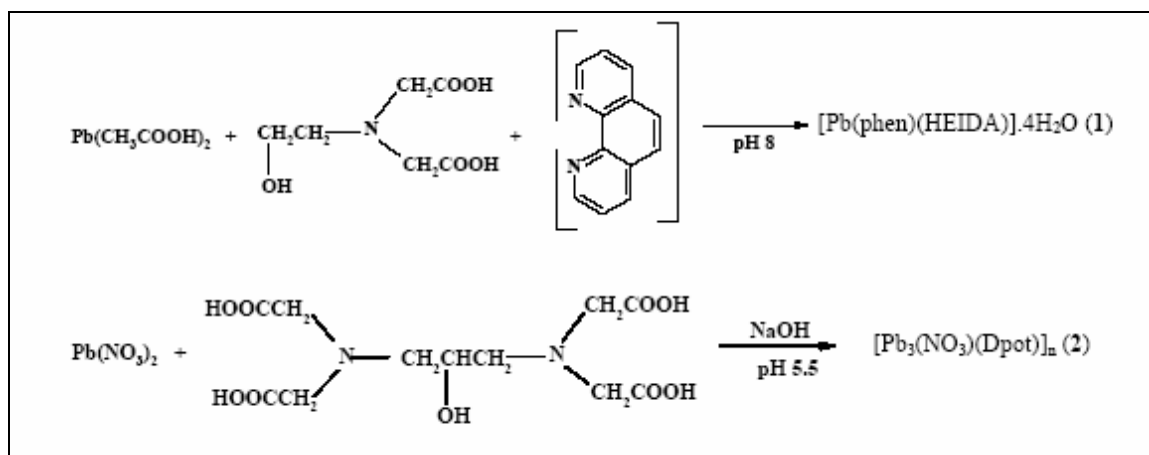
Experimental Section

We investigated the aqueous chemistry of Pb(II) with two different substrates 2-

hydroxyethyl-iminodiacetic acid (HEIDA) and 1,3-diamino-2-propanol-N,N,N,N-tetraacetic acid, from which two new species were isolated.

The synthesis of the new species of Pb(II) was carried out in aqueous media, with the use of simple reagents. Specifically the reaction between $\text{Pb}(\text{CH}_3\text{COOH})_2$ and 2-hydroxyethyl-iminodiacetic acid (HEIDA) in aqueous media at pH~8 and hydrothermal conditions led to the isolation of a colorless crystalline material with molecular formula $[\text{Pb}(\text{phen})(\text{HEIDA})] \cdot 4\text{H}_2\text{O}$ (**1**).

In a similar way the reaction of $\text{Pb}(\text{NO}_3)_2$ and 1,3-diamino-2-propanol-N,N,N,N-tetraacetic acid (Dpot) in aqueous media in the pH~4.5 and hydrothermal conditions led to the isolation of a colorless crystalline material with a molecular formula $[\text{Pb}_3(\text{NO}_3)(\text{Dpot})]_n$ (**2**).



Results and Discussion

The synthesized complexes were well characterized by elemental analysis, FT-IR spectroscopy and X-Ray crystallography.

The FT-IR spectra of the complexes were recorded in KBr and reflected the presence of vibrationally active carboxylate groups. Specifically, antisymmetric stretching vibrations $\nu_{\text{as}}(\text{COO}^-)$ were present for the carboxylate carbonyls in the range 11583-1518 cm^{-1} for (**1**) and at 1573 cm^{-1} for (**2**), respectively. Symmetric vibrations $\nu_{\text{s}}(\text{COO}^-)$ for the same groups were present around 1404-1332 cm^{-1} for (**1**) and in the range of 1453-1283 cm^{-1} for (**2**).

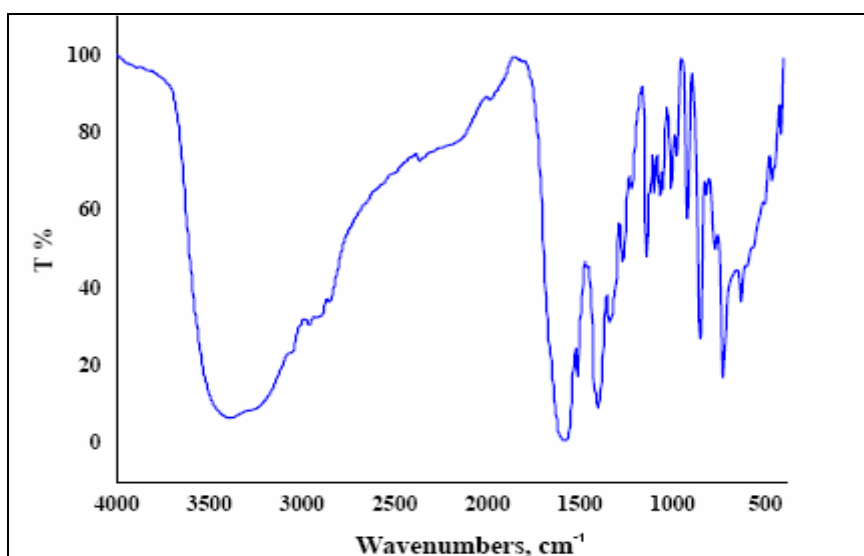


Figure 1: FT-IR spectrum of 1

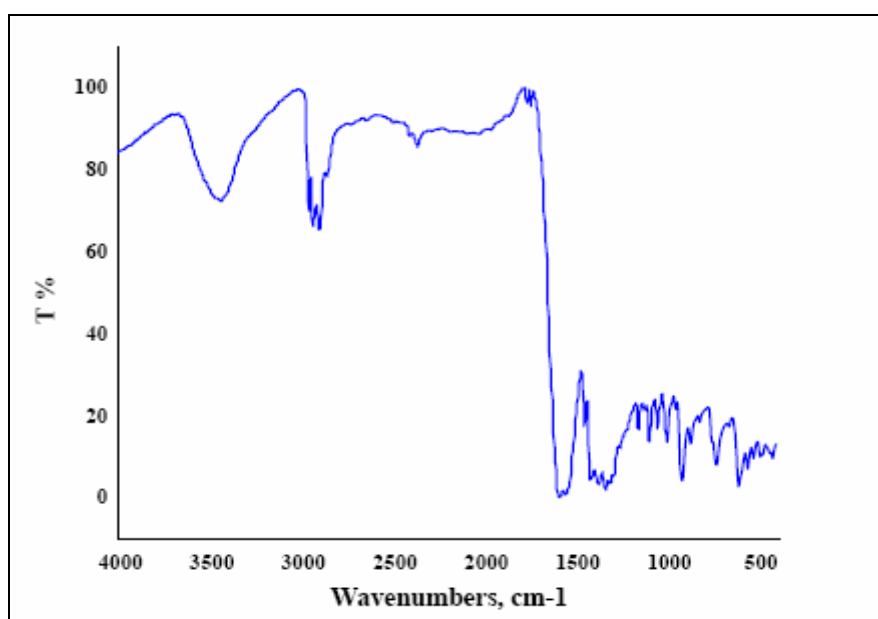


Figure 2: FT-IR spectrum of 2

Conclusions

- In this work we investigated the aqueous chemistry of Pb(II) with two different O- and N-substrates.
- The result of this reaction was the isolation of two new crystalline materials. One of them is mononuclear moiety [Pb(phen)(HEIDA)].4H₂O (**1**) and the other one is a polymer [Pb₃(NO₃)(Dpot)]_n (**2**).
- The use of 1,10-phenanthroline was very important because it was not only used in order to adjust the pH of the reaction mixture, but it also coordinated with the metal ion, Pb(II), and influenced the structure lattice of the new material.
- It is very important to use other cations like neocuproin or 2,2 bipyridyl instead of 1,10-phenanthroline to investigate the synthetic reaction mixtures of Pb(II).

- Finally we must emphasize the fact the N-moiety is coordinated to the metal ion of Pb(II), and this can lead us to the use of other Ncontaining substrates and the nvestigation of their interaction with Pb(II).

Acknowledgments

This work was supported by a “PENED” grant co-financed by the E.U. European Social Fund (75%) and the Greek Ministry of Development-GSRT (25%).

References

1. *Risk based standards for arsenic, lead, and cadmium in urban soils*. Edited by Chaney R. L., and Ryan J. A Dechema, Frankfurt, Germany, 1994.
2. Yang, Y-Y.; Jung, J-Y.; Song, W-Y.; Suh. H. S. ; Lee, L. *Plant Physiol.* **2000**,*124*, 1019-1026
3. De Abreu. C. A.; De Abreu. M. F.; De Andrade. J. C. *Bragantia* **1998**, *57*, 185-192
4. Johnson. M. S.; Eaton. J. W. *J. Environ. Qual.* **1980**, *9*, 175-179
5. Chen. A.; Dietrick. K. N.; Ware. J.H. *Environ Health Perspect.* **2005** *113(5)*,597-601.
6. Tong. S.; et al. *Bull World Health Organ.* **2000**, *78(9)*, 1068-1077.