Aqueous synthetic chemistry of Pb(II) with dicarboxylic acids

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Abstract

Contamination of soils by heavy metals is a widespread event throughout the globe because of human, agricultural and industrial activities. Among heavy metals, lead is a formidable pollutant that readily accumulates in soils and sediments. In this research work, we investigated the aqueous chemistry of Pb(II) with dicarboxylic acids, such as malic acid, maleic acid and fumaric acid. Through hydrothermal synthesis new species \([\text{Pb}_2(\text{Phen})_4(\text{fumarate})](\text{NO}_3)\)\(_2\)\(\cdot\)6\(\text{H}_2\text{O}\) (1), \([\text{Pb}_2(\text{Phen})_4(\text{fumarate})(\text{CO}_3)]\)\(\cdot\)3\(\text{H}_2\text{O}\) (2), and \([\text{Pb}_2(\text{Phen})(\text{fumarate})]n\) (3) were isolated and characterized by FT-IR spectroscopy and X-Ray crystallography.

Keywords: Lead, maleic acid, malic acid, fumaric acid, plant toxicity

1. Introducere

Lead (Pb) is one of the major heavy metals that has gained considerable importance as a potent environmental pollutant. Apart from natural weathering processes, Pb(II) contamination of the environment has occurred from mining and smelting activities, lead- containing paints, gasoline, explosives and the disposal of municipal sewage sludge enriched in lead.\(^1\) As many forms of lead pollutants are frequently used in modern human life, soil contamination with Pb is not likely to decrease in the near future.\(^2\) A significant increase in the Pb content of cultivated soils has also been observed near industrial areas. Pb tends to accumulate on the surface ground layer and its concentration decreases with soil depth.\(^3\) Pb(II) is easily taken up by plants from the soil and is accumulated in different organs. Pb is considered a general protoplasmic poison, which is cumulative, slow acting and subtle. Soils contaminated with Pb cause a decrease in crop productivity thereby posing a serious problem for agriculture.

On the other hand, Pb 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 pathological symptoms. However, it is more common for lead poisoning to build up slowly over time. This occurs from repeated exposure to small amounts of lead. In this case, there may not be any obvious symptoms, but the lead can still cause serious health problems in the long term, such as sleeping disorder or lowered IQ in children. Lead is much more harmful to children than adults are because it can affect children's developing nervous system and brain. 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, especially if they swallow the lead object. They can even get lead poison on their fingers from touching a dusty or peeling lead object, and then putting their fingers in their mouth or eating food afterward. Tiny amounts of lead can also be inhaled. The lack of knowledge of the chemistry involved with the interaction between Pb(II) and dicarboxylates and the absence of crystallographically charac-
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.

2. Materials and methods

We investigated the aqueous chemistry of the ternary systems Pb(II)-phenanthroline-malic, maleic and fumaric acid systems

\[ \text{Pb(NO}_3\text{)_2} + 2\text{ Malic} \xrightarrow{\text{NaOH, pH 8.5}} \text{[Pb}_2\text{(Phen)}_4\text{(fumarate)}\text{(NO}_3\text{)_2}]_2 } \]

In the same fashion, two more reactions took place, but instead of Pb(NO\textsubscript{3})\textsubscript{2}, Pb(CH\textsubscript{3}COO)\textsubscript{2} was used with maleic and fumaric acid respectively. The reactions leading to complexes 2 and 3 are shown schematically below:

\[ \text{Pb(CH}_3\text{COO)}_2 + 2\text{ Maleic} \xrightarrow{\text{NaOH, pH 9}} \text{[Pb}_2\text{(Phen)}_4\text{(CO}_3\text{)}_3\text{(fumarate)}\text{]}_2\text{6H}_2\text{O} \]

3. Results and discussions

The synthesized complexes were well characterized by elemental analysis, X-Ray crystallography and FT-IR spectroscopy. The structures of the complexes \([\text{Pb}_2\text{(Phen)}_4\text{(fumarate)}\text{(CO}_3\text{)}_3\text{]}_2\text{(NO}_3\text{)_2} \), \([\text{Pb}_2\text{(Phen)}_4\text{(fumarate)}\text{(CO}_3\text{)}_3\text{]}_2\text{6H}_2\text{O} \), and \([\text{Pb}_2\text{(Phen)}_4\text{(fumarate)}\text{]}_n \) reveal the presence of variable lattices, each with its own characteristic features, denoting a) the chemical reactivity of Pb(II), and b) its ability to get involved in chemistries leading to transformations of various dicarboxylic acids into fumarate. The arisen fumarate is eventually incorporated into diversely assembled solid-state lattices of Pb(II).

4. Conclusions

- Although three different dicarboxylic acids were used in the synthetic investigation, the isolated complexes contained the same ligand, i.e. fumarate.
- In the case of (1), lead facilitated the conversion of malic acid, a α-hydroxycarboxylic acid, into fumaric acid, through dehydration.
- In the case of (2), lead turned maleic acid, a trans isomer, into fumaric acid, the cis- isomer, of the same ligand.
- In the case (3), fumaric acid stayed intact.
- In all three cases, phenanthroline was coordinated in a different way to Pb(II).
- The first and the second species are dimers of lead, fumarate and phenanthroline, with the difference being that in the first compound NO\textsubscript{3}\textsuperscript{-} anions were present, whereas in the second case CO\textsubscript{3}\textsuperscript{2-} anions were presenting the lattice.
- The third compound is a polymer with two different moieties of lead atoms.
• The reasons for all the diverse chemical reactivity observed for Pb(II) is a matter of ongoing investigation in our lab.

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References