Short Communication



# Chemical speciation of binary complexes of Pb(II), Hg(II) and Cd(II) with 2-(1,5-Dimethyl-4-hexenyl)-3-hydroxy-5-methyl-1,4-benzoquinone (Perezone), a Sesquiterpene


## Abstract

Binary complexes of Pb(II), Hg(II) and Cd(II) with 2-(1,5-Dimethyl-4-hexenyl)-3-hydroxy-5-methyl-1,4-benzoquinone are reported. Their chemical composition and geometries are supported by elemental analysis and infrared spectroscopy studies. The lead metal content was estimated by flame atomic absorption method. The mercury metal content was estimated by preparing the metallic hydrides using the "cold vapor" atomic absorption technique. Finally, the cadmium metal content was estimated by the calcination, formation of the respective oxide and determined by flame atomic absorption spectrometry method.


**Keywords:** natural product, toxic metals, chelation therapy, heavy metal toxicity

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## Introduction

As a global problem, the potential health effects of metallic hazards should be a matter of public health concern, especially if the emissions of toxic metals into the environment continue at the current rate.[1] Lead has been known since ancient times. Although lead makes up only about 0.0013% of the earth's crust, it is not considered to be a rare element since it is easily mined and refined. Lead affects every organ of the body, especially the bones and teeth, the kidneys, the nervous, cardiovascular, immune and reproductive systems.[2] Lead and other heavy metals create reactive radicals which damage cell structures including DNA and membranes.[3] Mercury is the 80th element of the Periodic table of elements. Mercury exists in three forms: Hg° (zero valent), $Hg_2$II (Hg I) (monovalent) and HgII (divalent). Our daily intake is less than 0.01 milligrams (about 0.3 grams in a lifetime), and this we can cope with easily. However, in much higher doses it is toxic such as methylmercury is particularly dangerous. Mercury affects the immune system, alters genetics and enzyme systems, and damages the nervous systems, and the senses of touch, taste and vision.[4] Cadmium enters the environment through volcanic activity and forest fires.[5] Cadmium affects different kinds of organisms, ranging from microbes to humans. Human exposure to cadmium mainly occurs through cigarette smoking, but exposure can also occur through contaminated food, water or air.[6]. Cadmium is a known carcinogen to mammals.[7] Cadmium accumulates in plants, where it is detoxified by binding to phytochelatins,[8] a family of thiol-rich peptides. Perezone was first reported in 1852 by Leopoldo Río de la Loza[9] and the roots of Acourtia cuernavacana is used in laxative drinks, as a diuretic, analgesic, as a hypoglycemic.[10] The structure of perezone was determined by using NMR spectroscopic methods.[11] and its crystal structure was reported in 1986.[12] The main objective of this paper is to provoke and stimulate debate on the health effects of long-term, low-level exposure of human populations to toxic metals. Herein we report on the synthesis and spectroscopic characterization of Pb(II), Hg(II) and Cd(II) complexes of perezone in the solid state, in order to understand the molecular mechanism involve in the elimination of toxic metals in animals.

## Materials and methods

### Materials

All chemicals were available commercially and the solvents were purified as conventional methods before use.[13] Perezone was isolated from dry roots of *Acourtia cuernavacana* spp, and extracted three times by using maceration with hexane at room temperature. As a result orange crystals were obtained. Purity was checked by single spot test.

### Preparation of of binary complexes of Pb(II), Hg(II) and Cd(II) with Perezone

**Compound Pb-Perezone:** The solid lead-perezone complex was prepared by using a glass beaker of 250mL containing 25mL of 1mmol of alcoholic perezone solution with 25mL of 1mmol aqueous lead acetate. The addition of lead acetate solution was slowly with continuous stirring at room temperature for 1h. The presence of an excess of perezone in the flask is separated by a decanting process. A dark brown powder was formed in the beaker. The precipitated complexes were separated by filtration and the excess metal acetate was removed by three times washing with 10mL of deionized water. The complex was finally dried at room temperature. The powder was collected using a plastic spatula and the Pb-perezone complex is ready for the spectroscopic analysis.

**Compound Hg-perezone:** The solid mercury-perezone complex was prepared by using a glass beaker of 150mL containing 25mL of 1mmol of 1mmol aqueous solution of mercury acetate and adding 10mL of 1mmol alcoholic perezone solution. The addition of mercury acetate solution was slowly with continuous stirring at room temperature until the brick red was formed in the glass beaker. The product is rested for 12 hours. The precipitated complexes were separated by filtration and the excess metal acetate was removed by three times washing with 10mL of deionized water. The complex was finally dried at room temperature. The powder was collected using a plastic spatula and the Hg-perezone complex is ready for the spectroscopic analysis.

**Compound Cd-perezone:** The solid cadmium-perezone complex was prepared by using a glass beaker of 150mL containing 25mL of 1mmol aqueous cadmium acetate. Then, adding 15mL 1mmol of alcoholic perezone solution. The addition was slowly and continuous stirring with the help of a solid glass stirrer and the beaker glass surface during 5 minutes, a dark green precipitated was formed. The excess of perezone in the beaker is separated by a decanting process. The precipitated complexes were separated by using a vacuum filtration process and the excess metal acetate was removed by three times washing with 10mL of deionized water. The complex was finally dried at room temperature. The powder was collected using a plastic spatula and the Cd-perezone complex is ready for the spectroscopic analysis.

## Results

Keeping in view the applications of perezone complexes, we describe the synthesis, their chemical composition and geometries are supported by elemental analysis and infrared spectroscopy of binary complexes of Pb(II), Hg(II) and Cd(II) with perezone. The bonding of the metals (Pb, Hg and Cd) to the ligand is studied by comparing the IR spectrum of the ligand with those of the complexes. In the ligand spectrum, bands at 3304.6, 1626.8 and 1283.3 cm-1 are due to intramolecular hydrogen bonded of hydroxyl group at position 3 and the carbonyl oxygen at position 4, the υC=O) and υC-O), respectively. The spectra of the complexes in comparison show shifts in the above mentioned bands due to coordination to Pb and Cd ions. The band due to presence of an intramolecular hydrogen bond involving the hydroxyl group disappears in the spectra of the complexes as a result of the coordination to the metal ion through the oxygen atom of the hydroxyl and abstraction of protons.[14] In the complex of Pb(II), Hg(II) and Cd(II) bands at 3391.0, 2922.9 and 3303 cm-1 respectively are assigned in the stretching modes of coordinated water molecules. The bands at 608.6, 595.8 and 713.9 cm-1 are due to υPb-O), υHg-O) and υCd-O) stretching modes. The color, elemental analysis and IR analysis results are given in Table 1 suggest a molecular formula $[M(C_{15}H_{19}O_3)_2 \cdot 2H_2O]$ where M = Pb(II), Hg(II) and Cd(II).

## Discussion

In the present work, the first three new binary complexes of Pb(II), Hg(II) and Cd(II) with Perezone were synthesized, and their color, elemental and IR spectral analysis of these complexes were determined. The experimental data suggest a molecular formula $[M(C_{15}H_{19}O_3)_2 \bullet 2H_2O]$ where M=Pb(II), Hg(II) and Cd(II). The proposed geometries of the Pb, Hg and Cd complexes contain two ligand molecules and two water molecules arranged around a central metal atom defining the vertices of a distorted octahedron.

**Table 1** Colour, Elemental Analysis, and IR spectral analysis of the complexes

| Complex | Color | Elemental analysis (Calc./Found[a]) | | | IR Spectral bands ($cm^{-1}$) | | |
|---|---|---|---|---|---|---|---|
| | | C | H | M | υ (C=O) | υ (C-O) | υ (M-O) |
| $Pb(C_{15}H_{19}O_3)_2$ | Dark brown | 59.0/59.1 | 6.6/6.5 | 29.5/30.4 | 1550.3 | 1282.4 | 608.6 |
| $Hg(C_{15}H_{19}O_3)_2$ | Brick red | 59.1/60.4 | 7.0/6.9 | 28.9/30.4 | 1553.2 | 1281.9 | 595.8 |
| $Cd(C_{15}H_{19}O_3)_2$ | Green | 60.5/60.1 | 8.2/8.2 | 18.5/21.0 | 1549.9 | 1282.1 | 713.9 |

Each value corresponds to an average of 5 determinations.

## Conclusion

This work brings some useful experimental evidence regarding the molecular interaction between three toxic metal ions (Pb, Hg and Cd) with a Mexican natural product which may provide an incentive to understanding the mechanism of elimination of toxic metals present in the outdoors air pollution in the cities.

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## Conflicts of interest

Do not exists any financial or conflict of interest.

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