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## Structure and spectroscopic studies of homo- and heterometallic complexes of adipic acid dihydrazide



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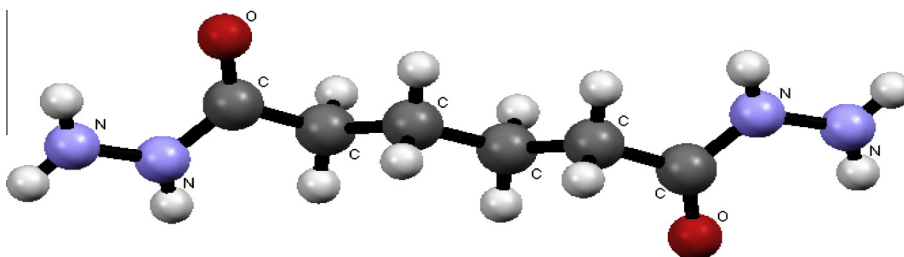
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### HIGHLIGHTS

- Series of metal complexes of adipic acid dihydrazide with  $\text{Co}^{2+}$ ,  $\text{Ni}^{2+}$ ,  $\text{Cu}$ ,  $\text{Zn}^{2+}$ ,  $\text{Cd}^{2+}$ ,  $\text{Hg}^{2+}$ ,  $\text{Ag}^+$ ,  $\text{Pd}^{2+}$  and  $\text{Pt}^{2+}$ .
- XRD analysis of ADH.
- Identification of the structure of the formed complexes.
- Molecular modeling of the ligand and its metal complexes.

### GRAPHICAL ABSTRACT

The reactions between adipic acid dihydrazide and  $\text{Co}^{2+}$ ,  $\text{Ni}^{2+}$ ,  $\text{Cu}^{2+}$ ,  $\text{Zn}^{2+}$ ,  $\text{Cd}^{2+}$ ,  $\text{Hg}^{2+}$ ,  $\text{Ag}^+$ ,  $\text{Pd}^{2+}$  and/or  $\text{Pt}^{2+}$  salts produced homometallic and heterometallic complexes; X-ray crystal structure of ADH is solved and described.



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### ABSTRACT

A single crystal of adipic acid dihydrazide, ADH, has been analyzed. Its reaction with  $\text{Co}^{2+}$ ,  $\text{Ni}^{2+}$ ,  $\text{Cu}^{2+}$ ,  $\text{Zn}^{2+}$ ,  $\text{Cd}^{2+}$ ,  $\text{Hg}^{2+}$ ,  $\text{Ag}^+$ ,  $\text{Pd}^{2+}$  and/or  $\text{Pt}^{2+}$  gave homometallic and heterometallic complexes which are characterized by partial elemental analysis, spectra (MS, ESR,  $^1\text{H}$  NMR, electronic; IR), thermal analysis and magnetic measurements. Some complexes:  $\text{Zn}_{0.73}\text{Cu}(\text{ADH})\text{Cl}_4 \cdot \text{H}_2\text{O}$ ;  $\text{Zn}_{0.71}\text{Hg}_{0.36}(\text{ADH})\text{Cl}_4 \cdot \text{H}_2\text{O}$ ;  $\text{Zn}_{0.65}\text{Cd}_{0.46}(\text{ADH})\text{Cl}_4 \cdot \frac{1}{2}\text{H}_2\text{O}$ ;  $\text{Zn}_{0.75}\text{Co}_{0.41}(\text{ADH}-2\text{H})\text{Cl}_2 \cdot 3\text{H}_2\text{O}$ ;  $\text{Cd}_{0.85}\text{Co}_{0.43}(\text{ADH})\text{Cl}_4 \cdot \frac{1}{2}\text{EtOH}$  were isolated having nonstoichiometric metal ratios. The ligand behaves as a neutral (bidentate or tetradentate) and/or bidentate tetradentate. A square-pyramidal, square-planar and tetrahedral structures were proposed for the homo  $\text{Co}(\text{II})$ ,  $\text{Cu}(\text{II})$  and  $\text{Ni}(\text{II})$  complexes, respectively. A similar and different stereochemistry around each metal ion (tetrahedral + tetrahedral; tetrahedral + tetrahedral and/or tetrahedral + octahedral) was suggested for the heterometallic complexes. Some complexes were found highly stable with stability point  $>240^\circ\text{C}$ ; the most stable is  $[\text{HgNi}(\text{ADH}-2\text{H})\text{Cl}_2]$ . The presence of diamagnetic atom (Zn, Cd or Hg) reduces the magnetic moments and gave anomalous moments. The degradation steps and the hydrated complexes are confirmed through the TGA study. The order of covalency of  $[\text{Zn}_{0.73}\text{Cu}(\text{ADH})\text{Cl}_4] \cdot \text{H}_2\text{O}$ ,  $[\text{CdCu}(\text{ADH})\text{Cl}_4] \cdot \text{H}_2\text{O}$  and  $[\text{HgCu}(\text{ADH}-2\text{H})\text{Cl}_2]$  matches with the size of the second metal (Zn complex  $>$  Cd complex  $>$  Hg complex). Some heterometallic complexes were found nonstoichiometric through the analysis of their metal content and supported by TGA.

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### Introduction

Adipic acid dihydrazide [hexanedioic acid dihydrazide or adipodihydrazide] is a symmetrical molecule with a C4 backbone

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and two CONHNH<sub>2</sub> as reactive groups. It offers amino- and amido functionality at either end of the molecule which makes it an excellent cross-linking agent for water-based emulsions. It is also used as a hardener for certain epoxy resins and in adhesive and coating-manufacturing applications [1]. It is used to prepare active forms of originally neutral mannans from pathogenic yeasts (*Candida albicans*, *Candida tropicalis*, *Candida glabrata*). Significant cross-linking effect of ADH was revealed, despite the high excess of ADH involved in the reaction [2]. Isophthalic and sebacic dihydrazides are used in proteomics and protein chromatography. They were utilized for purification and identification of fungal phytotoxin Fusaricocin, identifying RNA binding proteins that interact with RNA cis-elements, and enzyme purification such as peroxisomes from guinea pig liver [1]. Solvation and complexation of Co(II), Ni(II) and Cu(II) with adipic acid dihydrazide in aqueous and non-aqueous solutions were studied spectrophotometry and their formation constants were determined [3]. N-(2-hydroxybenzylidene-2-aminophenol) (L<sub>2</sub>) and adipic acid dihydrazide (L) react with Cu<sup>2+</sup>, Ni<sup>2+</sup>, Co<sup>2+</sup>, UO<sub>2</sub><sup>2+</sup>, VO<sup>2+</sup> and Fe<sup>3+</sup> to yield ML<sub>2</sub>L·nH<sub>2</sub>O. L<sub>2</sub> behaves as a bidentate ligand coordinating through OH and NH<sub>2</sub>. Similarly, L behaves as a bidentate through N of both amino groups. The data reveal that the ligand was bound through O and N. The microbial activities of the complexes have been screened *in vitro* against *A. niger*, *A. flavus*, *S. aureus* and *E. coli* [4]. Periodate oxidation of sodium alginate was controlled to form isolatable beads with Ca<sup>2+</sup> ions. The beads were covalently cross linked with adipic acid dihydrazide (ADH) in addition to ionic cross links. SEM revealed that the beads were spherical having smooth surfaces. The drug entrapment efficiency decreased (90–86%) with increasing concentration of ADH (2–6% w/v) in the gelation medium. The beads prepared with 2% ADH swelled more rapidly and led to faster drug release in either pH 1.2 HCl solution or pH 7.2 phosphate buffer solution. The FTIR spectroscopy indicated stable nature of flurbiprofen in the beads and therefore had potential as sustained oral delivery system for the drug [5]. Heterometallic complexes of diacetylmonoxime thiosemicarbazone (H<sub>2</sub>L) with Ag<sup>+</sup>, Fe<sup>3+</sup>, Co<sup>2+</sup>, Ni<sup>2+</sup> and Cu<sup>2+</sup> individually and in combination with Ag<sup>+</sup> has been studied [6]. The ligand chelated as neutral in [Ag(H<sub>2</sub>L)(H<sub>2</sub>O)]NO<sub>3</sub>·H<sub>2</sub>O, [Ag<sub>2</sub>(H<sub>2</sub>L)<sub>2</sub>](NO<sub>3</sub>)<sub>2</sub>·H<sub>2</sub>O and [Ag<sub>2</sub>(H<sub>2</sub>L)(OH)]NO<sub>3</sub>; monobasic in [Co(HL)<sub>2</sub>·EtOH], [Fe(HL)<sub>2</sub>]NO<sub>3</sub>, [FeAg<sub>2</sub>(HL)<sub>2</sub>(NO<sub>3</sub>)<sub>2</sub>]NO<sub>3</sub>, and [Cu<sub>2</sub>(HL)<sub>2</sub>(EtOH)(NO<sub>3</sub>)<sub>2</sub>]NO<sub>3</sub>·EtOH and dibasic molecule in [Ni(L)(EtOH)], [NiAg<sub>2</sub>(L)(OAc)<sub>2</sub>(EtOH)], [NiAg<sub>2</sub>(L)(NO<sub>3</sub>(H<sub>2</sub>O)<sub>2</sub>]NO<sub>3</sub>, [Cu<sub>2</sub>Ag<sub>2</sub>(L)<sub>2</sub>(H<sub>2</sub>O)(NO<sub>3</sub>)<sub>2</sub>]NO<sub>3</sub> and [Cu<sub>2</sub>Ag<sub>2</sub>(L)<sub>2</sub>(H<sub>2</sub>O)<sub>3</sub>(OAc)<sub>2</sub>(NO<sub>3</sub>)<sub>2</sub>]NO<sub>3</sub>·H<sub>2</sub>O. The nitrates were investigated by IR spectra; ionic by a strong band at ≈ 1380 cm<sup>-1</sup> and coordinated by bands at ≈ 1440 and ≈ 1220 cm<sup>-1</sup>. Iron, cobalt, nickel and copper complexes of butylmalonyldihydrazide (H<sub>2</sub>BMD) have different (octahedral, tetrahedral and square-planar) geometries [7]. The coordination compounds containing carbonic, benzoic and m-hydroxybenzoic acids were characterized. Complexes with carbonic acid dihydrazides were classified depending on the M: DH ratio and the nature of the acido ligand. [8]. Transition metal complexes of mono-, di- and tetrahydrazides were prepared electrochemically by electrochemical oxidation of Co, Ni and Cu in acetone solution of benzoic, malonic and 1,1,3,3'-propanetetra-carbo hydrazides to form 1:2, 1:1, 2:1 and 4:1 (metal: ligand) ratios in good yields. When 1,10-phenanthroline or triphenylphosphine was present in solution, adducts were formed [9].

Up to date, no work was done on heterometallic complexes with adipic acid dihydrazide. The aim is to extend our early work on this type of complexes [10,11] and to prepare, characterize and confirm homo- and heterometallic complexes. Trials will be done to grow single crystals for these complexes.

## Experimental

CoCl<sub>2</sub>·6H<sub>2</sub>O, NiCl<sub>2</sub>·6H<sub>2</sub>O, CuCl<sub>2</sub>·2H<sub>2</sub>O, ZnCl<sub>2</sub>·2H<sub>2</sub>O, CdCl<sub>2</sub>·2H<sub>2</sub>O, HgCl<sub>2</sub>·2H<sub>2</sub>O, AgNO<sub>3</sub>, K<sub>2</sub>PdCl<sub>4</sub> and K<sub>2</sub>PtCl<sub>4</sub>, diethyladipate, hydrazine hydrate, ethanol, diethyl ether, DMF and DMSO were obtained from the BDH chemicals and used without additional purification.

### Synthesis of ADH

Adipic acid dihydrazide was prepared by heating 10 g (0.05 mol) of diethyladipate with 5.5 ml (0.1 mol) of hydrazine hydrate in 10 ml EtOH on a water bath for 3 h. Complete reaction is tested by TLC. The precipitate was filtered off, recrystallized from ethanol and dried. The ligand was characterized by spectral studies and elemental analysis. The <sup>1</sup>H NMR spectrum of the ligand (Fig. 1) gives different signals at δ = 8.922, 4.15, 2.07 and 1.42 ppm corresponding to the protons of NH (N<sub>9</sub>, N=, 2P), NH<sub>2</sub> (N<sub>10</sub>, N<sub>12</sub>, 4P), COCH<sub>2</sub>CH<sub>2</sub> (C<sub>2</sub>, C<sub>5</sub>, 4P) and CH<sub>2</sub>—CH<sub>2</sub>—CH<sub>2</sub> (C<sub>3</sub>, C<sub>4</sub>, 4P), respectively. Its <sup>13</sup>C NMR spectrum consists of different peaks at 171.91, 40.57, 33.671 and 25.24 due to the carbons of C=O, CH<sub>2</sub>CH<sub>2</sub>, CH<sub>2</sub>CO and CONH, respectively. Its elemental analyses are: Calcd (Found) [C = 41.37 (41.87), H = 8.10 (8.09) and N = 32.16 (31.33)] and FT-IR bands at 3315; 3290; 3180; 1630; 1533 and 1034 cm<sup>-1</sup> due to ν(NH<sub>2</sub>), νs(NH<sub>2</sub>); ν(NH); ν(C=O); amide II and ν(N—N), respectively. Its single crystal was grown by slow evaporation of its dichloromethane solution.

### Preparation of the complexes

The homometallic complexes were prepared by heating under reflux a mixture of the ligand (0.174 g; 1 mmol), in 30 ml absolute ethanol, and the metal salt (2 mmol), in 20 ml absolute ethanol on a water bath for 2–4 h.

The heterometallic complexes were prepared by heating the same mixture on a water bath for 4–6 h but in the presence of 1 mmol of the second metal salt in 20 ml absolute ethanol. In case of AgNO<sub>3</sub>, it dissolved in 10 ml bidistilled water and the reaction takes place in a round flask surrounded with aluminum foil. As example, ZnNi(ADH)Cl<sub>4</sub>·2EtOH·4H<sub>2</sub>O was prepared as: to 100 ml reaction flask, 0.348 g (2 mmol) of ADH, in 30 ml ethanol, and 0.474 g (2 mmol) of NiCl<sub>2</sub>·6H<sub>2</sub>O, in 20 ml ethanol were added and heated on a water bath for 5 min, then 0.344 g (2 mmol) of ZnCl<sub>2</sub>·2H<sub>2</sub>O, in 20 ml ethanol, was added and the reaction mixture was heated for 4 h. The green precipitate thus formed was removed by filtration, washed with EtOH and then dried at 80 °C. Cd(ADH)(NO<sub>3</sub>)<sub>2</sub> was isolated during the preparation of heterometallic complex containing Cd and Ag by reacting Cd(NO<sub>3</sub>)<sub>2</sub>·2H<sub>2</sub>O (0.272 g, 1 mmol) and AgNO<sub>3</sub> (0.17 g, 1 mmol) in 20 ml H<sub>2</sub>O with 0.35 g (2 mmol) of ADH, in 30 ml ethanol. A white precipitate is formed after washing several times by hot water. The analysis of the formed complex gave the above stoichiometry. The preparation of [Cd<sub>3</sub>(ADH)Cl<sub>6</sub>] proceeds through the addition of 0.174 g of ADH to 0.27 g of Cd(NO<sub>3</sub>)<sub>2</sub>·2H<sub>2</sub>O in 50 ml ethanol.

Trials to grow single crystals for all complexes in DMSO solution (most are easily soluble) but failed because powdered were formed in this solvent. More effort will be done with changing the solvent.

### Equipment and analysis

The elemental analysis of ADH and its complexes was determined at the Microanalytical Unit (VarianMicro V1.5.8, CHNS Mode, 15073036) of Kuwait University, Kuwait. The metal content was determined using ICP-OES GBC Quantum Sequential. The IR

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