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Solution and structural studies of the Cd(II) – Aconitate system

George E. Kostakis [a,b,d,*], Gerasimos Malandrinos [a,*], Ebbe Nordlander [b], Matti Haukka [c], John C. Plakatouras [a]

[a] *Department of Chemistry, University of Ioannina, 451 10 Ioannina, Greece*
[b] *Inorganic Chemistry Research Group, Chemical Physics, Center for Chemistry and Chemical Engineering, Lund University, Box 124, SE-221 00 Lund, Sweden*
[c] *Department of Chemistry, University of Joensuu, P.O. Box 111, FIN-80101 Joensuu, Finland*
[d] *Institut für Anorganische Chemie der Universität Karlsruhe, Engessertsr. Geb. 30.45, D-76131 Karlsruhe, Germany*

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This work is dedicated to Dr. Aris Terzis on the occasion of his retirement.

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ABSTRACT

The complexing ability of the binary system *trans*-aconitic acid (H_3L) with regard to Cd(II) and the crystal structures of the binary system Cd(II)–(H_3L), $[Cd_3L_2(H_2O)_6]$ n(**1**) and ternary systems of Cd(II)–(H_3L)–Lewis base [Lewis base = 1,10-phenanthroline (**2**) and 2,2′-bipyridine (**3**)] have been determined. Compound **1** is a rare binodal four-connected three-dimensional (3D) metal-organic framework possessing a moganite (**mog**) topology. Compounds **2** and **3** represent infinite one-dimensional (1D) chains forming three-dimensional metal-supramolecular structures through H-bond and π–π stacking interactions. All compounds have been characterized by spectroscopic and thermogravimetric techniques.

1. Introduction

Cadmium belongs to a group of heavy metals ions that has gradually attracted increased attention over the years, due to the revelation of the toxicity of its complexes that initiates carcinogenesis and teratogenesis in humans [1], e.g. Itai–Itai, proteinuria, aminoaciduria diseases, and also affects plants [2]. Cd(II) is largely associated with Zn(II), and a number of its toxic effects are believed to arise from the competitive binding of Cd(II) to zinc-binding proteins [3]. As a toxic metal, Cd(II) is absorbed by the liver, ultimately finding its way to the kidney, in which metallothioneins strongly bind cadmium with Cd–S bonds in order to remove it from the organism. A concentration of 200 μg Cd/gr is crucial, in order to cause damage to the kidney or the liver. The exact mechanism(s) by which Cd(II) toxicity arises still remain(s) unknown.

trans-Aconitic acid (H_3L) is an isomer of *cis*-aconitic acid that has been found to be a competitive inhibitor of aconitase in the Krebs cycle [4], and the mechanism of its action is still unclear. Recently, it has been found that the methyl esterification of *trans*-aconitate significantly reduces its ability to inhibit aconitase activity [5]. In the solid state, *trans*-1,2,3-propenetricarboxylic acid (H_3L), a small flexible open chain tricarboxylate, has been used as hydrogen-bonding building block [6–8] and for the preparation of metal-organic frameworks [9–12]. In particular, it was found that *trans*-aconitate in its dianionic or trianionic forms behaves as a μ_3-, μ_4-, or μ_5-ligand in different coordination modes, leading to polymeric complexes.

To date, in the solution state no information exists on the complexing ability of *trans*-aconitic acid in solution. Moreover, Cd(II) is a labile metal center with a large ionic radius and flexible coordination environment so that geometries can vary; consequently, severe distortions of the ideal coordination polyhedra occur easily.

Previous studies have shown that the small flexible tricarboxylic acids, *trans*-aconitic acid [12] and tricarballylic acid [13] in reactions with Zn(II) in the presence of chelating Lewis bases, lead to the formation of multidimensional metal organic networks or 3D metal-supramolecular architectures through H-bonding and stacking interactions.

Bearing this in mind and continuing our growing interest in the coordination behavior of flexible polycarboxylic acids, we here present a study of the complexing ability of *trans*-aconitic acid (H_3L) with respect to Cd(II), and the synthesis, isolation, spectroscopic, thermal and X-ray structural characterization of $[Cd_3L_2(H_2O)_6]_\infty$ (**1**), as well as of two *trans*-aconitate bridged 1D coordination polymers $\{[Cd(HL)(phen)(H_2O)]_n \cdot n(H_2O)\}$ (**2**) and $\{[Cd(HL)(bpy)(H_2O)]_n \cdot n(H_2O)\}$ (**3**). In the binary system, correlation between its behavior in the solid state and in solution with that of species arising from solution speciation studies may be made. The

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[*] Corresponding authors. Present address: Institut für Anorganische Chemie der, Universität Karlsruhe, Engessertsr. Geb. 30.45, D-76131 Karlsruhe, Germany. Tel.: +49 724 782 8920 (G.E. Kostakis).

E-mail address: kostakis@aoc.uni-karlsruhe.de (G.E. Kostakis).

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present work is an extension of our research efforts on coordination polymers [12,14–20] and hydrogen-bonded frameworks [21,22].

2. Experimental

2.1. General

All reagents and solvents were of commercially available reagent quality unless otherwise stated. All reactions were performed at room temperature and no special conditions were required.

2.2. Instrumentation

^{13}C and ^{113}Cd NMR spectra were recorded on a Bruker AMX 400 MHz spectrometer. For ^{113}Cd NMR spectra a 0.1 M $Cd(NO_3)_2{\cdot}4H_2O$ solution was used as an external standard. The samples for solution NMR studies were prepared by dissolving $Cd(NO_3)_2{\cdot}4H_2O$ and *trans*-aconitic acid in D_2O; the pH of the D_2O solutions was adjusted with NaOD. Mass spectra were measured on an Agilent 1100 series LC-MSD-TRAP-SL-Spectrometer. The samples for ESI-MS spectra were prepared by dissolving $Cd(NO_3)_2{\cdot}4H_2O$ and *trans*-aconitic acid in a solvent mixture (H_2O/CH_3CN: 90/10) and the pH of the solutions was adjusted using NaOH. The FT-IR spectra were recorded on a Perkin–Elmer Spectrum GX FT-IR spectrophotometer with the samples as KBr pellets. The TG-DTA analysis was carried out under nitrogen, at a scan speed of 5 °C/min, on a Shimadzu DTG 60 apparatus. The weight of the samples was about 5 mg. C, H and N analyses were conducted by Microanalytical Service at the University of Ioannina, Greece.

2.3. Potentiometry

Potentiometric titrations of free ligand (H_3L) and its complexes with Cd(II) ions were carried out at 25 °C, using a total volume of 10.0 mL. The titrations were performed in the presence of 0.1 M KNO_3 over the pH range 2–8 on a Mettler Toledo DL50 automatic titrator and a combined glass-silver chloride electrode calibrated in hydrogen concentrations using HNO_3 [23]. About 0.1 M KOH was used as titrant. The concentrations of *trans*-aconitic acid and the metal ion was 4 mM at a1:1 metal:ligand molar ratio. The experimental data were analyzed using the HYPERQUAD program [24]. Standard deviations computed by HYPERQUAD refer to random errors.

2.4. Preparation of the compounds

2.4.1. Synthesis of $[Cd_3L_2(H_2O)_6]_n$ (**1**)

$Cd(NO_3)_2{\cdot}4H_2O$ (46.4 mg, 0.15 mmol) was dissolved in H_2O (4 mL). To this, an aqueous solution of *trans*-aconitic acid (17.4 mg, 0.1 mmol), was added. The pH of the resulting solution was adjusted to 6.2. This molecular ratio affords the optimum yield for compound **1**. A microcrystalline powder was formed after 1 h, it was collected and washed with ethanol and diethyl ether, and dried in vacuum. Yield 80% (31.4 mg based on L). For the preparation of a suitable sample for crystallographic analysis 1.7 mg of *trans*-aconitic acid were dissolved in 6 mL H_2O. To this solution, 4.64 mg of $Cd(NO_3)_2{\cdot}4\,H_2O$ (dissolved in 4 mL H_2O) was added. The resulting solution was left undisturbed for slow evaporation. The first crop of colourless crystals was isolated after 5 days; a second crop of crystals isolated after 3 weeks. *Anal.* Calc. for $C_{12}H_{18}O_{18}Cd_3$, (**1**): C, 18.30; H, 2.30. Found: C, 17.96; H, 2.22%. IR (KBr, cm^{-1}) = 3448 (s), 2965 (w), 2925 (w), 1638 (m), 1564 (s), 1400 (s), 1307 (w), 1264 (m), 1222 (w), 1106 (w), 964 (w), 941 (m), 887 (m), 791 (m), 700 (m).

2.4.2. Synthesis of $\{[Cd(HL)(1,10\text{-phen})(H_2O)]_n{\cdot}n(H_2O)\}$ (**2**)

$Cd(NO_3)_2{\cdot}3H_2O$ (46.4 mg, 0.15 mmol) was dissolved in H_2O (4 mL). To this, a solution of 1,10-phenanthroline (15 mg, 0.075 mmol) in hot H_2O (1 mL), was added. Separately, *trans*-aconitic acid, (17.4 mg, 0.1 mmol) was dissolved in water (5 mL) and was added to the metal solution. The resulting solution was left undisturbed for slow evaporation. The first crop of colorless crystals was isolated after 5 days; a second crop of colorless crystals was isolated after 1 week. Yield 75% (28.1 mg based on phen). *Anal.* Calc. for $C_{18}H_{16}N_2O_8Cd$, (**2**): C, 43.03; H, 3.21; N, 5.58. Found: C, 42.96; H, 3.18; N, 5.45%. IR (KBr, cm^{-1}) = 3448 (s), 3071 (m), 2992 (w), 2607 (w) (–OH), 1700 (m) (–COOH), 1649 (m), 1567 (s), 1517 (m), 1411 (s), 1332 (m) [phen], 1294 (w), 1273 (w), 1210 (m) [phen], 1103 (m), 924 (w), 848 (m) [phen], 801 (w), 727 (m) [phen].

2.4.3. Synthesis of $\{[Cd(HL)(2,2'\text{-bipy})(H_2O)]_n{\cdot}n(H_2O)\}$ (**3**)

The synthesis of **3** was carried out as for **2** but using 2,2′-bipy instead of 1,10-phenanthroline. The formation of the colorless crystals was slower and the last crop of crystals was collected after almost 8 weeks. Overall yield: 72% (23 mg based on 2,2′-bipy). *Anal.* Calc. for $C_{16}H_{16}N_2O_8Cd$, (**3**): C, 40.17; H, 3.37; N, 5.86. Found: C, 40.06; H, 3.33; N, 5.78%. IR (KBr, cm^{-1}) = 3425 (s), 3296 (m), 3072 (w), 2983 (w), 2951 (w), 2604 (w) (–OH), 1703 (m) (–COOH), 1639 (m), 1576 (s), 1475 (m), 1438 (m), 1377 (s), 1317 (w), 1210 (m), 1171 (m), 1077 (w), 1016 (m), 851 (w), 770 (m).

2.5. X-ray crystallography

The crystals of **1–3** were immersed in cryo-oil, mounted in a Nylon loop, and measured at a temperature of 120 K. The X-ray diffraction data were collected on a Nonius KappaCCD diffractometer using Mo Kα radiation (λ = 0.71073 Å). The EVALCCD [25] program package was used for cell refinements and data reductions. The structures were solved by direct methods using the SIR92 [26] or SIR97 [27] programs with the WINGX [28] graphical user interface. A semi-empirical absorption correction (SADABS) [29] was applied to all data. Structures were refined using the SHELXL-97 program [30]. The H_2O and OH hydrogen atoms were located from the difference Fourier map but constrained to ride on their parent atom, with U_{iso} = 1.5. Other hydrogens were positioned geometrically and constrained to ride on their parent atoms, with C–H = 0.95–0.99 Å and $U_{iso} = 1.2U_{eq}$ (parent atom). The crystallographic details are summarized in Table 1 and selected bond lengths and angles in Tables 2 and 3.

3. Results and discussion

3.1. Description of the structures

The molecular structure of **1** is depicted in Fig. 1 and bond distances and angles are listed in Table 2. The crystal structure of **1** reveals the formation of a neutral 3D metal-organic framework $[Cd_3L_2(H_2O)_6]_n$. [31]. The formation of **1** has been reported under hydrothermal conditions [11]. There are two independent Cd(II) atoms in the asymmetric unit (Table 2). Cd(2) is coordinated to three oxygen atoms belonging to water molecules and three oxygen atoms of three different *trans*-aconitates, forming a distorted octahedral geometry. The three water molecules are placed around the centre in a meridional plane. Cd(1) is coordinated to eight oxygen atoms, which belong to two chelating and two chelating-bridging carboxylates with two elongated Cd(1)–O(6) distances of 2.671(2) Å. In the reported compound, the authors considered that Cd(1) is six coordinate and adopts a distorted octahedral geometry [11]. A detailed analysis of the molecular geometry reveals that