

Structural characterization of ladder-type cadmium(II) citrate complex, $(C_3H_{12}N_2)[\{Cd(H_2O)(C_6H_5O_7)\}_2] \cdot 6H_2O$

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Abstract: The title complex, $(C_3H_{12}N_2)[\{Cd(H_2O)(C_6H_5O_7)\}_2] \cdot 6H_2O$, **I**, has been prepared and its structure characterized by FT-IR, EDS, elemental analysis, ICP-AES, and X-ray single crystallography. It is triclinic system, $P\bar{1}$ space group with $a = 10.236(2)$, $b = 11.318(2)$, $c = 13.198(2)\text{\AA}$, $\alpha = 77.95(1)^\circ$, $\beta = 68.10(1)^\circ$, $\gamma = 78.12(1)^\circ$, $V = 1373.5(3)\text{\AA}^3$, $Z = 2$. Complex **I** has constituted by protonated 1,3-diaminopropane cations, citrate coordinated cadmium(II) anions, and free water molecules. The central cadmium atoms have a capped trigonal prism geometry by seven coordination with six oxygen atoms of three different citrate ligands and one water molecule. Citrate ligands are bridged to three different cadmium atoms. Each cadmium atom is linked by carboxylate and hydroxyl groups of citrate ligand to construct an one-dimensional ladder-type assembly structure. The polymeric crystal structure is stabilized by three-dimensional networks of the intermolecular O-H \cdots O and N-H \cdots O hydrogen-bonding interaction.

Key words : cadmium ion, citrate ligand, 1,3-diaminopropane, crystal structure, ladder-type assembly

1. Introduction

A category of heavy metal ions such as cadmium, lead, mercury, chromium and copper are well-known as toxic, carcinogenic and mutagenic agents, and giving a serious effect to human populations and various organisms.¹⁻³ Many industries such as electroplating, leather tanning, textile use heavy metals in the process of manufacturing. The wastes and waste waters from these industries contains some heavy metal ions. Therefore, the discharge of these metal ions into aquatic bodies and sources of drinking water must be strictly controlled.

The remediation methods for heavy-metal such as activated carbon adsorption, chemical precipitation, electrolytic treatment, *in situ* vitrification and biological treatment have been extensively explored.⁴⁻⁶ Chemical precipitation is one of the most efficient and cheap methods to remove heavy metal ions from waters and industrial residues. However, a considerable concentration of toxic heavy metals remains in wastewater after chemical treatments or precipitation processes. These traditional processes are not efficient enough to satisfy pollution control limits and have some disadvantages such as the need for excess chemicals for pH control.⁷

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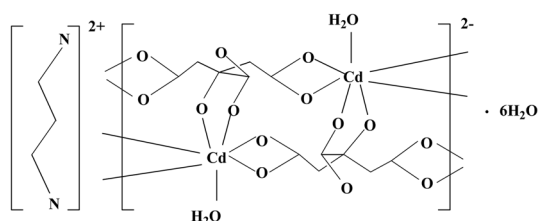


Fig. 1. Chemical structural diagram of complex I.

On the other hand, organic ligand process has a good capacity to remove heavy metals in wastewater comparing with that of traditional chemical treatment or precipitation process.⁸⁻¹⁰ Organic ligands can easily control the reaction selectivity between heavy metal ions by various functional groups and increase the stability of chelate complex formed by metal ions. As a strategy for development of novel heavy metal remediation agents, we have introduced organic ligands containing hard amine donor, carboxylate donor and/or soft thiolate donor.¹¹⁻¹⁴ Carboxylate ligands such as citric acid and tartaric acid are known to be useful as a various metal chelating agents. Herein, we report the preparation and structural characterization of the cadmium(II)-citrate complex, I, as shown in Fig. 1.

2. Experimental

2.1. Preparation and analysis of complex I

$\text{CdCl}_2 \cdot 2.5\text{H}_2\text{O}$ (1.14 g, 5 mmol) was dissolved in 25 mL aqueous solution. 1,3-diaminopropane (0.5 mL, 5 mmol) was added to this solution dropwise with stirring. The pH of mixture solution was adjusted to 8 by adding citric acid and 2-aminoethanol. A small amount of white precipitate was filtered off. The resulting solution was allowed to stand in a refrigerator at 5 °C. After a few weeks the colourless block crystals were obtained. *Calc. for* $\text{C}_{15}\text{H}_{38}\text{N}_2\text{O}_{22}\text{Cd}_2$: C 21.88, H 4.65, N 3.40, O 42.76, Cd 27.31 %. *Anal. Found*: C 21.55, H 4.55, N 3.74, O 38.50, Cd 27.23 %.

FT-IR spectrum of the crystal was recorded with a BioRad Digilab FTS-165 infrared spectrophotometer. The EDS spectrum obtained on an EDAX Phoenix energy-dispersive X-ray spectrometer with

Philips XL-30S FEG scanning electron microscope. The contents of the carbon, hydrogen, nitrogen, oxygen and cadmium were analyzed by CE EA-1110 elemental analyzer and Jobin-Yvon Ultima-C inductively coupled plasma-atomic emission spectrometer, respectively.

2.2. X-ray crystallography

A colourless block crystal of dimensions $0.38 \times 0.32 \times 0.18$ mm for the title complex was coated with epoxy glue in order to prevent spontaneous liberation of water molecules from the specimen under ambient conditions. The epoxy-coated crystal was mounted on a Bruker P4 four-circle X-ray diffractometer with graphite-monochromated Mo $K\alpha$ radiation ($\lambda = 0.71073$ Å). The intensity data were collected in the θ - 2θ scan mode with operating 50 kV, 30 mA at a temperature 291 ± 2 K. The cell parameters and orientation matrix were determined from the least-squares fit of 39 reflections in the θ range of 4.72 – 12.50° . Three standard reflections were measured every 97 reflections: no remarkable

Table 1. Crystallographic and experimental data for complex I

Formula	$\text{C}_{15}\text{H}_{38}\text{N}_2\text{O}_{22}\text{Cd}_2$
Formula weight	823.27
Crystal system	triclinic
Space group	$P\bar{1}$
<i>a</i> (Å)	10.236(2)
<i>b</i> (Å)	11.318(2)
<i>c</i> (Å)	13.198(2)
α (°)	77.95(1)
β (°)	68.10(1)
γ (°)	78.12(1)
<i>V</i> (Å ³)	1373.5(3)
<i>Z</i>	2
<i>D_c</i> (g/cm ³)	1.991
μ (Mo- $K\alpha$) (mm ⁻¹)	1.647
<i>F</i> (000)	828
θ range for data collection (°)	1.9–26.5
Index range	$-1 \leq h \leq 12$, $-13 \leq k \leq 14$, $-15 \leq l \leq 16$
Reflections collected	6648
Independent reflections	5665 [$R_{\text{int}} = 0.0193$]
Data/restraints/parameters	5665/0/420
Goodness-of-fit on F^2	1.093
Final <i>R</i> indices [$I > 2\sigma(I)$]	$R_1 = 0.0296$, $wR_2 = 0.0809$

decays were observed throughout data collection. Lorentz and polarization corrections were applied to the intensity data, and a semi-empirical absorption correction based on the psi-scans was applied.¹⁵

All calculations in the structural solution and refinement were performed using the Bruker SHELXTL crystallographic software package.¹⁶ The structure was solved by the direct method and refined by successive full-matrix least-squares method followed by difference Fourier maps. All the non-

hydrogen atoms were refined anisotropically; all the hydrogen atoms were put into calculated positions with the isotropic thermal parameters. Final difference of electron density maps contained no significant features.

3. Results and Discussion

The characteristic peaks of the citrate, 1,3-diaminopropane, and water molecules were assigned

Table 2. Selected bond lengths (Å) and angles (°) for complex I

Cd(1)-Ow1	2.298(2)	Cd(1)-O(5)	2.503(2)
Cd(1)-O(6)	2.297(2)	Cd(1)-O(12) ⁱ	2.396(2)
Cd(1)-O(13) ⁱ	2.428(2)	Cd(1)-O(28)	2.334(2)
Cd(1)-O(30)	2.293(2)	Cd(1) ⁱⁱ -O(12)	2.396(2)
Cd(1) ⁱⁱ -O(13)	2.428(2)	Cd(2)-Ow2	2.320(2)
Cd(2)-O(8)	2.320(2)	Cd(2)-O(10)	2.267(2)
Cd(2)-O(25) ⁱⁱ	2.432(2)	Cd(2)-O(26) ⁱⁱ	2.353(2)
Cd(2)-O(32)	2.435(2)	Cd(2)-O(33)	2.365(2)
Cd(2) ⁱ -O(25)	2.432(2)	Cd(2) ⁱ -O(26)	2.353(2)
Ow1-Cd(1)-O(5)	80.49(9)	Ow1-Cd(1)-O(6)	105.07(9)
Ow1-Cd(1)-O(12) ⁱ	79.01(9)	Ow1-Cd(1)-O(13) ⁱ	93.24(9)
Ow1-Cd(1)-O(28)	97.64(9)	Ow1-Cd(1)-O(30)	166.53(9)
O(5)-Cd(1)-O(6)	54.26(7)	O(5)-Cd(1)-O(28)	86.35(7)
O(5)-Cd(1)-O(30)	101.50(8)	O(5)-Cd(1)-O(12) ⁱ	158.59(8)
O(5)-Cd(1)-O(13) ⁱ	133.56(7)	O(6)-Cd(1)-O(28)	128.89(8)
O(6)-Cd(1)-O(30)	86.50(8)	O(6)-Cd(1)-O(12) ⁱ	138.33(8)
O(6)-Cd(1)-O(13) ⁱ	84.17(7)	O(12) ⁱ -Cd(1)-O(13) ⁱ	54.18(7)
O(28)-Cd(1)-O(30)	69.35(7)	O(28)-Cd(1)-O(12) ⁱ	90.31(7)
O(28)-Cd(1)-O(13) ⁱ	139.95(7)	O(30)-Cd(1)-O(12) ⁱ	97.05(8)
O(30)-Cd(1)-O(13) ⁱ	94.81(7)	Ow2-Cd(2)-O(8)	91.09(9)
Ow2-Cd(2)-O(10)	158.33(9)	Ow2-Cd(2)-O(32)	77.51(9)
Ow2-Cd(2)-O(33)	94.84(9)	Ow2-Cd(2)-O(25) ⁱⁱ	74.53(9)
Ow2-Cd(2)-O(26) ⁱⁱ	114.24(9)	O(8)-Cd(2)-O(10)	69.67(7)
O(8)-Cd(2)-O(32)	85.49(7)	O(8)-Cd(2)-O(33)	136.72(7)
O(8)-Cd(2)-O(25) ⁱⁱ	93.46(7)	O(8)-Cd(2)-O(26) ⁱⁱ	126.46(8)
O(10)-Cd(2)-O(32)	90.68(8)	O(10)-Cd(2)-O(33)	92.83(8)
O(10)-Cd(2)-O(25) ⁱⁱ	115.22(8)	O(10)-Cd(2)-O(26) ⁱⁱ	86.03(8)
O(25) ⁱⁱ -Cd(2)-O(32)	152.00(8)	O(26) ⁱⁱ -Cd(2)-O(25) ⁱⁱ	54.37(7)
O(26) ⁱⁱ -Cd(2)-O(32)	143.57(7)	O(26) ⁱⁱ -Cd(2)-O(33)	89.45(7)
O(32)-Cd(2)-O(33)	54.44(7)	O(33)-Cd(2)-O(25) ⁱⁱ	129.42(7)
Cd(1)-O(5)-C(4)	87.23(17)	Cd(1)-O(6)-C(4)	96.29(17)
Cd(1)-O(28)-C(27)	120.22(17)	Cd(1)-O(30)-C(22)	121.81(15)
Cd(1) ⁱⁱ -O(12)-C(11)	92.88(17)	Cd(1) ⁱⁱ -O(13)-C(11)	91.05(17)
Cd(2)-O(10)-C(7)	122.03(15)	Cd(2)-O(8)-C(7)	119.82(17)
Cd(2)-O(32)-C(31)	90.16(17)	Cd(2)-O(33)-C(31)	93.12(16)
Cd(2) ⁱ -O(25)-C(24)	90.52(17)	Cd(2) ⁱ -O(26)-C(24)	93.99(16)

Symmetry transformations used to generate equivalent atoms: ⁱ $x-1, y, z$, ⁱⁱ $x+1, y, z$.

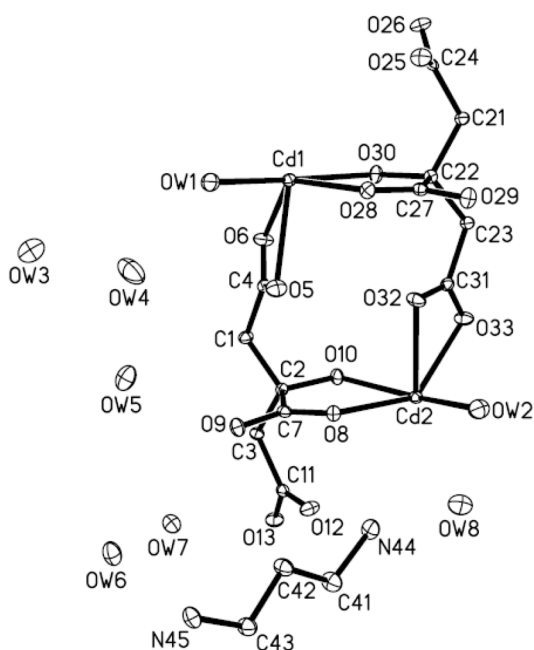


Fig. 2. An ORTEP diagram of complex **I** with the atom-numbering scheme. H atoms are omitted for clarity.

by the relevant IR absorption bands of the complex, respectively.¹⁷ The EDS spectrum showed the presence of C, N, O and Cd. The composition of the crystal was deduced from the elemental analyses and ICP-AES analysis; the formula of $(C_3H_{12}N_2)[\{Cd(H_2O)(C_6H_5O_7)\}_2] \cdot 6H_2O$, **I**, is consistent with the results of X-ray single crystallography.

Details of the crystallographic and experimental data are given in Table 1. The selected bond lengths and bond angles are listed in Table 2. The chemical structural diagram and an ORTEP diagram of complex **I** are shown in Fig. 1 and Fig. 2, respectively. The complex **I** has constituted by doubly protonated 1,3-diaminopropane cations, citrate and water coordinated cadmium(II) anions and un-coordinated free water molecules. Each cadmium atom is seven coordinated by six oxygen atoms of three different citrate ligands and one water molecule. Environment of cadmium atoms exists in a capped trigonal prism geometry. Two carboxylate groups from two different citrate ligands spontaneously chelate cadmium atom. Each hydroxyl and carboxylate group from one different citrate ligand is

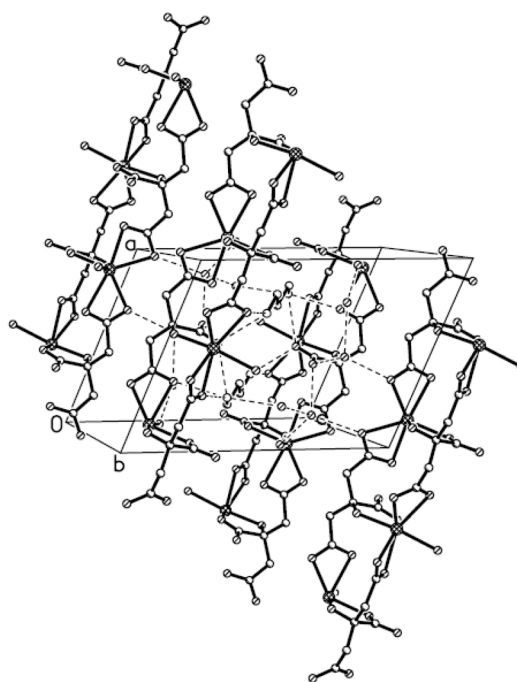


Fig. 3. Perspective view of the complex **I** along the *b* axis. Hydrogen bonds are shown by broken lines.

chelate to cadmium atom. The remaining coordination site is occupied by a water molecule. As listed in Table 2, bond lengths of $Cd-O_{\text{citrate}}$ and $Cd-O_{\text{water}}$ are $2.267(2) \sim 2.435(2)$ and $2.309(2) \text{ \AA}$, respectively. The bond lengths and angles of the citrate and 1,3-diaminopropane ligands are very similar to those of the previously reported results.¹⁸⁻²¹

Each cadmium atom is linked to three different citrate ligands and each citrate ligand is linked to three different cadmium atoms as shown in Fig. 1 and Fig. 2. A repeating unit of -cadmium-citrate- running in parallel to the *ac*-plane forms one-dimensional (1D) chains as shown in Fig. 3. This 1D chain is successively linked to adjacent chain running

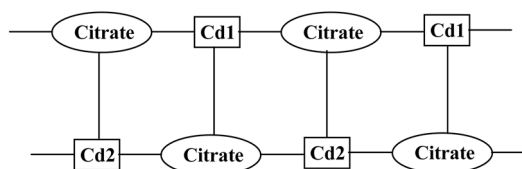


Fig. 4. Schematic diagram of one-dimensional ladder-type complex **I**.

Table 3. Hydrogen bonds for complex I

D-H...A Interaction	H...A (Å)	D...A (Å)	D-H...A (°)
O(9)-H(9)...O _w 5	2.33	2.783(4)	115.4
O(29)-H(29)...O _w 3 ^{#3}	1.95	2.699(3)	150.7
N(44)-H(44a)...O(25) ^{#2}	2.09	2.797(3)	135.7
N(44)-H(44a)...O(28) ^{#2}	2.57	3.220(4)	131.0
N(44)-H(44b)...O _w 8	1.99	2.842(4)	161.6
N(44)-H(44c)...O(8)	2.02	2.832(3)	151.4
N(44)-H(44c)...O(12)	2.60	3.116(3)	118.4
N(45)-H(45a)...O(28) ^{#4}	2.26	3.004(3)	152.3
N(45)-H(45a)...O(32) ^{#4}	2.42	2.843(3)	113.4
N(45)-H(45b)...O _w 6	2.06	2.828(4)	156.5
N(45)-H(45c)...O(8) ^{#4}	2.17	2.895(3)	148.0
N(45)-H(45c)...O(5) ^{#4}	2.31	2.830(3)	122.4
O _w 1-H _w 1a...O _w 7 ^{#1}	1.83(5)	2.783(4)	177(4)
O _w 1-H _w 1b...O _w 4	1.89(5)	2.663(4)	169(5)
O _w 2-H _w 2a...O _w 8 ^{#5}	1.98(5)	2.833(4)	173(5)
O _w 2-H _w 2b...O _w 3 ^{#6}	2.03(5)	2.788(4)	171(5)
O _w 3-H _w 3a...O(29) ^{#7}	2.02(6)	2.901(4)	164(5)
O _w 3-H _w 3b...O(29) ^{#3}	2.17(5)	2.699(3)	141(6)
O _w 4-H _w 4a...O _w 5	2.00(8)	2.802(5)	175(7)
O _w 4-H _w 4b...O _w 3	2.17(7)	2.838(5)	170(9)
O _w 5-H _w 5a...O(6) ^{#8}	1.98(6)	2.760(4)	161(5)
O _w 5-H _w 5b...O(9)	2.05(6)	2.783(4)	170(6)
O _w 6-H _w 6a...O _w 7	1.89(5)	2.822(4)	173(4)
O _w 6-H _w 6b...O(29) ^{#9}	1.93(5)	2.788(3)	173(5)
O _w 7-H _w 7a...O(13) ^{#10}	1.93(5)	2.759(3)	171(4)
O _w 7-H _w 7b...O(9)	2.03(5)	2.796(3)	174(5)
O _w 8-H _w 8a...O _w 6 ^{#4}	2.15(5)	2.930(4)	154(5)
O _w 8-H _w 8a...O _w 2	2.64(5)	3.090(4)	115(4)
O _w 8-H _w 8b...O _w 5 ^{#4}	1.97(6)	2.732(4)	170(5)

Symmetry transformations used to generate equivalent atoms: ^{#1}; x-1, y, z, ^{#2}; x+1, y, z, ^{#3}; -x, -y+1, -z+1, ^{#4}; -x+1, -y+1, -z+1, ^{#5}; -x+1, -y+2, -z+1, ^{#6}; x, y+1, z, ^{#7}; x, y-1, z, ^{#8}; -x+1, -y+1, -z, ^{#9}; x+1, y-1, z, ^{#10}; -x+2, -y+1, -z.

in almost parallel mode. And thus, the polymeric cadmium-citrate complex I forms an one-dimensional ladder-type assembly structure as shown in Fig. 3 and 4. There are many intermolecular O_{citrate}-H...O_{water}, O_{water}-H...O_{citrate}, O_{water}-H...O_{water}, N_{1,3}-diaminopropane-H...O_{citrate} and N_{1,3}-diaminopropane-H...O_{water} hydrogen-bonds as listed in Table 3. The crystal structure is stabilized by three-dimensional networks of hydrogen-bonding interaction between the water molecules and citrate ligands and protonated 1,3-diaminopropane cations.

In summary, we have prepared and characterized of the cadmium(II)-citrate complex, (C₃H₁₂N₂)[{Cd(H₂O)(C₆H₅O₇)₂}]·6H₂O, with novel ladder-type

framework. The framework structure is different from the other cadmium-citrate complexes, [Cd(H₂O)(C₆H₅O₇)₂]_n,¹⁸ [Cd₃(H₂O)₅(C₆H₅O₇)₂]_n·H₂O,¹⁹ {(NH₄)₂[Cd₂(C₆H₅O₇)₂]_n},²⁰ [Cd₃(H₂O)₂(C₆H₅O₇)₂]_n,²¹ with various coordination modes of citrate ligands. Further work on the subject is in progress.

Supporting Information Available

Tables of crystallographic details, atomic coordinates, interatomic distances and angles, torsional angles, hydrogen atom coordinates, anisotropic displacement parameters, and structure factors for title compound are available.

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