

Geometrical Aspects of Trinuclear Tetra- μ -Chloro-Cadmium Complex with 5-Methyl-4*H*-1,2,4-Triazole-3,4-Diamine

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ABSTRACT

In this work, a cadmium complex $[\text{Cd}_3(\text{L})_2(\text{HL})_2(\mu\text{-Cl})_4\text{Cl}_4]$ (**1**) with the ligand L, 5-methyl-4*H*-1,2,4-triazole-3,4-diamine, was prepared and identified by elemental analysis, FT-IR spectroscopy and single-crystal X-Ray diffraction. The cadmium atom in the crystal structure of **1** has distorted octahedral geometry by coordination of the two nitrogen atom of L and four chloride ions. Two chloride and a N-N bridges connect two adjacent cadmium atoms.

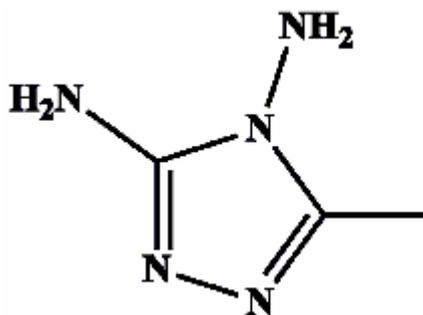
Key words: Trinuclear, Cadmium Complex, Triazole, X-ray Crystal Structure.

INTRODUCTION

Amongst five-membered ring systems available, the presence of the three nitrogens in triazoles provides an interesting class of compounds. Triazoles in particular, substituted-1,2,4-triazole are among various heterocycles that have received the most attention during last two decades as potential antimicrobial agents, antifungal, antitubercular, anti-HIV, antiinflammatory, CNS stimulants, sedatives, antianxiety¹. A larger variety of 1,2,4-triazole-based ligands have been used for preparation of polymeric coordination networks² and synthesis of nitrogen-rich energetic materials³.

In the past few years we have studied complexation of multi N-donor ligands⁴⁻⁸. In continuation of our previous studies, in this work

the preparation of cadmium(II) complex, $[\text{Cd}_3(\text{L})_2(\text{HL})_2(\mu\text{-Cl})_4\text{Cl}_4]$ (**1**), with 5-methyl-4*H*-1,2,4-triazole-3,4-diamine (L, scheme 1) was described. This complex was characterized by elemental analysis, IR spectroscopy and X-ray crystallography.



Scheme 1: The structure of ligand

MATERIALS AND METHODS

General methods

All starting chemicals and solvents were reagent or analytical grade and used as received. The infrared spectrum of a KBr pellet was recorded in the range 4000–400 cm^{-1} using a FT-IR 8400-Shimadzu spectrometer. The carbon, hydrogen and nitrogen contents were determined in a Thermo Finnigan Flash Elemental Analyzer 1112 EA. Melting point was determined using a Barnsted Electrothermal 9200 electrically heated apparatus.

Synthesis of $[\text{Cd}_3(\text{L})_2(\text{HL})_2(\mu\text{-Cl})_4\text{Cl}_4]$, **1**

A solution of L. HCl (1.3 mmol, 0.19 g), dissolved in 10 mL EtOH, were added to a 10 mL ethanolic solution of CdI_2 (1 mmol, 0.36 g). The reaction mixture was stirred at 60 °C for 2 h and a white precipitate was formed and then filtrated. The resulting solution was left at room temperature for several days and colorless crystals suitable for X-ray diffraction were collected. The results of melting point, CHN analysis and IR spectroscopy of the crystals were identical to those of the initial precipitate. Yield (0.25 g) 83%; Decomposed > 270 °C. Anal. Calcd for $\text{C}_{12}\text{H}_{30}\text{Cd}_3\text{Cl}_8\text{N}_{20}$ (%): C, 13.40; H, 2.81; N, 26.05. Found: C, 13.42; H, 2.81; N, 25.88. IR (KBr, cm^{-1}): 3317 s ($\nu_{\text{as}} \text{NH}_2$), 3240 m ($\nu_{\text{s}} \text{NH}_2$), 3183 m (νNH), 1697 s ($\nu \text{C}=\text{N}$), 1643 m (δNH_2), 1435 w ($\delta_{\text{as}} \text{CH}_3$), 1381 w ($\delta_{\text{s}} \text{CH}_3$), 1281 w (νCN), 1092 w (νNN).

Crystal structure determination and refinement

Intensity data were collected on a Bruker APEX-II CCD area detector diffractometer with graphite monochromated Mo K_{α} radiation (50 kV, 30 mA) using the APEX-II⁹ data collection software. The collection method involved w -scans of width 0.5° and 512 × 512 bit data frames. Data reduction was carried out using the program SAINT⁹ and face indexed absorption corrections were made using the program XPREP¹⁰. The crystal structure was solved by direct methods using SHELXTL¹¹. Non-hydrogen atoms were first refined isotropically followed by anisotropic refinement by full matrix least-squares calculations based on F^2 using SHELXTL. Hydrogen atoms were first located in the difference map then positioned geometrically and allowed to ride on their respective parent atoms. Crystallographic data and details of the data

collection and structure refinement are listed in table 1. Selected bond lengths and angles are listed in table 2.

RESULTS AND DISCUSSION

Reactions between L.HCl and ethanolic solution of cadmium(II) iodide provided colorless crystals of **1**. This complex was characterized by IR, Raman, ^1H NMR spectroscopy and X-ray crystallography. This complex is air-stable and soluble in DMSO and DMF.

Presence of the RNH_2 group in **1** affect IR spectrum in two regions including 3317 and 3240 cm^{-1} for asymmetric and symmetric NH_2 stretches

Table 1: Crystal data and structure refinement for **1**

Empirical formula	$\text{C}_{12}\text{H}_{30}\text{Cd}_3\text{Cl}_8\text{N}_{20}$
Formula weight (g mol^{-1})	1075.36
Temperature (K)	173(2)
Crystal system	Monoclinic
Space group	$P2_1/n$
Unit cell dimensions (\AA , °)	
<i>a</i>	9.1524(2)
<i>b</i>	9.3816(2)
<i>c</i>	18.8619(3)
β	101.5050(10)
Volume (\AA^3 , <i>Z</i>)	1587.02(5), 2
Calculated density (g cm^{-3})	2.25
Absorption coefficient (mm^{-1})	2.7
<i>F</i> (000)	1044
Crystal size (mm^3)	0.27 × 0.23 × 0.11
θ range for data collection (°)	2.20–28.00
<i>h</i> , <i>k</i> , <i>l</i> ranges	-12:12, -12:12, -24:24
Reflections collected	24192
Independent reflections	3833
R_{int}	0.0528
Data / restraints / parameters	3833 / 8 / 226
Goodness-of-fit on F^2	1.051
Final <i>R</i> indices [$>2\sigma(I)$]	$R_1 = 0.0284$, $wR_2 = 0.0713$
<i>R</i> indices (all data)	$R_1 = 0.0341$, $wR_2 = 0.0734$
Largest diff. peak and hole (e.\AA^{-3})	0.68 and -1.22

Table 2: Selected bond lengths (Å) and angles (°) for 1

Bond lengths (Å)		Angles (°)	
Cd1-N1	2.358(3)	N1-Cd1-N6	177.20(9)
Cd1-N6	2.477(3)	N1-Cd1-Cl1	92.67(7)
Cd1-Cl1	2.5578(8)	N1-Cd1-Cl2	94.69(7)
Cd1-Cl2	2.5743(8)	N1-Cd1-Cl3	88.78(7)
Cd1-Cl3	2.6379(8)	Cl1-Cd1-Cl2	96.41(3)
Cd1-Cl4	2.6666(8)	Cl1-Cd1-Cl4	92.82(3)
Cd2-N2	2.277(3)	N2-Cd2-N2 ⁱ	180.0
Cd2-Cl3	2.7182(7)	N2-Cd2-Cl3	84.61(7)
Cd2-Cl4	2.6724(8)	N2-Cd2-Cl4	89.17(8)

Symmetry code: (i) - x + 1, - y + 1, - z + 1.

and 1643 cm⁻¹ for NH₂ bending. The bands at 1697, 1281 and 1092 cm⁻¹ which were assigned to the ν (C=N), ν (CN) and ν (NN), respectively, confirm the presence of the triazole ring.

Description of the crystal structure

The crystal structure of **1** was determined by X-ray single-crystal diffraction. The molecular graphic was drawn with ORTEP-III¹².

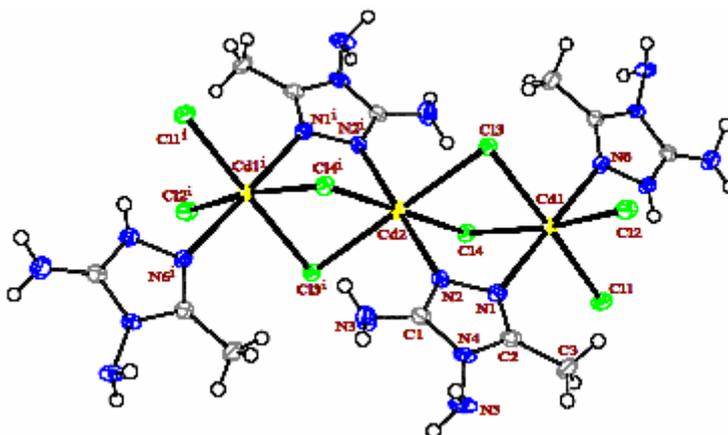


Fig. 1: The ORTEP-III diagram of the molecular structure of 1. The ellipsoids are drawn at the 50% probability level

In the crystal structure of **1** (figure. 1), the three cadmium atoms have a distorted octahedral coordination environment. Four sites are occupied by chloride ions with the Cd-Cl bond lengths in the range of 2.5578(8)–2.7182(7) Å. The two other sites are occupied by two nitrogen atoms of L. The ligand L coordinated by two different coordination modes. Two chloride and a N-N bridges connect two adjacent cadmium atoms. The complex has a center of inversion on the copper atom and *C*_i symmetry.

Supplementary material

CCDC 913232 for [Cd₃(L)₂(HL)₂(μ-Cl)₄Cl₄] contain the supplementary crystallographic data for this paper. These data can be obtained free of charge *via* www.ccdc.cam.ac.uk/conts/retrieving.html.

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