Reaction and Theoretical Study of the Coordination of an N₂O-Donor Amino Alcoholic Ligand Toward Group 12 Metals Mixtures

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ABSTRACT. A series of reactions between an amino alcoholic ligand, *cis*-2-((2-((2-hydroxyethyl)amino)ethyl)amino)cyclohexan-1-ol (HEAC), with the mixtures of group 12 metals including, $HgCl_2/CdCl_2$, $HgCl_2/CdL_2$, $ZnCl_2/CdCl_2$ and $ZnCl_2/CdCl_2/HgCl_2$ was experimentally and theoretically studied to determine the most stable product of these reactions. Furthermore, the Cambridge Structural Database (CSD) studies were done to evaluate the theoretical results. The products were characterized by elemental analysis, FT-IR, Raman, ¹H NMR spectroscopy and single-crystal X-ray diffraction. Based on these investigations a binuclear structure of cadmium, $[Cd_2(HEAC)_2(\mu-Cl)_2Cl_2]$ (1), is the most stable product that was formed in all studied reactions between HEAC and metals mixtures. In this structure, the cadmium atom has a $CdN_2O(\mu-Cl)_2Cl$ environment and distorted octahedral geometry.

Key words: Cadmium, Group 12, Amino alcohol, Metal mixture, DFT study

INTRODUCTION

Recently we have reported a mixed metal Cd/Hg complex, [Cd(HEAC)₂][HgI₄], in reaction between *cis*-2-((2-((2-hydroxyethyl)amino)ethyl)amino)cyclohexan-1-ol (HEAC) and CdI₂/HgI₂ mixture. In this reaction, two HEAC ligand have been coordinated selectively to the cadmium atom and iodo ligands coordinated to the mercury atom. Based on this observation we decided to examine the reaction between HEAC with other mixtures of the group 12 halide salts. It is interesting issue that the HEAC and halido ligands prefer which metal from the mixture.

Study of the Cambridge Structural Database (CSD)¹ revealed that there are a few examples for mixed metal complexes of the group 12 elements. Also this study revealed that there is no example containing Zn/Cd/Hg metals at the same time. Although the mixed metal compounds of the group 12 elements have been considered rarely, but they can form a variety of compounds including heterometal-lic host-guest cages,² sensors for detecting the palladium,³ coordination polymers,^{4–9} non-centrosymmetric (NCS) materials,¹⁰ metal clusters,¹¹ luminescence active compounds,¹² MOFs¹³ and nonlinear optical (NLO) materials.⁶

In this work, the reaction between HEAC with HgCl₂/ CdCl₂, HgCl₂/CdI₂, ZnCl₂/CdCl₂ and ZnCl₂/CdCl₂/HgCl₂ mixtures is investigated by spectral (FT-IR, Raman, ¹H NMR), structural (X-ray) and theoretical (DFT) methods along with structural investigations of the CSD database.

EXPERIMENTAL

All starting chemicals and solvents were obtained from Merck and were used as received. The HEAC ligand was synthesized according to the literature.^{14,15} Infrared spectra (from KBr pellets) in the range 4000–400 cm⁻¹ were recorded with an FT-IR 8400-Shimadzu spectrophotometer. Raman spectra were obtained using a Nicolet Model 910 Fourier-transform spectrometer. The carbon, hydrogen and nitrogen contents were determined using a Thermo Finnigan Flash Elemental Analyzer 1112 EA. The melting point was measured with a Barnsted Electrothermal 9200 electrically heated apparatus.

Synthesis of [Cd₂(HEAC)₂(µ-Cl)₂Cl₂], (1)

In all reactions the complex $[Cd_2(HEAC)_2(\mu-Cl)_2Cl_2]$ (1) was formed as a main product and crystallized from the reaction mixture. Thus its spectral data is gathered at the end of this section to avoid repetition.

HEAC + HgCl₂/CdCl₂

HEAC (0.20 g, 1 mmol), $HgCl_2$ (0.14 g, 0.50 mmol) and $CdCl_2 \cdot 2.5(H_2O)$ (0.11 g, 0.50 mmol) were placed in the large arm of a branched tube. Methanol was carefully added to fill both arms. The tube was then sealed and the ligand-

containing arm was immersed in a bath at 60 C while the other was maintained at ambient temperature.

After a few days, colorless crystals that were in the cooler arm were filtered off and dried in (0.17 g) 88%). Also same crystals were obtained filtrated solution (Yield (0.03 g) 16%).

HEAC + HgCl₂/CdI₂

The procedure for this reaction was similar to above except that CdCl₂ was replaced CdI₂ (0.18 g, 0.50 mmol). After five days did not form any product in the branched tube and reaction mixture was filtrated. Suitable crystals for X-ray diffraction studies were obtained by slow evaporation of the solution for three days and collected by filtration. Yield (0.07 g) 36%.

HEAC + ZnCl₂/CdCl₂

The procedure for this reaction was similar to the first method except that HgCl₂ was replaced by ZnCl₂ (0.07 g, 0.50 mmol). Yield (0.16 g) 83% for branched tube crystals and (0.02 g) 10% for crystals from the filtrated solution.

HEAC + ZnCl₂/CdCl₂/HgCl₂

The procedure for this reaction was similar to the first method along with addition of ZnCl₂ (0.11 g, 0.79 mmol) to the reaction mixture and using of 0.79 mmol for all reagents. After five days did not form any product in the branched tube and reaction mixture was filtrated. An oily compound was formed after evaporation of the solution. Suitable crystals for X-ray diffraction studies were obtained by recrystallization of this compound in the branched tube using the ethanol. Yield (0.06 g) 20%. mp. 222 °C. Anal. Calcd for C₂₀H₄₄Cd₂Cl₄N₄O₄ (%): C, 31.15; H, 5.75; N, 7.26. Found: C, 30.97; H, 5.69; N, 7.21. IR (cm⁻¹, KBr): 3355 s (v OH), 3224 s (v NH), 2931 s (v CH), 2862 m (v CH₂), 1450 w (δ_{as} CH₂), 1380 m (δ_s CH₂), 1200 w (ν CO), 1110 m (v C⁶N), 1056 m (v C⁷N). Raman (cm⁻¹): 2979 w (v CH), 2869 w (v CH₂), 1550 m, 1308 m (v CO), 1130 m (v CN), 986 m, 848 m, 694 m, 550 m (v CdN), 415 w (v CdO), 311 w (v CdCl_{terminal}), 249 w (v CdCl_{bridging}). ¹H NMR (300 MHz, DMSO): δ 6.5 (1H, O¹H), 4.8 (1H, O²H), 3.5 (2H, N¹H, N²H), 2.8-2.9 (7H, C⁶H, C⁷H₂, C⁸H₂ & C⁹H₂), 1.9-2.0 (3H, C¹H, $C^{10}H_2$), 1.6 (2H, C^2H_2), 1.1 (6H, C^3H_2 , C^4H_2 & C^5H_2).

Crystal Structure Determination and Refinement

Diffraction data were collected at 173 K on a Rigaku Oxford Diffraction Gemini Ultra diffractometer. Data processing and absorption correction was carried out using Crysalis Pro.¹⁷

5 Largest diff. peak / hole, e A 0.5 / -0.71The structures were solved with direct methods and refined with least squares using the OLEX2 package.¹⁹ All hydrogen atoms were placed at their calculated positions. Selected crystallographic data are presented in Table 1. Diagrams

Computational Details

Ortep-III.20,21

All structures were optimized with the Gaussian 09 software²² and calculated for an isolated molecule using Density Functional Theory (DFT)²³ at the B3LYP/LanL2DZ²⁶ level of theory for complexes. The X-ray structural data of complex 1 was used as input for the theoretical calculations.

of the molecular structure and unit cell were created using

RESULTS AND DISCUSSION

Reaction between HEAC and mixtures of the group 12 metals including, HgCl₂/CdCl₂, HgCl₂/CdI₂, ZnCl₂/CdCl₂ and ZnCl₂/CdCl₂/HgCl₂ were investigated. All crystals obtained from the four reactions were characterized by spectral, elemental analysis and single crystal X-ray dif-

 $C_{10}H_{22}CdCl_2N_2O_2$

 $0.18 \times 0.10 \times 0.08$

385.61

161

10-18	Empirical formula
e deposited	Formula weight, g mol ⁻¹
air (Yield	Crystal size, mm ³
ed from the	Temperature, K
	Crystal system

Temperature, K	173
Crystal system	Monoclinic
Space group	C2/c
Unit cell dimensions (Å, °)	
a	15.2804(10)
b	15.3998(10)
С	12.9314(9)
β	95.837(6)
Volume, Å ³	272.87(15)
Ζ	8
Calculated density, g cm ⁻³	1.692
Absorption coefficient, mm ⁻¹	1.79
<i>F</i> (000), e	1552.00
θ range for data collection (°)	1.6–25.4
h, k, l ranges	$-18 \le h \le 18, -18 \le k \le 18, -15 \le l \le 13$
Reflections collected /	13102 / 2778 / 0.088
independent / R _{int}	
Data / ref. parameters	2778 / 170
Goodness-of-fit on F ²	1.04
Final R indexes $[I \ge 2\sigma(I)]$	$R_1 = 0.0244, wR_2 = 0.0574$
Final R indexes [all data]	$R_1 = 0.0344, wR_2 = 0.0604$
Langest diff most / hale a Å-3	05/071

Table 1. Crystal data and structure refinement for 1

fraction. Our observations revealed that all crystals were same with formula of $[Cd_2(HEAC)_2(\mu-Cl)_2Cl_2]$ (1). The result of the HEAC + HgCl₂/CdI₂ reaction was the complex 1. This product is also formed in reaction between cadmium(II) iodide with mercury(II) chloride, confirming that the chloride ions transfer from mercury to the cadmium atom during the coordination process. It seems that the binuclear complex of the cadmium (1) is thermodynamically stable than the other products. The driving force of this reaction could be Hard-Soft-Acid-Base interaction.

Table 2. Optimized structure for possible homo- and hetero-atomic binuclear compounds of group 12 metals with HEAC along with their CSD average



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HEAC has hard O and N (softer than O) donor atoms in the second period and soft Hg(II) likes soft I^- (HgI₂ is more stable than HgCl₂).

Based on this assumption a series of the DFT calculations were run to find the most thermodynamically stable product among the six possible homo- and hetero-atomic binuclear structures of the group 12 metals for an isolated molecule (*Table* 2). The complex **1** is air-stable, and soluble in DMSO. We have reported the structure of the complex **1** previously in reaction between HEAC with cadmium(II) chloride.¹⁵

In all CSD searches which have been presented, for more precise results, the structures containing any error or disorder have been omitted.

Spectroscopic Characterization

The v (O–H) and v (N–H) in the IR spectrum of the **1** shifted 88 and 127 cm⁻¹ to the higher frequency than those of the free ligand,¹⁵ confirming coordination through these donor sites. In the Raman spectrum, the bridging Cd–Cl stretching frequency is observed at 249 cm⁻¹ which was lower than the terminal Cd–Cl stretching frequency (311 cm⁻¹) and both are in agree with the literature values.²⁷

Numbering used for the ¹H NMR spectra of the free ligand is given in *Scheme* 1. After coordination, O¹H signal shifted by 1.73 ppm to lower magnetic field compared to the free ligand.¹⁵

Similar shifts were observed for the N¹H and N²H signals (1.45 ppm) while no significant shift was observed for the O²H. These observations revealed that the potentially N₂O₂-donor HEAC act as the N₂O-donor in reaction toward the cadmium(II) chloride.

Theoretical Studies

Based on the experimental data, it seems that the complex 1 is the most stable product that can be formed in reaction between HEAC with group 12 metals mixture. In the binuclear structure of 1, (*Fig.* 1) the cadmium atom has an octahedral geometry by coordination of one HEAC, one terminal and two bridging chloro ligands. Based on



Scheme **1.** Structure of the *cis*-2-((2-((2-hydroxyethyl)amino) ethyl)amino)cyclohexan-1-ol (HEAC).



Figure **1**. The ortep diagram of the molecular structure of the complex **1**. The ellipsoids are drawn at the 50% probability level.

this structure, other possible isostructural binuclear complexes were optimized to determine the most stable ones (Table 2). For finding a reasonable structure for all studied compounds, all theoretically structures were compared with the CSD analogues average. In all optimized structures, the $M(\mu$ -Cl)₂M unit has a rectangular-like structure and thus all M-Cl bond lengths are not equal. In 1°pt, the Cd-Cl bond lengths are longer than the CSD average but are in range that have been observed for their analogues (Table 2), thus the formula of $[Cd_2(HEAC)_2(\mu-Cl)_2Cl_2]$ is reasonable for 1^{opt}. In 2^{opt}, only one of the Zn–Cl^a (2.463 Å) can be consider as a coordinate bond thus this structure has not a binuclear structure. In 3^{opt}, although two Hg–Cl bond lengths are longer than their analogues average whilst are within the acceptable range for Hg-Cl bond lengths and thus this structure can be considered as a binuclear. In 4^{opt}, the short M-Cla bond lengths of cadmium and zinc atoms are within the CSD range whilst the longer one is out of this range. This observation conducts us to conclude that this structure does not have a binuclear structure and cadmium and zinc complexes are placed in side of each other separately. There is not any CSD example containing Cd(µ-Cl)₂Zn unit. All coordinated bond lengths in 5^{opt} are acceptable thus this structure has a hetero atomic binuclear structure. Study of the CSD revealed that there is only one example for complexes containing the Cd(μ -Cl)₂Hg unit.²⁸

In the last optimized structure, 6^{opt} , among the four M–Cl^{bridging} bond lengths, only Zn–Cl^b distance (3.556 Å) is not acceptable as coordinate bond and this structure can be considered as a hetero atomic binuclear with one chloro bridge. There is not any example for complexes with Hg(μ -Cl)₂Zn moiety. Based on these DFT calculations, among the six possible binuclear complexes only three of them really can be consider as a binuclear structure with formula of [MCl (HEAC)(μ -Cl)₂M'Cl(HEAC)] including 1^{opt}, 3^{opt} and 5^{opt}. The total energy of 1^{opt}, 3^{opt} and 5^{opt} were calculated to be -1464.65, -1453.91 and -1459.28 a.u., respectively, confirming that the 1^{opt} is thermodynamically stable than the others and in agree with the result of the experiments.

CONCLUSION

In this work, reaction of *cis*-2-((2-((2-hydroxyethyl) amino)ethyl)amino)cyclohexan-1-ol (HEAC) with group 12 metals mixtures including HgCl₂/CdCl₂, HgCl₂/CdI₂, ZnCl₂/CdCl₂ and ZnCl₂/CdCl₂/HgCl₂ was studied. Based on the structural (X-ray), spectral (FT-IR, ¹H NMR) and theoretical (DFT) investigations a binuclear cadmium complex, $[Cd_2(HEAC)_2(\mu-Cl)_2Cl_2]$ (1) was determined as a most stable compound. In the structure of 1, the cadmium atom has a CdN₂O(µ-Cl)₂Cl environment and distorted octahedral geometry in which two chloro ligands were located in the axial positions and a N2O-donor HEAC was lied on the equatorial plane along with another chloro ligand. Theoretical and CSD studies revealed that among the six possible homoand hetero-atomic binuclear structures only three of them can form [MCl(HEAC)(µ-Cl)₂M'Cl(HEAC)] structure (1^{opt}, 3^{opt} and 5^{opt}). Also these studies revealed that the mixed metal structure containing $Cd(\mu-Cl)_2Hg$ unit is more stable than the other hetero-atomic mixtures. Qualitatively HEAC seems not like hardest Zn²⁺ and softest Hg²⁺, and the computation results may reflect this. So HEAC seems like Cd^{2+} .

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