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Structural study of the coordination behavior of a tetradentate NO$_3$-donor amino alcohol ligand toward a Cd^{II}:Hg^{II} mixture

Abstract: In this work, the reaction of 2,2′,2″-nitrilotriethanol (NTE) with a 1:1 mixture of CdI$_2$ and HgI$_2$ is investigated. The complex [Cd(NTE)$_2$][Hg$_2$(μ-I)$_2$I$_4$] was synthesized and identified by elemental analysis, FT-IR, ^{1}H NMR spectroscopy and single-crystal X-ray diffraction. The structure of the [HNTE]Cl salt is also presented. In the crystal structure of the complex, the cadmium atom has a CdN$_2$O$_6$ environment in a slightly distorted cube geometry. This geometry is one of the rare cube geometries with a minimum distortion among the Cambridge Structural Database structures for cadmium complexes. The anionic moiety has a binuclear structure with the mercury atoms being in tetrahedral environments. In the network of the complex, in addition to O−H···I hydrogen bonds, there are I···I interactions which lead to ten-membered rings.

Keywords: amino alcohol; Cd/Hg mixed-metal complex; coordination behavior; cube geometry; X-ray crystal structure.

1 Introduction

Amino alcohol functional groups are often found in biologically active molecules, ligands and chiral auxiliaries [1–3]. These types of ligands contain several coordination sites, which may interact with a metal center in different ways. An example of such ligands is 2,2′,2″-nitrilotriethanol (NTE), which [based on Cambridge Structural Database (CSD) data [4]] can act as NO$_3$-, NO$_2$-, NO-, O$_3$- and O$_2$-donor; the NO$_3$-donor form is the most commonly observed. Complexes containing both cadmium and mercury atoms are rare and only 14 structures have been reported [5–18]. These structural motifs are present in a variety of compounds including the heterobimetallic RHg/Cd species [15], heteronuclear complexes of cyanometallates [14], coordination polymers [8, 9, 11, 12, 16], clathrates [ML$_n$M′(CN)$_4$.2G] [7, 13] and noncentrosymmetric materials [18]. Cadmium-mercury thiocyanates exhibit good second-order nonlinear optical effects, a wide transparency wavelength region [11, 17, 18] and piezoelectricity properties [18]. In this paper, the preparation, characterization and crystal structure of [Cd(NTE)$_2$][Hg$_2$(μ-I)$_2$I$_4$] are presented.

2 Results and discussion

The reaction between NTE and an ethanol solution of a CdI$_2$/HgI$_2$ mixture afforded crystals of a complex which is air-stable and soluble in DMF and DMSO. In the IR spectrum of the complex, the ν (O−H) band is shifted by about 100 cm^{-1} to higher frequency than that of the free ligand [19], indicating coordination through the oxygen atoms. In the ^{1}H NMR spectra of NTE [19] and of the complex, there are two groups of signals in the region of 2.5–3.5 and above 4.5 ppm. The broad singlet above 4.5 ppm is assigned to protons of the alcoholic moiety and the multiplet is assigned to protons of the aliphatic hydrogen atoms. After coordination of NTE, the OH signal is shifted by about 1 ppm to a lower field, consistent with coordination of all alcoholic groups toward the metal atom. No significant shift was observed for the aliphatic hydrogen atoms.

The crystal structure of the complex has been determined. In addition to the complex, the structure of the [HNTE]Cl salt is presented in this work (Fig. 1). Owing to the previous reports on similar structures [20, 21], details about this structure will only briefly be discussed here. It should be mentioned that the collection of the data for this salt was carried out of a different temperature (93 K)

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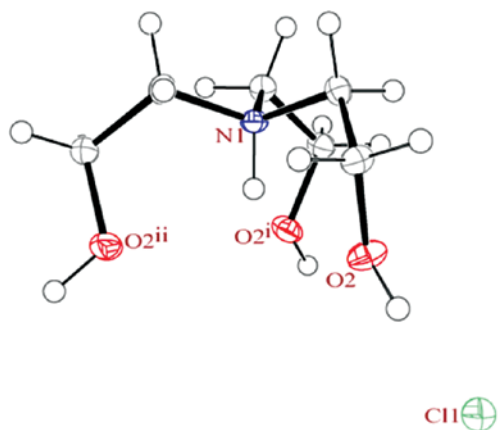
Fig. 1: Ortep-III diagram of the molecular structure of the [HNTE]Cl salt.

than before (100 and 283–303 K). A structural comparison of [HNTE]Cl with the previous results revealed that bond lengths and angles of them are slightly different as well as the properties of hydrogen bonds. Crystallographic data and details of the data collection and structure refinement are listed in Table 1, selected bond lengths and angles in Table 2 and hydrogen bond geometries in Table 3.

The compound consists of $[Cd(NTE)_2]^{2+}$ cations and binuclear $[I_2Hg(\mu\text{-}I_2)_2HgI_2]^{2-}$ anions (Fig. 2). The cadmium atom has a slightly distorted cube coordination geometry of six oxygen and two nitrogen atoms of two NTE ligands (Fig. 3). The averages of the six Cd–O (2.4460 Å) and two Cd–N bond lengths (2.4345 Å) are shorter than the CSD average [4] for compounds with a $Cd(N_{tert\text{-}amine})(O_{alcohol})_3$ environment (2.4615 and 2.4671 Å, respectively). Each ligand forms three five-membered non-planar chelate rings. Similar donor atoms of the two coordinated NTE ligands lie in *trans* positions to each other. The three alcoholic arms of the free ligand (Fig. 1) and its complex (Fig. 2) are co-orientated. In the structural network of the ligand salt, there are O–H···Cl, C–H···O and C–H···Cl interactions. Among them, the O–H···Cl hydrogen bonds participate in the formation of one $R_6^3(30)$ hydrogen bond motif (three acceptors, six donors with degree of 30) [1, 22] between three [HNTE]⁺ units (Fig. 4). If the distortion of alcoholic groups in the cationic unit of the [HNTE]Cl salt is disregarded, with a C_3 axis on the nitrogen atom, it has C_3 symmetry.

A study of the angles at cadmium atoms with coordination number eight in the CSD reveals that coordination of two ligands including 4,7,13,16,21,24-hexaoxa-1,10-diazabicyclo-[8.8.8]hexacosan [23] and tris(2-pyridylmethyl)

Table 1: Crystal data and structure refinement for $[Cd(NTE)_2][Hg_2(\mu\text{-}I)_2I_4]$ and [HNTE]Cl.

	Complex	[HNTE]Cl
Empirical formula	$C_{12}H_{30}CdHg_2I_6N_2O_6$	$C_6H_{16}ClNO_3$
Formula weight, g mol⁻¹	1573.40	185.65
Crystal size, mm³	0.12×0.10×0.10	0.20×0.20×0.20
Temperature, K	93	93
Crystal system	Monoclinic	Trigonal
Space group	$P2/c$	$R3c$
Unit cell dimensions		
a, Å	17.031(2)	8.226(3)
b, Å	8.6213(9)	8.226(3)
c, Å	21.377(3)	22.763(7)
β, deg	105.787(3)	90
Volume, Å³	3020.4(6)	1333.9(8)
Z	4	6
Calculated density, g cm⁻³	3.46	1.39
Absorption coefficient, mm⁻¹	17.0	0.4
$F(000)$, e	2760	600
θ range for data collection (deg)	2.4–27.4	3.4–27.3
h, k, l ranges	$-20 \leq h \leq 20, -10 \leq k \leq 10, -17 \leq l \leq 25$	$-9 \leq h \leq 9, -9 \leq k \leq 9, -26 \leq l \leq 26$
Reflections collected/independent/R_{int}	15 569/5471/0.045	4440/549/0.054
Data/ref. parameters	5471/286	549/40
Goodness-of-fit on F^2	0.960	1.10
$R1/wR2$ ($I > 2\sigma(I)$)	0.0249/0.0521	0.0315/0.0673
$R1/wR2$ (all data)	0.0289/0.0531	0.0317/0.0674
Flack parameter	–	−0.04(4)
Largest diff. peak/hole, e Å⁻³	1.60/−2.35	0.20/−0.19

Table 2: Selected bond lengths (Å) and angles (deg) for [Cd(NTE)$_2$][Hg$_2$(μ-I)$_2$I$_4$] with estimated standard deviations in parentheses[a].

Bond lengths		Angles	
Cd(1)–N(1)	2.440(5)	Hg(1)–I(1)–Hg(1)^i	80.861(14)
Cd(1)–N(2)	2.424(5)	Hg(2)–I(4)–Hg(2)^{ii}	90.607(17)
Cd(1)–O(2)	2.499(5)	I(1)–Hg(1)–I(1)^i	99.138(14)
Cd(1)–O(4)	2.424(4)	I(2)–Hg(1)–I(3)	124.917(17)
Cd(1)–O(6)	2.419(5)	I(4)–Hg(2)–I(4)^{ii}	89.271(18)
Cd(1)–O(8)	2.425(5)	I(6)–Hg(2)–I(5)	128.595(19)
Cd(1)–O(10)	2.491(4)	N(2)–Cd(1)–N(1)	173.42(16)
Cd(1)–O(12)	2.427(5)	O(4)–Cd(1)–O(12)	173.35(16)
Hg(1)–I(1)	2.8835(5)	O(10)–Cd(1)–O(2)	174.17(17)
Hg(1)–I(2)	2.6863(5)	O(8)–Cd(1)–O(6)	171.00(16)
Hg(1)–I(3)	2.7220(6)	O(4)–Cd(1)–O(2)	107.57(16)
Hg(2)–I(4)	2.8996(6)	N(2)–Cd(1)–O(2)	108.41(15)
Hg(2)–I(5)	2.6781(5)	O(12)–Cd(1)–O(2)	69.91(18)
Hg(2)–I(6)	2.6768(5)	N(1)–Cd(1)–O(2)	69.73(15)

[a]Symmetry codes: i −x, −y+1, −z+1; ii −x+1, y, −z+0.5.

amine [24], to the cadmium atom produces the cube geometry with the lowest distortion, and our complex with the NTE ligand is now the third example to show this geometry.

The [I$_2$Hg(μ-I$_2$)$_2$HgI$_2$]$^{2-}$ anion is a binuclear complex of mercury(II), containing two types of iodide ligands (bridging and terminal) and two mercury atoms with coordination number four in tetrahedral environment. The averages of the four Hg–I$_{terminal}$ and two Hg–I$_{bridging}$ bond lengths are 2.6910 and 2.9540 Å, respectively, which are comparable with the CSD averages (2.6931 and 2.9230 Å, respectively). The tetracoordinate geometry of the mercury atom can adopt either a tetrahedral or a square planar configuration. To determine the geometry of such structures, the formula of Hakimi et al. [25] was applied in which the angular structural parameter (τ_{sq}) is represented as the index of tetragonality. The parameter $\tau_{sq} = (\theta_{max} - \theta_{min})/90$, where θ_{max} and θ_{min} are the maximum and minimum bond angles, respectively. An ideal square plane will have $\theta_{max} = 180°$ and $\theta_{min} = 90°$, and therefore $\tau_{sq} = 1$, but an ideal tetrahedron will have $\theta_{max} = 109.28°$, $\theta_{min} = 109.28°$ and therefore $\tau_{sq} = 0$. The τ_{sq} value is calculated to be 0.29 and 0.44 for Hg1 and Hg2, respectively, thus indicating an inclination to a tetrahedral geometry [25]. In the structure of the complex, two [I$_2$Hg(μ-I$_2$)$_2$HgI$_2$]$^{2-}$ anions have different point group symmetries. The anion containing an Hg1 atom has one center of inversion on the

Table 3: Hydrogen bond geometries (Å, deg) for [Cd(NTE)$_2$][Hg$_2$(μ-I)$_2$I$_4$].

D−H···A	d(D−H)	d(H···A)	<(DHA)	d(D···A)	Symmetry code
O(2)–H(2)···I(4)	0.98	2.81	154	3.715(5)	1−x, y, 0.5−z
O(4)–H(4)···I(6)	0.98	2.65	157	3.578(6)	x, −1+y, z
O(6)–H(6)···I(3)	0.98	2.71	163	3.662(4)	x, −1+y, z
O(8)–H(8)···I(5)	1.0	2.7	151	3.574(4)	x, y, z
O(10)–H(10)···I(4)	0.98	2.74	147	3.604(5)	1−x, −1+y, 0.5−z
O(12)–H(12)···I(3)	1.0	2.8	159	3.748(5)	x, y, z
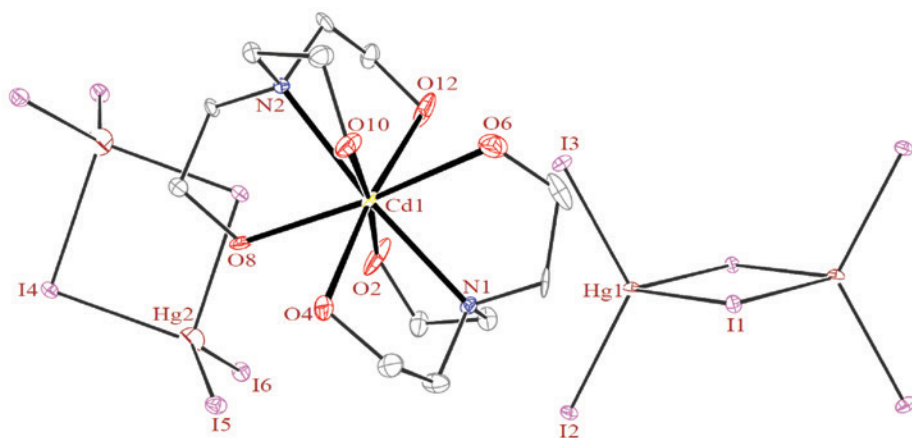
Fig. 2: ORTEP-III diagram of the molecular structure of [Cd(NTE)$_2$][Hg$_2$(μ-I)$_2$I$_4$]. The displacement ellipsoids are drawn at the 35% probability level. The hydrogen atoms of the ligand were omitted for clarity.
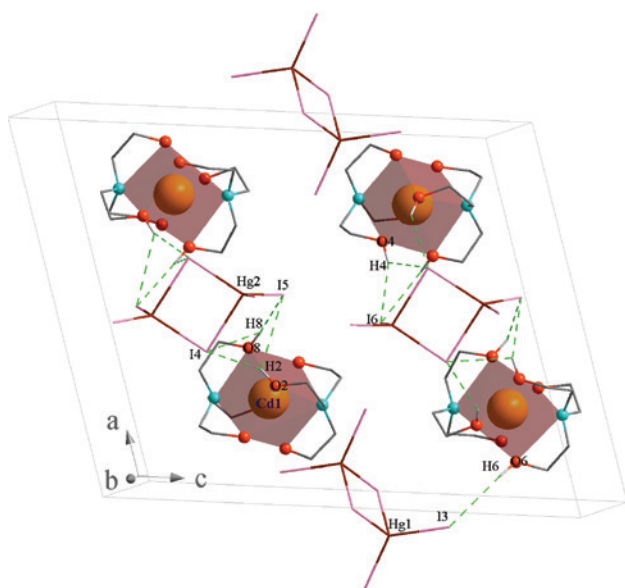
Fig. 3: Packing of complex, showing the hydrogen bonds in the *ac* plane. Only the hydrogen atoms involved in hydrogen bonding are shown. Each CdN$_2$O$_6$ unit is shown as a cube.
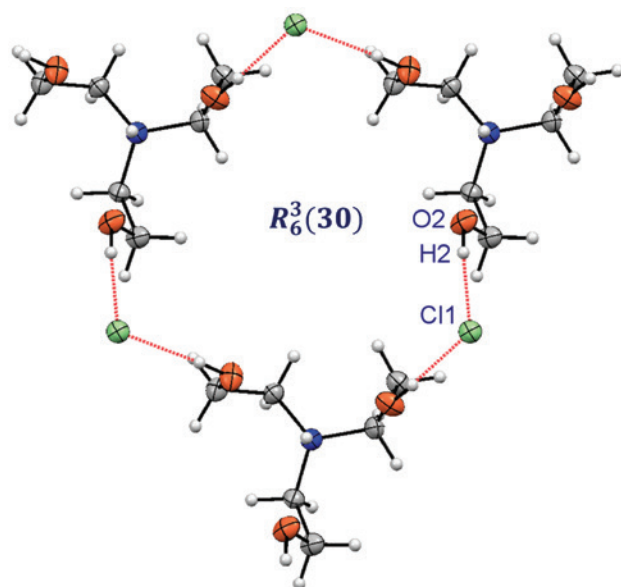

Fig. 4: Packing in crystals of [HNTE]Cl, showing the hydrogen bonds and R$_6^3$(30) motifs.

center of the Hg1/I1/Hg1^i/I1^i plane and C_i symmetry, while another anion has a C_2 axis perpendicular to the Hg2/I4/Hg2^i/I4^i plane and C_2 symmetry.

In the structural network of the complex (Fig. 3), there are intermolecular O−H⋯I and I⋯I interactions. Two I5⋯I6 interactions are evident between adjacent [I$_2$Hg(μ-I$_2$)$_2$HgI$_2$]$^{2-}$ units to form a ten-membered ring and extend the network in the *bc* plane (Fig. 5).

3 Conclusion

In this work, a new complex of NTE, [Cd(NTE)$_2$][Hg$_2$(μ-I)$_2$I$_4$], was synthesized and its spectral (IR, ^{1}H NMR) and structural properties were investigated. The structure of the [HNTE] Cl salt was also then determined by X-ray diffraction analysis and reported. The NTE ligand acts as an NO$_3$-donor in this complex by forming three five-membered non-planar chelate rings. X-ray analysis of the complex revealed a cadmium atom with a slightly distorted cube geometry (CdN$_2$O$_6$) and mercury atoms in a binuclear structure [I$_2$Hg(μ-I$_2$)$_2$HgI$_2$]$^{2-}$ with a tetrahedral geometry. On the basis of CSD studies, we observe that the coordination geometry around the cadmium atom is a cube with only modest distortion.

4 Experimental section

4.1 Materials and instrumentation

All chemicals and solvents were reagent or analytical grade and used as received. The carbon, hydrogen and nitrogen contents were determined in a Thermo Finnigan Flash Elemental Analyzer 1112 EA. The infrared spectra of KBr pellets were recorded in the range of 400−4000 cm^{-1} using an FT-IR 8400-Shimadzu spectrometer. The melting point was determined using Barnstead Electrothermal 9200 electrically heated apparatus. The ^{1}H NMR spectrum was recorded on a Bruker Aspect 3000 instrument operating at 250 MHz; chemical shifts are given in parts per million, with values in reference to an internal standard of tetra methyl silane.

4.2 [HNTE]Cl

NTE (0.15 g, 1 mmol) dissolved in EtOH (10 mL) was added with stirring to a solution containing 0.27 g (1 mmol) of HgCl$_2$ in ethanol (10 mL). The reaction mixture was refluxed for 6 h and then filtered. The colorless crystals suitable for X-ray diffraction were obtained from the solution after standing for a week. Yield: 0.01 g, 5%; m.p.: 168°C. −C$_6$H$_{16}$ClNO$_3$ (185.65): calcd. C 38.82, H 8.69, N 7.54; found C 38.47, H 8.66, N 7.68. − IR (KBr disk): $\nu = 3314$ (OH), 3158 (NH), 2938 (CH), $\delta_{as} = 1459$ (CH$_2$), $\delta_s = 1404$ (CH$_2$), $\nu = 1253$ (CO), 1095 (CN) cm^{-1}.

4.3 [Cd(NTE)$_2$][Hg$_2$(μ-I)$_2$I$_4$]

NTE (0.30 g, 2 mmol) dissolved in EtOH (15 mL) was added with stirring to a solution containing 0.37 g (1 mmol) of
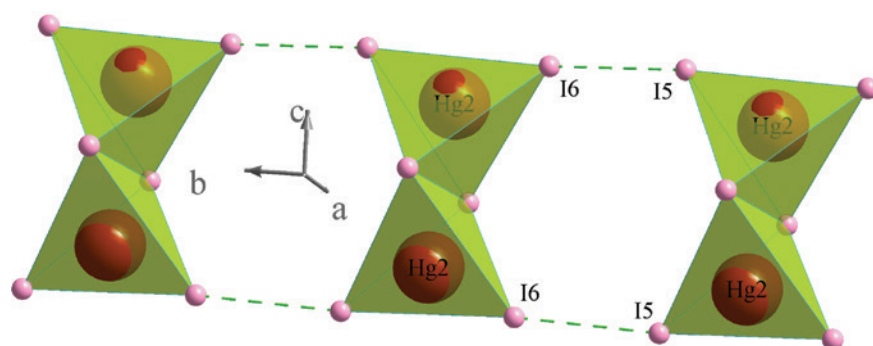
Fig. 5: Participation of I···I interactions in forming ten-membered rings. Each HgI$_4$ unit is shown as a tetrahedron.

CdI$_2$ and 0.45 g (1 mmol) of HgI$_2$ in ethanol (25 mL). The reaction mixture was refluxed for 6 h and then filtered. The yellow crystals suitable for X-ray diffraction were obtained from the solution after standing for 5 days. Yield: 0.64 g, 82%; m.p.: 160°C. −C$_{12}$H$_{30}$CdHg$_2$I$_6$N$_2$O$_6$ (1573.40): calcd. C 9.13, H 1.92, N 1.78; found C 8.12, H 2.01, N 1.85. − IR (KBr disk): ν = 3442 (OH), 2953 (CH), δ_{as} = 1446 (CH$_2$), δ_s = 1369 (CH$_2$), ν = 1251 (CO), 1060 (CN) cm^{-1}. −^{1}H NMR (250 MHz, [D$_6$]DMSO): δ = 5.56 (s, 3H, OH), 3.50 (m, 6H, OCH), 2.68 (m, 6H, NCH) ppm.

4.4 X-ray structure determinations

Data were collected at 93.0 K using a Rigaku FRX (Mo-K, confocal optic) and Dectris P200. The structures were solved and refined with SHELX [26]. Diagrams of the molecular structure and unit cell were created using ORTEP-III [27–29] and DIAMOND [30, 31]. In all CSD searches which have been presented, the structures containing any error or disorder have been omitted.

CCDC 1530145 and 1506871 for [Cd(NTE)$_2$][Hg$_2$(μ-I)$_2$I$_4$] and [HNTE]Cl, respectively, contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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