

Coordination of an Amino Alcohol Schiff Base Ligand Toward Cd(II)

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ABSTRACT. A potentially tetradentate Schiff base ligand, 2-((2-((pyridin-2-ylmethylene)amino)ethyl)amino)ethan-1-ol (PMAE), and its cadmium(II) complex, [Cd(PMAE)₂] (**1**), were prepared and characterized by elemental analysis, FT-IR, Raman, ¹H and ¹³C NMR spectroscopies and single-crystal X-ray diffraction. In the crystal structure of **1**, the cadmium atom has a slightly distorted square-pyramidal geometry and a CdN₃I₂ environment in which the PMAE acts as an N₃-donor. In the crystal packing of the complex, the alcohol and amine groups of the coordinated ligands participate in hydrogen bonding with iodide ions and form R₂²(14) and R₂²(8) hydrogen bond motifs, respectively. In addition to the hydrogen bonds, the crystal network is stabilized by π - π stacking interactions between pyridine rings. The thermodynamic stability of the isolated ligand and its cadmium complex along with their charge distribution patterns were studied by DFT and NBO analysis.

Key words: β -Amino alcohol, Cadmium complex, X-ray crystal structure, Schiff base ligand, Microwave

INTRODUCTION

β -Amino alcohols exhibit a broad spectrum of biological activities such as anti-hypertensive,¹ antibacterial agents² and HIV protease inhibitors.³ β -Amino alcohols have been used as intermediates and chiral auxiliaries in organic synthesis,⁴ as well as organocatalysts.⁵ Amino alcohols such as mono- and diethanolamine are known to fix CO₂ and are used as absorbents for the chemical absorption of CO₂.⁶ Chiral amino alcohol Schiff base ligands⁷ comprise of a group of ligands that are widely employed in asymmetric transformations such as asymmetric oxidations,⁸ asymmetric alkynylations⁹ and enantioselective trimethylsilyl-cyanations.¹⁰ An example of such ligands is 2-((2-((pyridin-2-ylmethylene)amino)ethyl)amino)ethan-1-ol (PMAE, Scheme 1) which is potentially tetradentate ligand. In this work, in order to extend the chemistry of this class of compounds, microwave assisted preparation, characterization (elemental analysis, FT-IR, Raman, ¹H and ¹³C NMR spectroscopy) of PMAE ligand and its cadmium(II) complex is presented along with the X-ray structure and theoretical studies.

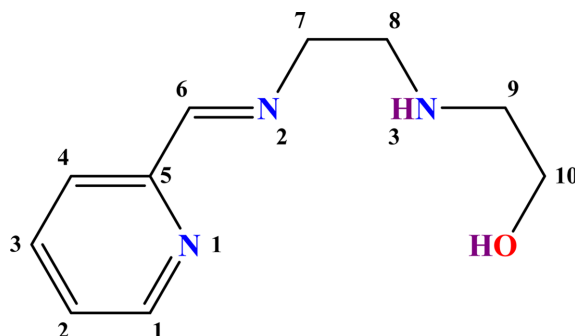
EXPERIMENTAL

All chemicals and solvents were reagent or analytical grade and used as received. The infrared spectra of KBr

pellets in the range 4000–400 cm⁻¹ were recorded with a FT-IR TENSOR 27 spectrometer. ¹H and ¹³C NMR spectra were recorded on Bruker Aspect 3000 instrument. The carbon, hydrogen and nitrogen contents were determined by a Thermo Finnigan Flash Elemental Analyzer 1112 EA. The melting points were determined with a Barnsted Electrothermal 9200 electrically heated apparatus. The microwave-assisted synthesis of compound was carried out using a Microwave Laboratory Systems MicroSYNTH, Milestone s.r.l. Raman spectrum was obtained using a Nicolet Model 910 Fourier-transform spectrometer.

Synthesis of 2-((2-((pyridin-2-ylmethylene)amino) ethyl) amino)ethan-1-ol, PMAE

A mixture of 1.07 g (10 mmol) pyridine-2-carbaldehyde



Scheme 1. Structures of the PMAE ligand.

and 1.04 g (10 mmol) 2-((2-aminoethyl)amino)ethan-1-ol was irradiated inside a microwave oven for 10 min under reflux condition with a power up to 1000 W. After microwave irradiation a brown oily liquid was obtained. All volatile components were removed by rotary evaporation and the resultant was dissolved in water (15 mL) and then washed three times with chloroform (15 mL). The isolated water layer was evaporated to dryness. A viscous brown oil was obtained. Yield 1.00 g, 52%. Anal. calcd for $C_{10}H_{15}N_3O$ (193.25): C 62.15, H 7.82, N 21.74; found C 63.04, H 7.98, N 22.15%. IR (KBr): 3325 (ν O–H), 3254 (ν N–H), 3063 (ν C–H)^{ar}, 2939 (ν C–H), 1613 (ν C=N), 1574 (ν C=N)^{py}, 1471 (ν C=C), 1435 (δ_{as} CH₂), 1366 (δ_s CH₂), 1227 (ν C–O), 1142 (ν C–N), 779 and 664 (γ py) cm^{-1} . ¹H NMR (250 MHz, CDCl₃, atom numbering as in Scheme 1): δ = 8.33 (d, 1H, C¹H), 8.10 (s, 1H, C⁶H), 6.99–7.49 (m, 3H, C²H–C⁴H), 5.55 (s, 1H, OH), 2.55–3.43 (m, 9H, C⁷H–C¹⁰H, N³H) ppm. ¹³C NMR (63 MHz, CDCl₃): δ = 122.8–159.0 (C¹–C⁶), 82.8 (C¹⁰), 53.2–60.20 (C⁷–C⁹) ppm.

Synthesis of [Cd(PMAE)I₂]

0.19 g (1 mmol) of PMAE dissolved in EtOH (15 mL) was added with stirring to a solution containing 0.37 g (1 mmol) of CdI₂ in ethanol (25 mL). The reaction mixture

was refluxed for 6 h and then filtered. Yellow crystals suitable for X-ray diffraction were obtained from the solution after standing for four days. Yield 0.47 g, 84%; m. p. 208 °C. Anal. calcd for $C_{10}H_{15}CdI_2N_3O$ (559.47): C 21.47, H 2.70, N 7.51; found C 21.22, H 2.70, N 7.82%. IR (KBr): 3328 (ν O–H), 3301 (ν N–H), 3063 (ν C–H)^{ar}, 2939 (ν C–H), 1651 (ν C=N), 1589 (ν C=N)^{py}, 1443 (δ_{as} CH₂), 1373 (δ_s CH₂), 1219 (ν C–O), 1126 (ν C–N), 772 and 661 (γ py) cm^{-1} . Raman: 3073 (ν C–H)^{ar}, 2978 (ν C–H), 1630 (ν C=N), 1332 (δ_s CH₂), 1166 (ν C–N), 677 (γ py), 553 (ν Cd–N), 132 (ν Cd–I) cm^{-1} . ¹H NMR (300 MHz, [D₆]-DMSO, atom numbering as in Scheme 1): δ = 8.85 (s, 1H, C⁶H), 7.83–8.67 (m, 4H, C¹H–C⁴H), 4.80 (s, 1H, OH), 2.82–3.89 (m, 9H, C⁷H–C¹⁰H, N³H) ppm.

Computational Details

All structures were optimized with the Gaussian 09 software¹¹ and calculated for an isolated molecule using Density Functional Theory (DFT)¹² at the B3LYP/6-31G(d,p) level of theory for ligand and B3LYP/LanL2DZ for complex as well as for NBO analysis. The coordination from the cif file of complex **1** was used as input file for theoretical calculations.

Table 1. Crystal data and structure refinement for complex **1**

Empirical formula	$C_{10}H_{15}CdI_2N_3O$
Formula weight, $g\ mol^{-1}$	559.45
Crystal size, mm^3	$0.11 \times 0.1 \times 0.06$
Temperature, K	150
Crystal system	monoclinic
Space group	$P2_1/n$
Unit cell dimensions (\AA , deg)	
<i>a</i>	7.9869(3)
<i>b</i>	15.8553(5)
<i>c</i>	12.2474(4)
β	102.071(3)
Volume, \AA^3	1516.65(8)
<i>Z</i>	4
Calculated density, $g\ cm^{-3}$	2.505
Absorption coefficient, mm^{-1}	6.171
<i>F</i> (000), e	1048.0
2θ range for data collection (deg)	4.26–58.68
<i>h</i> , <i>k</i> , <i>l</i> ranges	$-9 \leq h \leq 10$, $-12 \leq k \leq 20$, $-10 \leq l \leq 15$
Reflections collected / independent / R_{int}	7122 / 3494 / 0.0326
Data / ref. parameters	3494 / 155
Goodness-of-fit on F^2	1.018
Final <i>R</i> indexes [$I > 2\sigma(I)$]	$R_1 = 0.0399$, $wR_2 = 0.1041$
Final <i>R</i> indexes [all data]	$R_1 = 0.0452$, $wR_2 = 0.1087$
Largest diff. peak / hole, $e\ \text{\AA}^{-3}$	1.26 / –2.68

Table 2. Selected bond lengths (Å) and angles (deg) for complex **1** with estimated standard deviations in parentheses

Bond lengths (Å)			Angles (°)		
	1	1^{opt}		1	1^{opt}
Cd1–N1	2.443(4)	2.483	N1–Cd1–N2	68.8(1)	68.15
Cd1–N2	2.320(4)	2.385	N2–Cd1–N3	72.7(1)	71.23
Cd1–N3	2.395(3)	2.507	N3–Cd1–I2	114.87(9)	99.99
Cd1–I1	2.839(4)	2.810	I2–Cd1–I1	110.54(1)	129.26
Cd1–I2	2.757(4)	2.814	I1–Cd1–N1	96.8(9)	96.07

Table 3. Hydrogen bond dimensions (Å and deg) in complex **1**

D–H⋯A	<i>d</i> (D–H)	<i>d</i> (H⋯A)	<(DHA)	<i>d</i> (D⋯A)	Symmetry code on A atom
O(1)–H(1)⋯N(2)	0.82	2.49	119	2.97(5)	2– <i>x</i> , 1– <i>y</i> , 2– <i>z</i>
N(3)–H(3)⋯I(2)	0.91	2.96	143	3.73(3)	2– <i>x</i> , 1– <i>y</i> , 2– <i>z</i>
O(1)–H(1)⋯I(1)	0.82	3.00	148	3.72(3)	1– <i>x</i> , 1– <i>y</i> , 2– <i>z</i>
C(2)–H(2)⋯I(1)	0.93	3.16	160	4.04(5)	1– <i>x</i> , 1– <i>y</i> , 1– <i>z</i>
C(6)–H(6)⋯I(1)	0.93	3.36	100	3.65(5)	1+ <i>x</i> , <i>y</i> , <i>z</i>
C(7)–H(7A)⋯I(2)	0.97	3.33	123	3.95(5)	1– <i>x</i> , 1– <i>y</i> , 1– <i>z</i>

Crystal Structure Determination and Refinement

Diffraction data were collected at 150 K on a Rigaku Oxford Diffraction Gemini Ultra diffractometer. Data processing and absorption correction was carried out using CrysAlis Pro.¹³ The structures were solved with direct methods and refined with least squares using the OLEX2 package.¹⁴ All hydrogen atoms were placed at their calculated positions. Selected crystallographic data are presented in *Table 1*. Diagrams of the molecular structure and unit cell were created using Ortep-III¹⁵ and Diamond.¹⁶ Selected bond lengths and angles are displayed in *Table 2* and hydrogen bond geometries in *Table 3*.

CCDC 981063 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.

RESULTS AND DISCUSSION

The PMAE formed in the reaction between 2-((2-aminoethyl)amino)ethan-1-ol and pyridine-2-carbaldehyde under solvent free conditions using microwave irradiation.¹⁷ The reaction between an ethanolic solution of CdI₂ with PMAE afforded yellow crystals of **1**, which are air-stable and soluble in DMF and DMSO. A study of the literature revealed, that a similar structure to complex **1**¹⁸ has been reported previously using a different method than used in this study. We prepared the ligand using microwave irradiation and then used it for preparation of the complex while Purkait et al.¹⁸ prepared the complex by a template reaction without isolating the ligand. Also full spectroscopic

data of the ligand and its cadmium complex have not been reported previously and are present at this paper. The temperature of the X-ray data collection in our report (150 K) is different than the previous work (room temperature).

Spectroscopic Characterization

In the FT-IR spectrum of the ligand (Supplementary Materials), frequencies above and under 3000 cm⁻¹ which can be assigned to the stretching vibration of the C–H bonds, reveal the aromatic and aliphatic moieties in these structures, respectively. Frequencies near 3300 and 3250 cm⁻¹ can be attributed to the stretching vibrations of the ν(O–H) and ν(N–H), respectively. After complexation, no significant shift was observed for ν(O–H) while ν(N–H) shifted 47 cm⁻¹ to higher frequencies, confirming the coordination of the amine moiety of the ligand. In the FT-IR spectra of the ligand and complex, two peaks are observed near 1600 cm⁻¹ which can be assigned to the ν(C=N) vibrations of the imine and pyridine units. The ν(C=N) of the imine and pyridine in **1** is shifted 38 and 15 cm⁻¹, respectively, to the higher frequencies than the free ligand. Based on these observations we may infer that the PMAE acts as N₃-donor towards the cadmium atom. The ring wagging vibrations of the pyridine ring are also observed at near 770 and 660 cm⁻¹ in both spectra.^{17b,19}

Information about the low frequency metal-ligand vibrations was obtained by Raman spectroscopy. In this spectrum, the Cd–N stretching vibration appeared at 553 cm⁻¹. The presence of a band at 132 cm⁻¹ can be attributed to the terminal Cd–I stretching vibrations (100–200 cm⁻¹ for M–I^{terminal}).²⁰

In the ^1H NMR spectra of the ligand and **1** (see Scheme 1 for numbering), the peaks are observed in three regions, 7–9 ppm for aromatic and imine protons, 5 ppm for the alcohol unit and 2.5–4 ppm for aliphatic and amine moieties. Comparison of the ^1H NMR spectra of ligand and complex revealed that all peaks of the ligand are shifted to lower magnetic field after complexation. Among them, the proton of the imine shows the highest shift by 0.75 ppm. In the ^{13}C NMR spectrum of the ligand, the imine and aromatic carbon atoms are observed at 120–160 ppm and others at 50–80 ppm. Among the aliphatic carbon atoms, the C10 atom which was attached to the alcohol moiety is observed at the lowest chemical shift.

Description of the Crystal Structure

In the crystal structure of **1** (Fig. 1), the cadmium atom has a $\text{Cd}(\text{N}^{\text{py}})(\text{N}^{\text{imine}})(\text{N}^{\text{amine}})(\text{I}^{\text{terminal}})_2$ environment and is coordinated by one N_3 -donor PMAE ligand and two iodide ions with coordination number of five. A penta-coordinate geometry of **1** may adopt either a square pyramidal or a trigonal bipyramidal structure which is determined by applying the formula of Addison et al.^{19,21} The angular structural parameter, $\tau = (\beta - \alpha)/60$, was calculated to be 0.05 for the cadmium atom indicating a slightly distorted square-pyramidal geometry. Searching the Cambridge Structural Database (CSD)^{20a} for analogues of **1** containing $\text{Cd}(\text{N}^{\text{py}})(\text{N}^{\text{imine}})(\text{N}^{\text{amine}})(\text{I}^{\text{terminal}})_2$ environments with two five-membered chelate rings revealed that there are five examples²² (one structure containing one five-membered and one six-membered chelate rings¹⁸ was omitted for precise comparison). The average geometrical parameters for these structures were calculated and are presented in Scheme 2. Comparison of these data with those of **1** revealed that, all geometrical parameters in **1** are comparable with the CSD averages, except that the Cd1–I1 bond length is 0.092 Å

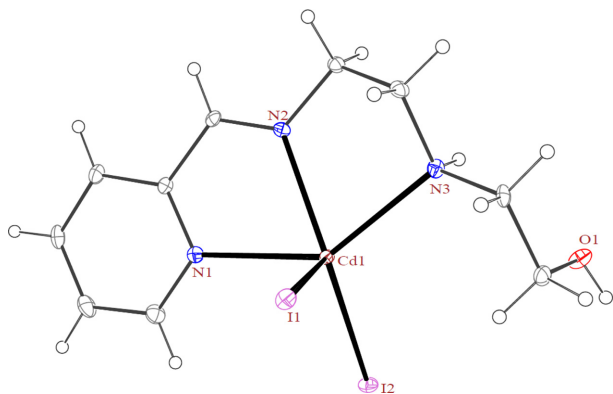
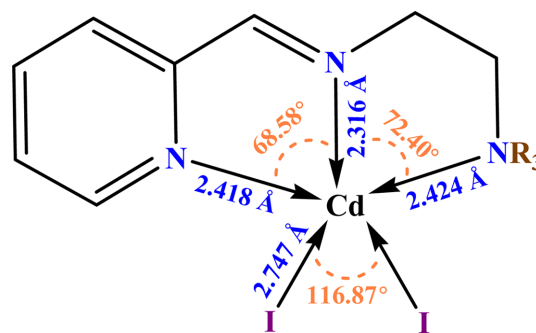


Figure 1. The ortep diagram of the molecular structure of **1**. The ellipsoids are drawn at the 25% probability level.



Scheme 2. CSD average for the $\text{Cd}(\text{N}^{\text{py}})(\text{N}^{\text{imine}})(\text{N}^{\text{amine}})(\text{I}^{\text{terminal}})_2$ environment.

longer than the average and also I–Cd–I bond angle in **1** is 6.33° smaller than the average. A study of the crystal packing of **1** revealed that the longest Cd–I has more interactions with adjacent molecules than the other one. For all analogues of **1**, the τ value was calculated to be in the range of 0.07–0.32, showing that **1** is closer to ideal square-pyramidal geometry than its analogues.

The PMAE ligand forms two five-membered planar and non-planar chelate rings. This ligand does not have a chiral center, but upon coordination a new chiral center at N3 is produced. Although complex **1** has one chiral center, the crystals are racemic.^{17b,c}

Each tridentate ligand can coordinate to a metal center in facial or meridional forms. In the *mer* form there are two angles of 90° and one of 180° , in the *fac* form there are three angles of 90° .^{17a,20b} In **1**, two of the relevant bond angles of PMAE deviate slightly from 90° due to the chelating bite angle, whilst the third one is $141.4(1)^\circ$ and thus consistent with the *mer* form (135° is exactly half way between *fac* and *mer*).

In the packing of **1**, there are $\text{C}-\text{H}\cdots\text{I}$, $\text{N}-\text{H}\cdots\text{I}$, $\text{O}-\text{H}\cdots\text{I}$ and $\text{O}-\text{H}\cdots\text{N}$ interactions (Fig. 2). Among them, the $\text{O}-\text{H}\cdots\text{I}$ hydrogen bonds participate in the formation of $\text{R}^2_2(14)$ hydrogen bond motifs (two acceptors, two donors with degree of 14)^{17f} between two molecules of **1**. Another hydrogen bond motif ($\text{R}^2_2(8)$) is formed between two adjacent complexes connected by two $\text{N}-\text{H}\cdots\text{I}$ hydrogen bonds. In addition to the hydrogen bonds, the network is stabilized by π – π stacking interactions between pyridine rings of the ligands of adjacent complexes. The pyridine rings are exactly parallel to each other (dihedral angle between planes: 0°) and nitrogen atoms of the pyridine rings have anti direction. The centroid–centroid distance and the perpendicular distance between the pyridine planes are 3.719 and 3.527 Å, respectively. Thus the slippage of pyridine rings was calculated to be 1.180 Å.²³

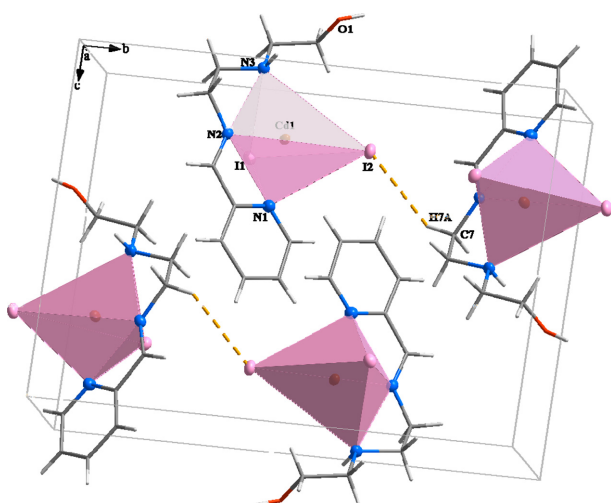


Figure 2. Packing of the **1**, showing the hydrogen bonds.

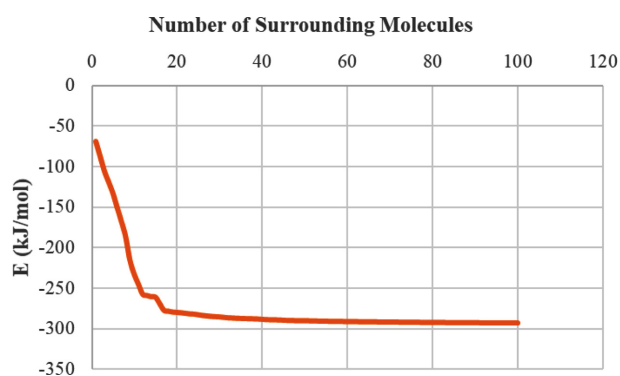


Figure 3. Variation diagram of total intermolecular interactions energy (E) for **1** with increasing number of surrounding molecules.

The total intermolecular interactions energy²⁴ for one complex unit of **1** was calculated using the CSD-materials tool in Mercury²⁵ (Fig. 3).²⁶ For this aim, the sum of intermolecular interactions energies in a molecular pack-

ing shell containing 100 molecules around one molecule of **1** was calculated to be -293.3 kJ/mol. In **1**, 56 and 95 % of the calculated stabilization energy corresponds to the interactions with 6 and 18 surrounding molecules, respectively.

Computational Studies

For comparing the structure of the complex **1** in solid state with an isolated one, DFT calculations were performed and optimized structures are presented in Fig. 4. For the optimized structure **1**^{opt}, the τ was calculated to 0.17, showing that the square-pyramidal geometry in solid phase is different from that in an isolated molecule. Comparing the geometrical parameters of **1** with **1**^{opt} revealed that in solid phase, the coordinated bond lengths formed by donor atoms that do not participate in hydrogen bonding (N1, N2) are similar to those of the isolated ones (Table 2) while others are different. In **1**^{opt}, similarly to **1**, two of the coordinated bond angles of the PMAE deviate slightly from 90° , whilst the third one is 139.37° and thus in the *mer* form. In the optimized structure of the ligand, the PMAE has *E* configuration and all nitrogen atoms have same direction as observed in the structure of the complex.

For studying the charge distribution pattern of ligand before and after coordination an NBO analysis was performed (Table 4). The results reveal that the calculated charge on the carbon atom of the imine moiety is positive while other carbon atoms have a negative charge. Among the three nitrogen atoms, the amine nitrogen has higher electronegativity than the others. In the complex, the calculated charge on the metal atom (+1.07) is lower than the formal charge (+2) owing to electron donation of the ligand upon complexation. After coordination of the PMAE, the variation of charge on the hydrogen atoms is not signif-

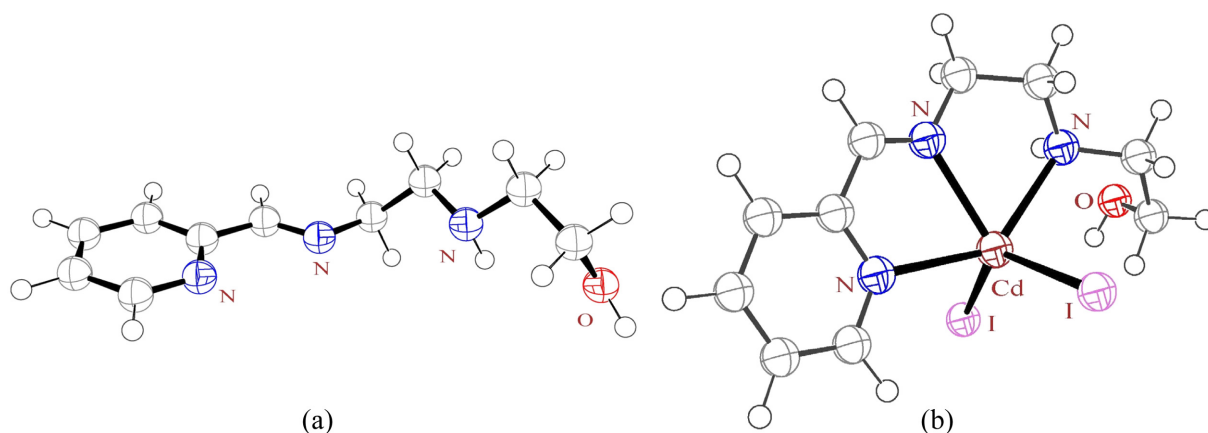
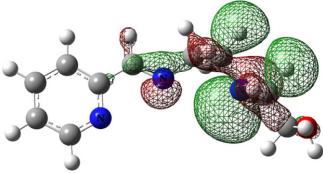
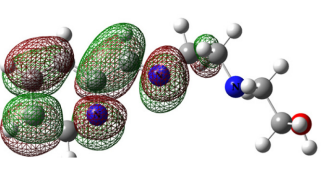
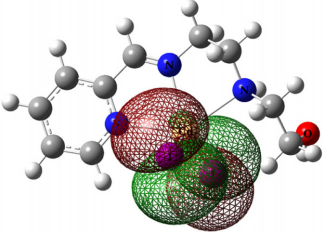
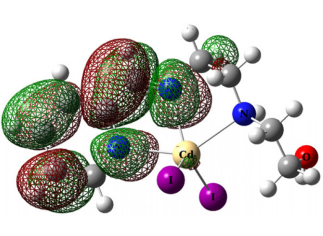


Figure 4. Optimized structures of the PMAE and its cadmium complex.

Table 4. The NBO analysis results for PMAE and complex **1**. The values are the average of charge on similar atoms

	C ^{aliph}	C ^{ar}	C ^{imine}	H ^{OH}	H ^{aliph}	H ^{ar}	H ^{imine}	N ^{imine}	N ^{NH}	N ^{py}	O	I	Cd
PMAE	-0.25	-0.12	0.06	0.50	0.22	0.25	0.17	-0.38	-0.72	-0.41	-0.80	–	–
Complex 1	-0.11	-0.05	0.21	0.51	0.19	0.23	0.18	-0.60	-0.83	-0.60	-0.86	-0.63	1.07

Table 5. HOMO and LUMO orbitals for optimized structures of two DFPT isomers

	HOMO	LUMO	Total Energy (kcal/mol)	HOMO/LUMO Gap(eV)
PMAE ^{opt}			-395060.3	4.15
1 ^{opt}			-435782.8	8.88

icant while the charges on the carbon atoms are positive compared to the free ligand as well as iodide ligands, showing that these atoms play an important role in electron donation toward metal atom and decreasing the charge of it. The nitrogen atoms of the ligand show the highest charge variation after coordination. The charge on these atoms are negative compared to the free ligand and the nitrogen atom of the imine moiety has the highest variation.

In the optimized structure of PMAE, the LUMO is mainly delocalized on the aromatic and imine portions whilst the HOMO is delocalized on the aliphatic and partially on the imine unit (Table 5). In **1**^{opt}, the LUMO has similar pattern with PMAE while the HOMO delocalized on the iodide ions. The cadmium atom does not have any quota in the frontier orbitals of the complex. DFT calculations reveal that the HOMO/LUMO energy gap in complex is 4.73 eV higher than the free ligand (Table 5).

CONCLUSION

In this work, a Schiff base ligand, 2-((2-((pyridin-2-ylmethylene)amino)ethyl)amino)ethan-1-ol (PMAE), and its cadmium complex, [Cd(PMAE)₂] (**1**), were synthesized and their spectral (IR, Raman, ¹H and ¹³C NMR) and structural properties were investigated. In the structure of **1**, the cadmium atom has slightly distorted square-pyramidal geometry and CdN₃I₂ environment by coordination of the one *mer*-(N^{py})(N^{imine})(N^{amine})-donor PMAE and two non-

bridging iodide ions. The complex contains one chiral center on an amine nitrogen atom with racemic mixture of isomers. In the crystal packing of the complex, the alcohol and amine groups along with the iodide ions have important roles in the hydrogen bonding map. The O–H···I and N–H···I hydrogen bonds form R²₂(14) and R²₂(8) hydrogen bond motifs, respectively. In addition to the hydrogen bonds, the crystal network is stabilized by π–π stacking interactions between pyridine rings of the PMAE ligands on the adjacent complexes. The DFT calculations revealed that among different atoms of the ligand, the carbon atoms have significant role in electron donation toward cadmium atom. Based on the theoretical studies, the HOMO/LUMO energy gap in complex is 4.73 eV higher than the free ligand.

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Supporting Information. Additional supporting information is available in the online version of this article.

REFERENCES

- (a) Frishman, W. H. Beta-adrenergic blockers. *Circulation* **2003**, *107*, e117. (b) Nash, D. Alpha-adrenergic blockers: Mechanism of action, blood pressure control, and effects on lipoprotein metabolism. *Clin. Cardiol.* **1990**, *13*, 764.
- Yendapally, R.; Lee, R. E. Design, synthesis, and evaluation of novel ethambutol analogues. *Bioorg. Med. Chem.*

- Lett.* **2008**, *18*, 1607.
- Kwon, S. J.; Ko, S. Y. Synthesis of statine employing a general syn-amino alcohol building block. *Tetrahedron Lett.* **2002**, *43*, 639.
 - (a) Ager, D. J.; Prakash, I.; Schaad, D. R. 1, 2-Amino alcohols and their heterocyclic derivatives as chiral auxiliaries in asymmetric synthesis. *Chem. Rev.* **1996**, *96*, 835. (b) Myers, A. G.; Yang, B. H.; Chen, H.; McKinstry, L.; Kopecky, D. J.; Gleason, J. L. Pseudoephedrine as a practical chiral auxiliary for the synthesis of highly enantiomerically enriched carboxylic acids, alcohols, aldehydes, and ketones. *J. Am. Chem. Soc.* **1997**, *119*, 6496.
 - Russo, A.; Lattanzi, A. Asymmetric Epoxidation of trans-Chalcones Organocatalyzed by β -Amino Alcohols. *Eur. J. Org. Chem.* **2008**, *2008*, 2767.
 - (a) Hunt, A. J.; Sin, E. H.; Marriott, R.; Clark, J. H. Generation, capture, and utilization of industrial carbon dioxide. *ChemSusChem* **2010**, *3*, 306. (b) Rainbolt, J. E.; Koech, P. K.; Yonker, C. R.; Zheng, F.; Main, D.; Weaver, M. L.; Linehan, J. C.; Heldebrant, D. J. Anhydrous tertiary alkanolamines as hybrid chemical and physical CO₂ capture reagents with pressure-swing regeneration. *Energ. Environ. Sci.* **2011**, *4*, 480. (c) Werner, T.; Tenhumberg, N. Synthesis of cyclic carbonates from epoxides and CO₂ catalyzed by potassium iodide and amino alcohols. *J. CO₂ Util.* **2014**, *7*, 39.
 - Pradeep, C. P.; Das, S. K. Coordination and supramolecular aspects of the metal complexes of chiral N-salicyl- β -amino alcohol Schiff base ligands: Towards understanding the roles of weak interactions in their catalytic reactions. *Coord. Chem. Rev.* **2013**, *257*, 1699.
 - Barbarini, A.; Maggi, R.; Muratori, M.; Sartori, G.; Sartorio, R. Enantioselective sulfoxidation catalyzed by polymer-supported chiral Schiff base-VO(acac)₂ complexes. *Tetrahedron: Asymmetry* **2004**, *15*, 2467.
 - Chen, C.; Hong, L.; Zhang, B.; Wang, R. Catalytic asymmetric addition of alkynylzinc reagents to ketones using polymer-supported chiral Schiff-base amino alcohols. *Tetrahedron: Asymmetry* **2008**, *19*, 191.
 - Gama, Á.; Flores-López, L. Z.; Aguirre, G.; Parra-Hake, M.; Somanathan, R.; Cole, T. A study of substituent effects on the enantioselective trimethylsilylcyanation of benzaldehyde catalyzed by chiral Schiff base-titanium(IV) complexes. *Tetrahedron: Asymmetry* **2005**, *16*, 1167.
 - Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Scalmani, G.; Barone, V.; Mennucci, B.; Petersson, G. A.; Nakatsuji, H.; Caricato, M.; Li, X.; Hratchian, H. P.; Izmaylov, A. F.; Bloino, J.; Zheng, G.; Sonnenberg, J. L.; Hada, M.; Ehara, M.; Toyota, K.; Fukuda, R.; Hasegawa, J.; Ishida, M.; Nakajima, T.; Honda, Y.; Kitao, O.; Nakai, H.; Vreven, T.; Montgomery Jr., J. A.; Peralta, J. E.; Ogliaro, F.; Bearpark, M. J.; Heyd, J.; Brothers, E. N.; Kudin, K. N.; Staroverov, V. N.; Kobayashi, R.; Normand, J.; Raghavachari, K.; Rendell, A. P.; Burant, J. C.; Iyengar, S. S.; Tomasi, J.; Cossi, M.; Rega, N.; Millam, N. J.; Klene, M.; Knox, J. E.; Cross, J. B.; Bakken, V.; Adamo, C.; Jaramillo, J.; Gomperts, R.; Stratmann, R. E.; Yazyev, O.; Austin, A. J.; Cammi, R.; Pomelli, C.; Ochterski, J. W.; Martin, R. L.; Morokuma, K.; Zakrzewski, V. G.; Voth, G. A.; Salvador, P.; Dannenberg, J. J.; Dapprich, S.; Daniels, A. D.; Farkas, Ö.; Foresman, J. B.; Ortiz, J. V.; Cioslowski, J.; Fox, D. J. *Gaussian 09*, Gaussian, Inc.: Wallingford, CT, USA, 2009.
 - Perdew, J. P. *Phys. Rev.* **1986**, *B33*, 8822.
 - Crysalis Pro, Rigaku Oxford Diffraction, Japan.* 2018.
 - Dolomanov, O. V.; Bourhis, L. J.; Gildea, R. J.; Howard, J. A. K.; Puschmann, H. *J. Appl. Crystallogr.* **2009**, *42*, 339.
 - (a) Farrugia, L. J. *J. Appl. Crystallogr.* **1997**, *30*, 565. (b) Burnett, M. N.; Johnson, C. K. Ortep-III, Report ORNL-6895. Oak Ridge National Laboratory, Oak Ridge, Tennessee, U.S. 1996.
 - Bergerhof, G.; Berndt, M.; Brandenburg, K. *J. Res. Natl. Inst. Stand. Technol.* **1996**, *101*, 221.
 - (a) Hakimi, M.; Mardani, Z.; Moeini, K.; Mohr, F.; Schuh, E.; Vahedi, H. Synthesis, Crystallographic and Spectral Characterization of a Cadmium Chloride Complex Containing a Novel Imidazo[1,5-a]Pyridine Derivative. *Z. Naturforsch. B*, **2012**, *67b*, 452. (b) Hakimi, M.; Mardani, Z.; Moeini, K.; Schuh, E.; Mohr, F. Complexation to Cadmium(II) of a Tetradentate Ligand Resulting from the Condensation of 2-Pyridinecarbaldehyde with N-(2-Aminoethyl)propane-1,3-diamine. *Z. Naturforsch. B*, **2013**, *68b*, 267. (c) Hakimi, M.; Mardani, Z.; Moeini, K.; Schuh, E.; Mohr, F. A Spectral and Structural Study of the New Cadmium Salt [(H₂L)₂][CdI₆][(NO₃)₂]. *Z. Naturforsch. B*, **2013**, *68b*, 272. (d) Hakimi, M.; Mardani, Z.; Moeini, K.; Minoura, M.; Raissi, H. Synthesis, Characterization and Crystal Structure of a Binuclear Cadmium Iodide Complex with a Multi-N-donor Oxazolidine Ligand. *Z. Naturforsch. B*, **2011**, *66b*, 1122. (e) Hakimi, M.; Mardani, Z.; Moeini, K.; Fernandes, M. A. Coordination geometries and crystal structures of cadmium(II) complexes with a new amino alcohol (NN'O) ligand. *J. Coord. Chem.* **2012**, *65*, 2221. (f) Hakimi, M.; Moeini, K.; Mardani, Z.; Mohr, F. Microwave-assisted template synthesis of diazacyclam-based macrocyclic copper complex and forming octahedral, square planar and square pyramidal geometries by ion exchanging and introducing a novel 2D square-grid copper-mercury coordination polymer. *Polyhedron* **2014**, *70*, 92.
 - Purkait, S.; Chakraborty, P.; Bauzá, A.; Frontera, A.; Masera, C.; Das, D. Halide Ion Mediated Aldehyde-Amine Condensation Leading to Schiff-base and Cyclized Non-Schiff-base Ligand Complexes of CdII: A Combined Experimental and Theoretical Investigation. *ChemistrySelect* **2016**, *1*, 4539.
 - Hakimi, M.; Mardani, Z.; Moeini, K.; Mohr, F. Coordination behavior of dimethyl pyridine-2,6-dicarboxylate towards mercury(II), cadmium(II) and chromium(III) in

- the solid- and gaseous state supported by CSD studies. *Polyhedron* **2015**, *102*, 569.
20. (a) Allen, F. H. *Acta Crystallogr.* **2002**, *B58*, 380. (b) Hakimi, M.; Mardani, Z.; Moeini, K.; Feizi, N.; Mohr, F. Using experimental methods and CSD data for investigating the products of the reaction between 2-((2-aminoethyl)amino)ethanol with CdI₂ and CdI₂/HgI₂-mixtures. *J. Coord. Chem.* **2017**, *70*, 1247.
21. Addison, A. W.; Rao, T.; Reedjik, J.; Rijn, J. V.; Verschoor, G. Synthesis, structure, and spectroscopic properties of copper(II) compounds containing nitrogen-sulphur donor ligands; the crystal and molecular structure of aqua[1,7-bis(N-methylbenzimidazol-2'-yl)-2,6-dithiaheptane]copper(II) perchlorate. *Dalton Trans.* **1984**, *7*, 1349.
22. (a) Kundu, S.; Roy, S.; Bhar, K.; Sutradhar, D.; Mitra, P.; Ghosh, B. K. *Indian J. Chem.* **2013**, *52A*, 1404. (b) Satapathi, S.; Roy, S.; Bhar, K.; Ghosh, R.; Srinivasa Rao, A.; Ghosh, B. K. Syntheses, structures, and properties of two binuclear cadmium(II) iodides containing a bis(tridentate) Schiff base/tetradentate tripodal amine: control of coordination numbers by varying ligand matrices. *Struct. Chem.* **2011**, *22*, 605. (c) Mondal, S.; Jana, A. D. Induction of chirality through change of substitution in cadmium (II) complexes of 2-benzoylpyridine and 2-acetylpyridine based Schiff bases - Crystal structure, luminescence and thermal properties. *J. Mol. Struct.* **2018**, *1154*, 348. (d) Hakimi, M.; Ahmadi, S.; Mardani, Z.; Mohr, F., A new amino alcohol N^{py}N^{imine}N^{amine}O^{alcohol}-donor ligand: coordination toward zinc(II) and cadmium(II) halides and enantioselective products. *J. Coord. Chem.* **2017**, *70*, 3513.
23. (a) Mardani, Z.; Golsanamlou, V.; Khodavandegar, S.; Moeini, K.; Slawin, A. M. Z.; Woollins, J. D. The coordination of a multidentate NxOy-donor (x and y ≤ 2) oxazolidine-based ligand with Cd(II) and Hg(II); Structural, spectral, and theoretical studies. *J. Coord. Chem.* **2018**, *71*, 120. (b) Marandi, F.; Moeini, K.; Mostafazadeh, B.; Krautscheid, H. Structural, spectral and theoretical aspects in the coordination of a triazine-based ligand toward lead(II) with a holodirected environment. *Polyhedron* **2017**, *133*, 146. (c) Saghatforoush, L.; Moeini, K.; Golsanamlou, V.; Amani, V.; Bakhtiari, A.; Mardani, Z. Structural, spectral and theoretical study of the coordination of 3,6-bis(2-pyridyl)tetrazine ligand with zinc(II) and mercury(II). *Inorg. Chim. Acta* **2018**, *483*, 392. (d) Marandi, F.; Moeini, K.; Alizadeh, F.; Mardani, Z.; Quah, C. K.; Loh, W.-S.; Woollins, J. D. Treatment of cadmium(II) and zinc(II) with N₂-donor linkages in presence of β-diketone ligand; supported by structural, spectral, theoretical and docking studies. *Inorg. Chim. Acta* **2018**, *482*, 717.
24. Mardani, Z.; Kazemshoar-Duzdüzani, R.; Moeini, K.; Hajab-bas-Farshchi, A.; Carpenter-Warren, C.; Slawin, A. M. Z.; Woollins, J. D. Anticancer activities of a β-amino alcohol ligand and nanoparticles of its copper(II) and zinc(II) complexes evaluated by experimental and theoretical methods. *RSC Adv.* **2018**, *8*, 28810.
25. Macrae, C. F.; Bruno, I. J.; Chisholm, J. A.; Edgington, P. R.; McCabe, P.; Pidcock, E.; Rodriguez-Monge, L.; Taylor, R.; Van De Streek, J.; Wood, P. A. *J. Appl. Crystallogr.* **2008**, *41*, 466.
26. (a) Gavezzotti, A.; Filippini, G. Geometry of the Intermolecular X-H...Y (X, Y = N, O) Hydrogen Bond and the Calibration of Empirical Hydrogen-Bond Potentials. *J. Phys. Chem.* **1994**, *98*, 4831. (b) Gavezzotti, A. Are Crystal Structures Predictable? *Acc. Chem. Res.* **1994**, *27*, 309.
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