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A Dinuclear Cadmium(II) Schiff Base Thiocyanato Complex: Crystal Structure and Fluorescence

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Abstract

A new dinuclear cadmium(II) complex, $[Cd(L)(NCS)]_2$ (**1**) has been synthesized using a potentially tetradentate Schiff base ligand HL, 2-((E)-(2-(diethylamino)ethylimino)methyl)-6-methoxyphenol, obtained by the condensation of 2-diethylaminoethylamine and *o*-vanillin, and characterized by different physicochemical techniques. Crystal structure of the title complex was unambiguously established by single crystal X-ray diffraction which reveals that metal centers are connected by bridging phenolato and chelating methoxy oxygen atoms of the coordinating Schiff bases and embedded in severely distorted octahedral geometries. Fluorescence properties of the ligand and its complex, studied at room temperature indicate that later may serve as strong fluorescent emitter.

Keywords: Cadmium(II), Schiff base, Characterization, Crystal structure, Fluorescence

1. Introduction

Schiff bases with strong donor atoms like phenolato oxygen and imine nitrogen are excellent in catalysis and biological replication due to their strong coordination abilities with transition metal ions.[1] Among various Schiff bases, salen-type Schiff bases constitute a unique class for their structural richness and wide range of applications. For example, salen-type bis-chelating N,O-donor Schiff bases in their nickel(II) complex serve as important models for enzyme like urease.[2] Tri- and tetradentate Schiff bases constitute another class since their complexes with certain transition metal ions exhibit unusual coordination, thermodynamic stability and kinetic inertness.[3] Their polynuclear homometallic copper(II) complexes serve as model compounds at the active sites of multi-metalloenzymes.[4] Salen-type tetradentate Schiff base complexes with N_2O_2 donors form different 'ligand complexes' which often combine with other metals of same/ different types through their O,O donors, thereby acting as precursors for new polynuclear homo-/ hetero-metallic complexes leading to rich coordination chemistry.[4] Schiff bases of this type also exhibit wide range of photo- and thermochromic properties observed in solution and/or in solid state based on keto-enol tautomerism arising through intra-molecular proton transfer between *ortho*-positioned keto- and hydroxyl-functionalities.[5] Moreover, dinuclear transition metal complexes of salen-type Schiff bases are very significant in magneto-chemistry[6] to understand the nature of exchange interactions operating between metals present in clusters and polymers, and also find wide biological applications as antibacterial, antiviral, antifungal,[7] and anticancer drugs.[8,9] Dinuclear metal complexes find applications as effective devices for recognition and assembly of external species.[10] Thus, designing structural and functional dinuclear complexes remain a topic of continuous investigation.

Among various transition and non-transition metals cadmium needs special attention due to its extreme toxicity in nature. Due to human activities its concentration gradually increases leading to development of suitable chelating ligand for its intoxication[11] since mobilization and immobilization of cadmium(II) ion in the environment, in organisms, and in some technical processes largely depend on its complexation by chelating organic molecules. For example, glutathione or other phytochelatins present in living cell act as chelating and sequestering agent for cadmium(II) and effectively compartmentalize the metal ion in less metabolically active cell parts, such as vacuoles; thereby acts as fist line of defence against cadmium toxicity in many cells.[12] The role of biosorbent for immobilization and removal of cadmium(II) from aqueous solution may also be mentioned in this regard as they often possess lignin, cellulose, and hemi-cellulose having various biomolecules such as proteins, carbohydrates, and polyphenolic compounds containing carboxyl, hydroxyl, sulfate, phosphate and amino groups that strongly bind cadmium(II) ions.[13] Due to inherent softness and lack of ligand field stabilization energy[14] resulting from its d^{10} configuration cadmium shows flexible coordination numbers in its complexes and exhibits rich coordination chemistry[15–17] which find wide applications in ligand exchange chromatography,[18] serve as catalytic center in a newly discovered carbonic anhydrase,[19] and also in other biological organisms. Cadmium phenolato complexes were seen in epoxide activation and ring-opening reactions.[20] Moreover, due to d^{10} configuration, its complexes with conjugated π systems containing aromatic rings favor the development of fluorescent materials.[21–25]

Tri-/tetradentate Schiff bases derived from *o*-vanillin (2-hydroxy-3-methoxybenzaldehyde) and its derivatives and 2-dimethylaminoethylamine have been extensively explored, while Schiff bases derived from *o*-vanillin and its derivatives with 2-diethylaminoethylamine has been explored very little.[26,27]

In this paper, we report the synthesis, spectral, structural, and thermal characterization of a new dinuclear cadmium(II) complex $[Cd(L)(NCS)]_2$ (**1**), derived from the Schiff base HL, 2-((E)-(2-(diethylamino) ethylimino) methyl)-6-methoxyphenol, obtained by condensation of 2-diethylaminoethylamine and *o*-vanillin (Scheme I). Structural characterization reveals that two cadmium(II) ions adopt octahedral geometries, associated with different degrees of distortions in spite of same chemical environment. Strong fluorescent emission at room temperature indicates that **1** may be a potential photoactive material.

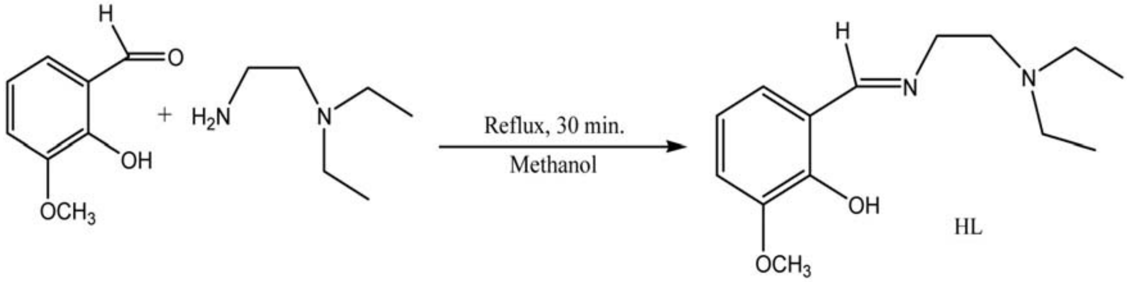
2. Experimental Section

2. 1. Materials and Instrumentations

All chemicals and solvents used for the synthesis were of reagent grade. 2-Diethylaminoethylamine (Fluka, Germany), *o*-vanillin, and ammonium thiocyanate (Sigma-Aldrich, USA), cadmium(II) nitrate tetrahydrate (E. Merck, India) were used as received without further purification. Elemental analyses (carbon, hydrogen and nitrogen) were carried out with a Perkin Elmer 2400 II elemental analyzer. The FT-IR spectra (4000–400 cm^{-1}) were recorded on a Perkin Elmer RX I FT-IR system with solid KBr disc. Ground state absorptions for HL and **1** were recorded on a Perkin Elmer Lambda 40 UV/Vis spectrometer in methanol. ^{1}H NMR spectra of HL and **1** were recorded on a Bruker 300 MHz FT-NMR spectrometer using tetramethylsilane as internal standard in $CDCl_3$. Fluorescence spectra of HL and **1** were recorded on Perkin Elmer LS-55 spectrofluorimeter at room temperature (298 K). Solutions of HL and **1** were prepared in methanol and optical density (OD) of each solution at the wavelength for fluorescence excitation was also recorded. The fluorescence quantum yield (φ) of HL and **1** were determined using quinine sulfate as reference with a known φ_R of 0.70 in methanol. HL, **1** and the reference compound were excited at 370 nm and the emission spectra were recorded from 390 to 650 nm. The area of emission spectrum was integrated and quantum yield was calculated according to the following equation:

$$\varphi_S/\varphi_R = [A_{S/}A_R] \times [(OD)_R/(OD)_S] \times [\eta_S^2/\eta_R^2] \quad (1)$$

where φ_S and φ_R are the fluorescence quantum yield of sample and reference, respectively. A_S and A_R are the areas under the fluorescence spectra of sample and reference, respectively. $(OD)_R$ and $(OD)_S$ are the respective optical densities of reference and sample solution at the wavelength of excitation, and η_S^2 and η_R^2 are the values of refractive index for the respective solvents used for sample and reference.[1] Thermogravimetric analysis was carried out with a heating rate of 10°C/min with a Mettler-Toledo Star TGA/SDTA-851^e thermal analyser system in a dynamic atmosphere of N_2 (flow rate 80 mL/min), the sample



Scheme 1. Synthetic scheme for preparation of HL.

was in an alumina crucible, and the temperature range was 25–800 °C.

2. 2. Synthesis of 2-((E)-(2-(diethylamino) ethylimino)methyl)-6-methoxyphenol (*HL*)

Schiff base HL was prepared based on slight modification of the procedure reported earlier.[27] Briefly, *o*-vanillin (5 mM, 0.760 g) and 2-diethylaminoethylamine (5 mM, 0.710 g) in 20 mL methanol were refluxed for half an hour. The resulting yellow solution containing the Schiff base ligand (HL) was cooled and subjected to TLC which revealed the presence of some starting materials along with the Schiff base product. The Schiff base ligand was isolated by column chromatography over silica gel (SRL) 60–120 mesh size, using a mixture of light petroleum and ethyl acetate (v/v, 2:3); subsequent evaporation of this eluent yielded the ligand in liquid form which was then further purified and dried under reduced pressure to yield a gummy mass. The ligand was then stored and dried *in vacuo* over fused $CaCl_2$ for subsequent use. Yield: 0.814 g (65 %). $C_{14}H_{22}N_2O_2$ (FW: 250.34): Calcd. C, 67.17; H, 8.86; N, 11.19 %. Found: C, 67.10; H, 8.76; N, 11.12 %. ^1H NMR (300 MHz, $CDCl_3$): δ 1.29 (t, J =7.7 Hz, $6H^1$), 2.72 (t, J = 7.5 Hz, $2H^3$), 3.48 (q, J = 7.7 Hz, $4H^2$), 3.65 (t, J = 7.5 Hz, $2H^4$), 3.93 (s, $3H^9$), 6.97 (t, J = 7.9, $1H^7$), 7.17 (d, J = 7.8 Hz, $1H^6$), 7.21 (d, J = 7.8 Hz, $1H^8$), 8.53 (s, $1H^5$), 11.12 (s, $1H^{10}$) ppm (Supplementary information: Scheme S1).

2. 3. Synthesis of $[Cd(L)(NCS)]_2$ (1)

To a methanolic solution (10 mL) of cadmium(II) nitrate tetrahydrate (2 mM, 0.616 g), a methanolic solution (10 mL) of HL (2 mM, 0.501 g) was added with slow stirring. After 10 minutes an aqueous solution (5 mL) of NH_4SCN (2 mM, 0.152 g) was added. Resulting deep yellow mixture was stirred for additional 20 minutes and filtered. The filtarate kept undisturbed in refrigerator at 5 °C for 7 days from which diffraction quality hexagonal block shaped single crystals of **1** were collected by filtration. Yield: 0.461 g (55 % with respect to metal substrate). $C_{30}H_{41}Cd_2N_6O_4S_2$ (FW: 838.65): Calcd. C, 42.97; H, 4.93; N, 10.02 %. Found: C, 42.90; H, 4.88; N, 9.98 %. Main IR bands (KBr, cm^{-1}): 3463(w), 3056(w), 2971(m), 2937(m), 2881(m), 2064(s), 1637(s), 1600(m), 1560(w), 1450(s), 1397(m), 1344(m), 1292(s), 1240(s), 1217(s), 1167(w), 1083(s), 963(s), 913(w), 882(w), 847(m), 790(w), 742(s), 628(m), 552(w), 464(w), 439(w). ^1H NMR (300 MHz, $CDCl_3$): δ 1.86 (t, J = 7.6 Hz, $6H^1$), 2.66 (q, J = 7.6 Hz, $2H^2$), 2.83 (q, J = 7.6 Hz, $2H^{2A}$), 3.48 (t, J = 7.4 Hz, $2H^3$), 3.72 (t, J = 7.4 Hz, $2H^4$), 3.95 (s, $3H^9$), 6.66 (t, J = 7.5 Hz, $1H^7$) 6.86-6.92 (m, $2H^{6,\,8}$), 8.35 (s, $1H^5$) ppm (Supplementary information: Scheme S2).

2. 4. X-ray Crystallography

Diffraction quality hexagonal block shaped crystal of **1** was mounted on a Bruker SMART CCD area detector equipped with fine-focus sealed tube graphite-monochromatized MoK_α radiation (λ = 0.71073 Å). Crystal data for **1** were collected using Bruker SMART software[28] at 120(2) K temperature using φ and ω scans technique. Cell refinements and data reduction were carried out using Bruker SMART.[28] No significant intensity variation was observed. Multi-scan absorption correction was applied to the intensity values (T_{max} = 0.7887, T_{min} = 0.7692) empirically using SADABS.[29] Data reduction was performed using Bruker SAINT.[30] Crystal structure was solved by direct methods using the program SHELXS-97[31] and refined with full-matrix least-squares based on F^2 using SHELXL-97.[31] For all non-hydrogen atoms, the anisotropic displacement parameters have been refined successfully. Hydrogen atoms were first located in the Fourier difference map then positioned geometrically and allowed to ride on their respective parent atoms. S2 and C28 atoms were disordered over two sites as S2A, S2B and C28A, C28B with a relative occupancy ratio of 0.56(5):0.44(5) and 0.488(7):0.512(7), respectively. The molecular graphics and crystallographic illustrations of the complex were prepared using ORTEP[32] and Bruker SHELXTL[33] pro-

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

Crystal data	**1**
Empirical Formula	$C_{30}H_{41}Cd_2N_6O_4S_2$
Formula weight (g mol^{-1})	838.65
Crystal size (mm)	0.20 × 0.18 × 0.18
Cell setting, Space group	Tetragonal, $I4_1/a$
Unit cell dimensions	a = 21.916(5) Å
	b = 21.916(5) Å
	c = 28.976(5) Å
	$\alpha = \beta = \gamma = 90°$
Unit cell volume	13918(7) $Å^3$
Temperature (K)	120(2)
Z, Density [g/cm^{-3}]	8, 1.601
Absorption coefficient	1.384 mm^{-1}
$\lambda_{Mo\text{-}K\alpha}$	0.71073 Å
F (000)	6768
θ range (°)	1.2→27.0
h range	–27→25
k range	–26→27
l range	–36→36
Reflection collected/ unique	89973/ 7590 [R_{int} = 0.064]
Observed data [I>2σ(I)]	6031
N_{ref} ; N_{par}	7590; 424
Final R indices [I>2σ (I)][(a)]	R_1 = 0.0264
	wR_2 = 0.0567
R indices (all data)[(a)]	R_1 = 0.0423
	wR_2 = 0.0613
Goodness-of-fit on F^2	1.026
Largest diff. peak and hole	0.55 and –0.56 e. $Å^{-3}$

[(a)] $R = \Sigma(|F_o\text{-}F_c|)/\Sigma|F_o|$, $wR = \{\Sigma[w(|F_o\text{-}F_c|)^2]/\Sigma[w|F_o|^2]\}^{½}$

grams. Details concerning crystal data and refinement are summarized in Table 1.

3. Results and Discussions

3. 1. FT-IR Spectra

The FT-IR spectra of HL and **1** were recorded in solid KBr matrix in the range of 4000-400 cm^{-1} and compared. The IR spectrum of HL showed a strong band at 1631 cm^{-1}, corresponding to azomethine group ($\nu_{C=N}$).The alkyl C–H bond stretching of the methoxy group and aromatic–OH stretching vibration of free ligand were observed at 2970 and 3440 cm^{-1}, respectively. Aromatic C–O and non-aromatic C–N single bond vibrations were observed at 1254, and 1081 cm^{-1}, respectively.[3]

The azomethine ($\nu_{C=N}$) stretching vibration of free ligand was shifted to lower frequency in the spectrum of **1** (Supplementary information: Figure S1) and appeared at 1600 cm^{-1}, supporting the coordination of imino nitrogen. The aromatic–OH stretching band of free ligand disappeared and aromatic C–O stretching band also shifted to lower frequency which was observed at 1240 cm^{-1} in the spectrum of **1** supporting the deprotonation of phenolic oxygen during complexation. The coordination of SCN$^-$ to the metal center was indicated by a strong band at 2064 cm^{-1} corresponding to $\nu_{C\equiv N}$ vibration. The alkyl C–H stretching vibration of the methoxy group and non-aromatic C–N single bond vibrations appeared at 2971 and 1083 cm^{-1}, respectively in the spectrum of **1**. Formation of Cd–N bond was substantiated by the bands appearing at 464 and 439 cm^{-1}.[3,34]

3. 2. UV-Vis Spectra

The electronic spectra of HL and **1** (Supplementary information: Figures S2 and S3) were recorded on HPLC grade acetonitrile at room temperature within the wavelength range 800-200 nm. The ligand HL showed a weak band at 422 nm and a moderately strong band at 328 nm which may be assigned to $n\rightarrow\pi^*$ (forbidden) and intra-ligand charge transfer transitions, respectively. The ligand also showed two strong bands at 260 and 222 nm, both corresponding to $\pi\rightarrow\pi^*$ transitions. Due to the presence of cadmium(II) (a d^{10} metal ion), the electronic spectra of **1** did not show any band corresponding to *d-d* transition. However, bands corresponding to different transitions of HL were shifted in the spectrum of **1**. The $n\rightarrow\pi^*$ transition of free HL disappeared in the spectrum of **1** which supports the coordination of lone pair electrons of –C=N– group to the metal center. Intra-ligand charge transfer transitions was also shifted to lower energy region and observed at 357 nm. The bands corresponding to $\pi\rightarrow\pi^*$ transitions of the coordinated ligand were shifted to slightly lower energy region compared to that of HL and appeared at 272 and 233 nm.[35–37]

3. 3. Crystal Structure

An ORTEP view of [Cd(L)(NCS)]$_2$ (**1**) with atom numbering is shown in Figure 1 and its relavent bonding parameters are summerized in Table 2 . Crystal structure analysis reveals that the title complex is a neutral dinuclear unit and consists of two cadmium(II) centers, two deprotonated Schiff base ligands and two thiocyanate ions. Each Schiff base anion is chelated to the cadmium(II) atom through its amine and imine nitrogen atoms, and phenolato oxygen while bridges through methoxy and phenolato oxygen to the other cadmium(II) atom, thus acts as a bridging bidentate (totally tetra-dentate) ligand. Each cadmium(II) atom is hexa coordinated by similar donor sets (N$_3$O$_3$). Coordination polyhedron of Cd1 is satisfied by imine nitrogen (N1), amine nitrogen (N2) and phenolato oxygen (O2) atoms of the same Schiff base ligand while the other three donor sites are satisfied by methoxy oxygen (O3) and phenolato oxygen (O4) from the other Schiff base ligand, and nitrogen atom (N5) from the monodentate thiocyanate which acts as a terminal ligand and merely completes the coordination site of the cadmium(II) atom. The geometry around the Cd1 is best described as severely distorted octahedron based on bonding parameters (Table 2) as well as the parameters summarized in Table 3. The structure may be imagined to consist of two triangles (with N1, N5, O2 and N2, O3, O4 atoms) with an average side (*s*) of 3.228 Å and separated by a distance (*h*) of 2.813 Å. Thus the *s/h* ratio of ~1.15 (<1.22) indicates an elongated octahedral structure. The average

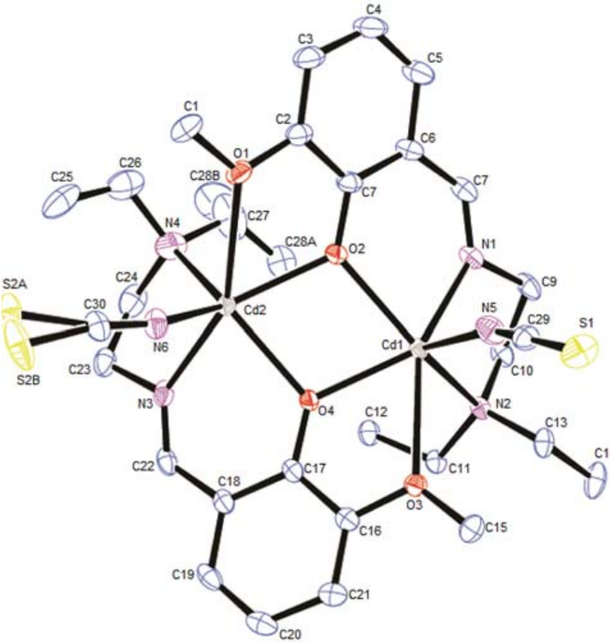


Figure 1. ORTEP view of **1** with atom labels (thermal ellipsoids are drawn at 30% probability level). Hydrogen atoms are omitted for clarity reasons.

triangular twist angle (φ) of 15.7° is very close to earlier reported structures[38–40] and is in support to the significant departure from a regular octahedral coordination. The average dihedral angle (θ, defined as the angle between the mean plane of the two triangles and the planes defined by the metal and each pair of near eclipsed donor vertices) of 47.55° is closer to an octahedral than to a trigonal prismatic geometry. The average *trans* angles (ρ, defined as the angle between the metal and trans donor sites) of ~133.11° and dihedral angle (ω, defined as the angle between the triangular faces defined by the metal and near eclipsed donor atoms) between the individual Cd1XY (X and Y are nearly eclipsed donor atoms) planes are averaged at only 67.17°, consistent with severe distortion (Table 3).[17,41,42] Similarly, coordination polyhedron of Cd2 is also considered as severely distorted octahedron.

However, in spite of same coordination environment its relative distortion is different to that of Cd1 center as evident from relative bonding parameters (Table 2), *s* and *h* values (3.216 and 2.809 Å), and average φ, θ, ρ, and ω values of 19.71, 48.94, 133.44, and 60.17° (Table 3), respectively, considering the two imaginary triangles consist of N3, O4, N6 and N4, O2, O1 atoms.[17,41,42]

Table 2. Selected bond distances (Å) and angles (˚) for **1**

Cd1–O2	2.2921(18)	Cd2–O1	2.6389(19)
Cd1–O3	2.6809(19)	Cd2–O2	2.2025(18)
Cd1–O4	2.2095(17)	Cd2–O4	2.2876(17)
Cd1–N1	2.322(2)	Cd2–N3	2.274(2)
Cd1–N2	2.371(2)	Cd2–N4	2.412(3)
Cd1–N5	2.180(3)	Cd2–N6	2.206(2)
O2–Cd1–O3	128.60(6)	N3–Cd2–N6	89.82(8)
O2–Cd1–O4	73.49(6)	N4–Cd2–N6	117.43(10)
O2–Cd1–N1	76.85(7)	O1–Cd2–O2	64.42(6)
O2–Cd1–N2	137.53(7)	O1–Cd2–O4	128.96(6)
O2–Cd1–N5	101.34(8)	O1–Cd2–N3	153.44(7)
O3–Cd1–O4	64.29(6)	O1–Cd2–N4	89.03(8)
O3–Cd1–N1	154.22(7)	O1–Cd2–N6	78.69(8)
O3–Cd1–N2	84.74(6)	O2–Cd2–O4	73.71(6)
O3–Cd1–N5	78.32(8)	O2–Cd2–N3	138.37(7)
O4–Cd1–N1	137.56(8)	O2–Cd2–N4	99.75(9)
O4–Cd1–N2	108.07(7)	O2–Cd2–N6	126.67(8)
O4–Cd1–N5	121.13(8)	O4–Cd2–N3	77.18(7)
N1–Cd1–N2	75.42(8)	O4–Cd2–N4	126.93(8)
N1–Cd1–N5	93.84(9)	O4–Cd2–N6	106.66(8)
N2–Cd1–N5	111.99(9)	N3–Cd2–N4	75.03(9)

In the severely distorted octahedron geometries of Cd1, the best equatorial plane is constituted by N2, N5, O2, and O4 atoms with N1 and O3 at the two apexes. Similarly, in the coordination geometry of Cd2, the best equatorial plane is constituted by N4, N6, O4, and O2 atoms with N3 and O1 at the two apexes. The Cd1 and Cd2 are out of mean basal plane by 0.103 and 0.045 Å, respectively. These small deviation from the mean basal plane are also in support of the distorted octahedron geometry rather than trigonal prism.[41] The phenolato oxygen atoms (O2 and O4) and methoxy oxygen atoms (O1 and O3) of the Schiff bases thus acts as bridge as well as chelate (totally tridentate) in a $\mu_{2,2}$-fashion between two cadmium(II) atoms leading to two five-membered {Cd-O-C-C-O}$_2$ metallacycles.[43] The long Cd···Cd separation

Table 3. Parameters for predicting the geometry of cadmium(II) centers in **1**

Parameters for	**Cd1**		**Cd2**		**For ideal octahedron**	**For ideal trigonal prism(TP)**
Imaginary triangle constituting atoms	N1,O2, O5 and N2, O4, O3		N3, O4, N6 and N4, O2, O1		–	–
s/ Å	3.228		3.216		–	–
h/ Å	2.813		2.809		–	–
s/*h* ratio	1.147		1.145		1.22	1
Twist angles [X–C_n–C_n'–Y](φ)/ °	10.93 16.40 19.87	15.70 (average)	4.42 24.91 29.82	19.72 (average)	60	0
θ/ °	83.22 30.10 29.40	47.55 (average)	27.74 73.10 45.98	48.94 (average)	54.7	90
ρ/ °	154.22 112.00	133.11 (average)	153.44 117.43	135.44 (average)	180	135.4
ω/ °	68.76 84.26 48.49	76.17 (average)	58.34 73.10 45.98	60.17 (average)	180	120

(i) X and Y are two nearly eclipsed donor atoms, and C_n and C_n' are the centroids of the two imaginary triangles (ii) *s* is average side distance of the triangles (iii) *h* is centroid to centroid separation (iv) θ is the angle between the mean plane of the two triangles and the planes defined by the metal and each pair of near eclipsed donor vertices (v) ρ is the angle between the metal and trans donor sites (vi) ω is the angle between the triangular faces defined by the metal and near eclipsed donor atoms.

(3.600 Å) suggests that there are no interactions between these two cadmium(II) atoms in the complex.

The complex reported herein may be compared to the complexes reported by Mitra et al.[3, 26] since both were derived from almost similar ligands bearing same donor set. In the reported dinuclear complex[3] the Schiff base was less steric crowded with respect to the amine moiety due to the methyl substituents while in the other reported complex[26] steric crowding in the ligand backbone was increased at the amine moiety due to ethyl substituents and simultaneously decreased by placing the methoxy substituent one position apart to that of phenolato group such that five coordinated distorted square pyramidal geometries resulted for the cadmium centers with the non-coordinating methoxy oxygen in these complexes.

However, in the complex reported herein the steric crowding in the Schiff base ligand is increased both due to amine moiety having ethyl substituents and methoxy substituent at the vicinity of phenolato group forcing cadmium(II) center to be six coordinated having severely distorted octahedral geometry. This steric effect is also evident from the smaller Cd–O(phenolato) separations in comparison to that found in the complexes reported earlier.[3, 26]

3. 4. Thermogravimetric Analysis

Thermogravimetric analysis of **1** (Supplementary information: Figure S4) was performed in the temperature range 25–800 °C in dynamic nitrogen atmosphere. It shows that the complex is thermally stable up to 255 °C after which it undergoes one step mass loss of 66.60% in the temperature range 256–490 °C corresponding to the loss of coordinated Schiff base and thiocyanate ligands. Residue does not show any mass loss upon heating up to 800 °C and it is identified as cadmium(II) oxide by qualitative analysis.

3. 5. Florescence Properties

The fluorescence spectra (Figure 2) of HL and **1** were recorded at room temperature (298 K) in methanol which reveals that HL exhibit emission at 502 nm (Figure 2: solid red line) while **1** shows an emission at 497 nm (Figure 2: solid black line) upon excitation at 370 nm. Therefore, for **1**, no emission originating from metal-centered MLCT/ LMCT excited states are expected, since cadmium(II) atom is difficult to oxidize or reduce due to its stable d^{10} configuration. Thus, the emission observed in **1** is tentatively assigned to the $^1(\pi-\pi^*)$ intraligand fluorescence. It is interesting that **1** shows much higher intensity than that of the free ligand (HL).This is also supported from their calculated quantum yield values as given in Table 4.

Enhanced fluorescence intensity of **1** is undoubtedly owing to chelation of ligand to the metal center. This is defined as chelation enhanced fluorescence intensity. Chelation of the ligand to cadmium(II) center via complexation enhances the rigidity of the ligand and thus reduces the loss of energy by radiation less decay of the intraligand emission excited state.[44–46] Enhancement of fluorescence through complexation is, however, of much interest as it opens up the opportunity for photochemical applications of these complexes.[47]

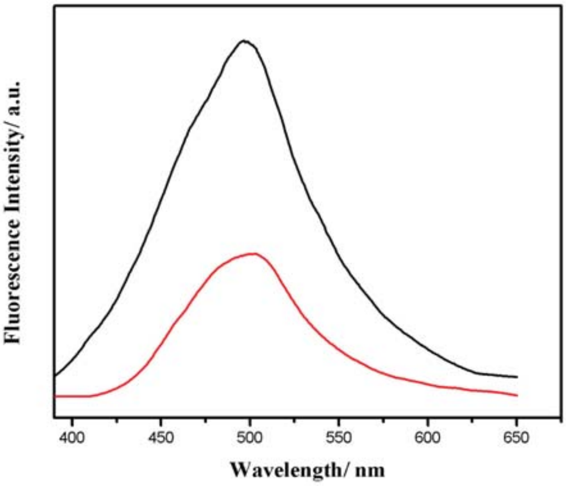


Figure 2. Fluorescence spectra of HL (solid red line) and **1** (solid black line) recorded in methanol at romm temperature (c = 1 × 10^{-6} Mol L^{-1}; λ_{exc} = 370 nm).

Table 4. Photophysical parameters of HL and **1** recorded in methanol at 298 K; excitation at 370 nm; reference compound is quinine sulfate (φ_R = 0.70 in methanol).

Compound	Abs (λmax), nm	Emission (λmax), nm	Quantum yield (φ)
HL	422	502	0.236
1	357	497	0.718

4. Conclusions

In this paper we have reported the synthesis, spectral, and structural characterization of a new dinuclear cadmium(II) Schiff base thiocyanato complex. Structural characterization reveals that in spite of same coordination environment two cadmium(II) atoms adopt distorted octahedral geometries associated with different degrees of severe distortions. Based on the comparison with earlier reported dinuclear cadmium complexes,[3, 26] it may be concluded that the coordination number as well as geometry of the cadmium(II) atom in the complex reported herein is controlled by steric modulation of the ligand backbone. The enhanced fluorescence intensities of the complex compared to that of ligand suggests its potentiality to be a photoactive material.

5. Acknowledgements

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5. 1. Appendix: Supplementary Data

Crystallographic data for **1** reported in this paper have been deposited with the Cambridge Crystallographic Data Centre, CCDC, 12 Union Road, Cambridge CB21EZ, UK. Copies of the data can be obtained free of charge on quoting the depository numbers CCDC-901794 (**1**) (Fax: +44-1223-336-033; E-Mail: deposit-@ccdc.cam.ac.uk,).

6. References

1. S. Basak, S. Sen, S. Banerjee, S. Mitra, G. Rosair, M. T. G. Rodriguez, *Polyhedron* **2007**, *26*, 5104–5112.
2. R. Vafazadeh, A. Gorji, S. Ansari, A. C. Willis, *Acta Chim. Slov.* **2012**, *59*, 897–903.
3. S. Sen, P. Talukder, S. K. Dey, S. Mitra, G. Rosair, D. L. Hughes, G. P. A. Yap, G. Pilet, V. Gramlich, T. Matsushita, *Dalton Trans.* **2006**, 1758–1767.
4 R. Vafazadeh, B. Khaledi, A. C. Willis, *Acta Chim. Slov.* **2012**, *59*, 954–958.
5. B. Kaitner, M. Zbačnik, *Acta Chim. Slov*. **2012**, *59*, 670–679.
6. C. R. Choudhury, S. K. Dey, R. Karmakar, C. D. Wu, C. Z. Lu, M. S. El. Fallah, S. Mitra, *New J. Chem.* **2003**, *27*, 1360–1366, and references therein.
7. S. Chandra, X. Sangeetika, *Spectrochim. Acta* **2004**, *A60*, 147–153.
8. D. Kessel, A. F. A. Sayyab, E. M. H. Jaffar, A. H. H. A. Lanil, *Iraqi J. Sci.* **1981**, *22*, 312.
9. E. M. Hodnett, W. J. Dunn, *J. Med. Chem.* **1970**, *13*, 768–770.
10. H. Keypour, A. H. Jamshidi, M. Rezaeivala, L. Valencia, *Polyhedron* **2013**, *52*, 872–878.
11. S. Sen, P. Talukder, G. Rosair, S. Mitra, *Struct. Chem.* **2005**, *16*, 605–610.
12. M. Glušič, P. Ropret, K. Vogel-Mikuš, J. Grdadolnik, *Acta Chim. Slov.* **2013**, *60*, 61–69.
13. B. Nagy, A. Măicăneanu, C. Indolean, S. Burcă, L. Silaghi-Dumitrescu, C. Majdik, *Acta Chim. Slov.* **2013**, *60*, 263–273.
14. P. Chakraborty, A. Guha, S. Das, E. Zangrando, D. Das, *Polyhedron* **2013**, *49*, 12–18.
15. M. A. Sharif, G. R. Najafi, *Acta Chim. Slov.* **2013**, *60*, 138–143.
16. L. Saghatforoush, H. A. Rudbari, F. Nicolò, P. Asgari, F. Chalabian, M. Hasanzadeh, V. Panahiazar, *Acta Chim. Slov.* **2013**, *60*, 300–309.
17. F. Marandi, S. Teimouri, H.-K. Fun, *Acta Chim. Slov.* **2013**, *60*, 328–334.
18. R. Karmakar, C. R. Choudhury, D. L. Hughes, S. Mitra, *Inorg. Chim. Acta* **2007**, *360*, 2631–2637, and references therein.
19. T. W. Lane, F. M. M. Morel, *Proc. Natl. Acad. Sci. USA* **2000**, *97*, 4627–4631.
20. D. J. Darensbourg, J. R. Wildeson, S. J. Lewis, J. C. Yarbrough, *J. Am. Chem. Soc.* **2002**, *124*, 7075–7083.
21. L.-L. Wen, D.-B. Dang, C.-Y. Duan, Y.-Z. Li, Z.-F. Tian, Q.-J. Meng, *Inorg. Chem.* **2005**, *44*, 7161–7170.
22. L. Wen, Y. Li, Z. Lu, J. Lin, C. Duan, Q. Meng, *Cryst. Growth Des.* **2006**, *6*, 530–537.
23. L. Wen, Z. Lu, J. Lin, Z. Tian, H. Zhu, Q. Meng, *Cryst. Growth Des.* **2007**, *7*, 93–99.
24. A. Sarkar, V. Bertolasi, D. Ray, *Polyhedron* **2012**, *44*, 113–123.
25. Q. Zhao, R.-F. Li, S.-K. Xing, X.-M. Liu, T.-L. Hu, X.-H. Bu, *Inorg. Chem.* **2011**, *50*, 10041–10046.
26. S. Basak, S. Sen, C. Marschner, J. Baumgartner, S. R. Batten, D. R. Turner, S. Mitra, *Polyhedron* **2008**, *27*, 1193–1200.
27. S.-J. Peng, Z.-L. You, *J. Chem. Crystallogr.* **2007**, *37*, 415–419.
28. *SMART*, *Data Collection Program for the CCD Area Detector System*.
29. G. M. Sheldrick, *SADABS*, *Program for Empirical Absorption Correction of Area Detector Data*, University of Göttingen, Göttingen (Germany), **1996**.
30. *SAINT*, *Data Reduction, Frame Integration Program for the CCD Area Detector System*, Bruker Analytical X-ray Instruments Inc., Madison, Wisconsin (U.S.A.) **2005**.
31. G. M. Sheldrick, *Acta Cryst*. **2008**, *A64*, 112–122.
32. L. J. Farrugia, *J. Appl. Crystallogr*. **1997**, *30*, 565–566.
33. G. M. Sheldrick, *SHELXTL (version 5.1), Program for the Solution and Refinement of Crystal Structures*, Bruker Analytical X-ray Instruments Inc., Madison, Wisconsin (U.S.A.) **1999**.
34. K. Nakamoto, Infrared and Raman Spectra of Inorganic and Coordination Compounds: Part A: Theory and Applications in Inorganic Chemistry, 5th ed., John Wiley & Sons, Inc., New York, **1997**, pp. 23
35. A. Golcu, M. Tumer, H. Demirelli, R. A. Wheatley, *Inorg. Chim. Acta* **2005**, *358*, 1785–1797.
36. S. Banerjee, A. Ray, S. Sen, S. Mitra, D. L. Hughes, R. J. Butcher, S. R. Batten, D. R. Turner, *Inorg. Chim. Acta* **2008**, *361*, 2692–2700.
37. A. B. P. Lever, Inorganic Electronic Spectroscopy, second ed., Elsevier, Amsterdam, **1984**.
38. J. L. Martin, J. Takats, *Inorg. Chem.* **1975**, *14*, 1358–1364.
39. E. I. Stiefel, G. F. Brown, *Inorg. Chem.* **1972**, *11*, 434–436.
40. W. O. Gillum, G. C. Huffman, W. E. Streib, R. A. D. Wentworth, *J. Chem. Soc., Chem. Commun.* **1969**, 843–844.
41. S. Banerjee, A. Ghosh, B. Wu, P.-G. Lassahn, C. Janiak, *Polyhedron* **2005**, *24*, 593–599.
42. F. Marandi, M. Jangholi, M. Hakimi, H. A. Rudbari, G. Bruno, *J. Mol. Struct.* **2013**, *1036*, 71–77.
43. S. Shit, J. Chakraborty, B. Samanta, G. Pilet, S. Mitra, *J. Mol. Struct.* **2009**, *919,* 361–365.

44. D. Das, B. G. Chand, K. K. Sarker, J. Dinda, C. Sinha, *Polyhedron* **2006**, *25*, 2333–2340.
45. S.-L. Zheng, J.-H. Yang, X.-L. Yu, X.-M. Chen, W.-T. Wong, *Inorg. Chem.* **2004**, *43*, 830–838.
46. L.-Y. Zhang, G.-F. Liu, S.-L. Zheng, B.-H. Ye, X.-M. Zhang, X.-M. Chen, *Eur. J. Inorg. Chem.* **2003**, 2965–2971.
47. A. Majumder, G. M. Rosair, A. Mallick, N. Chattopadhyay, S. Mitra, *Polyhedron* **2006**, *25*, 1753–1762, and references therein.

Povzetek

Nov dvojedrni kadmijev(II) kompleks, $[Cd(L)(NCS)]_2$ (**1**) je bil sintetiziran s potencialno tetradentatnim ligandom iz Schiffove baze HL, 2-((E)-(2-(dietilamino)etilimino)metil)-6-metoksifenol, ki je bila pripravljena s kondenzacijo 2-dietilaminoetilamina in *o*-vanilina. Kompleks je bil okarakteriziran z različnimi fizikalno-kemijskimi metodami. Kristalna struktura kompleksa je bila določena z rentgensko monokristalno analizo. Kovinska iona v dvojedrnem kompleksu sta povezana preko mostovne fenolatne skupine in kelatnega kisikovega atoma iz metoksi skupine Schiffove baze. Oba kadmijeva kationa imata popačeno oktaedrično geometrijo. Fluorescenčne lastnosti liganda in njegovega kompleksa pri sobni temperaturi kažejo, da je kompleks lahko uporaben kot močan fluorescenčni sevalec.

Supplementary Information

A Dinuclear Cadmium(II) Schiff Base Thiocyanato Complex: Crystal Structure and Fluorescence

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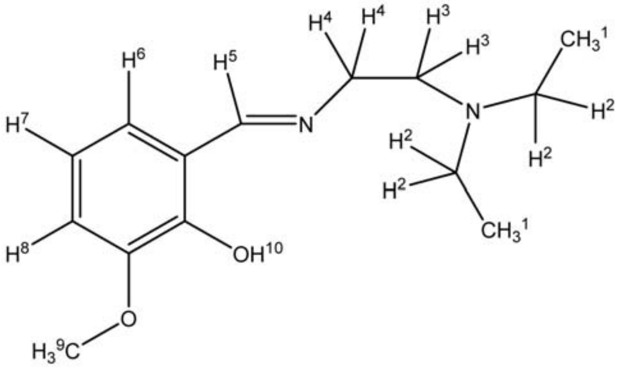


Scheme S1. Proton numbering scheme of HL

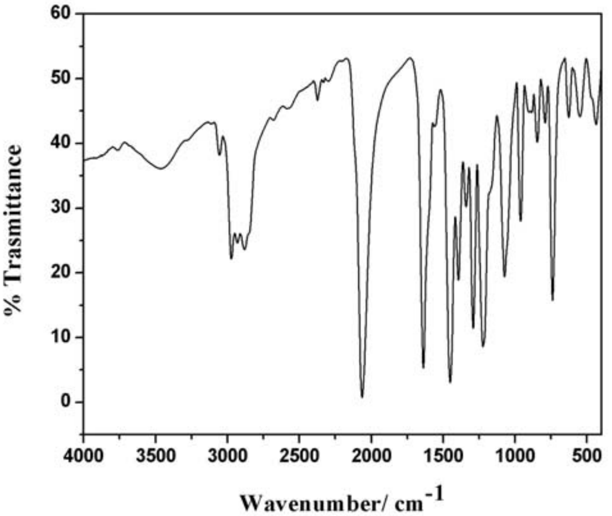
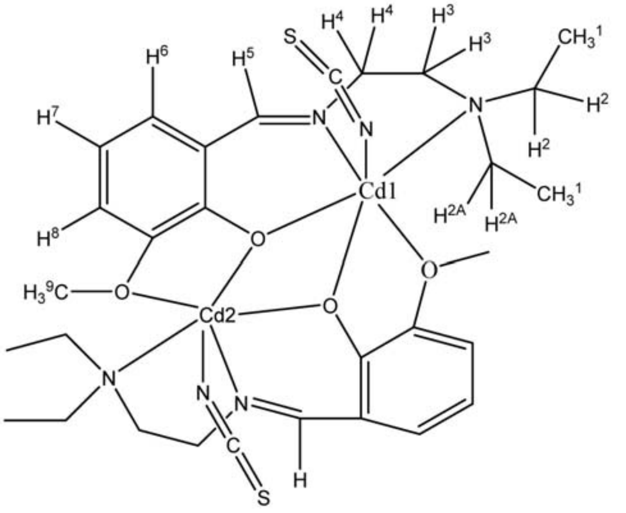


Figure S1. FT-IR spectrum of **1**



Scheme S2. Proton numbering scheme of L⁻ in **1**

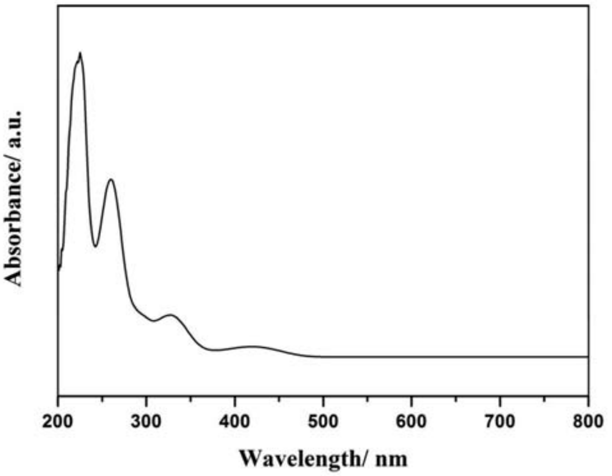


Figure S2. UV-Vis spectrum of Schiff base (HL)

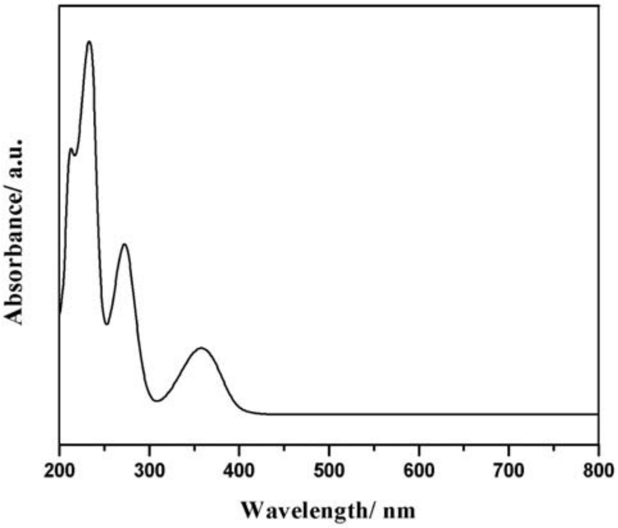


Figure S3. UV-Vis spectrum of **1**

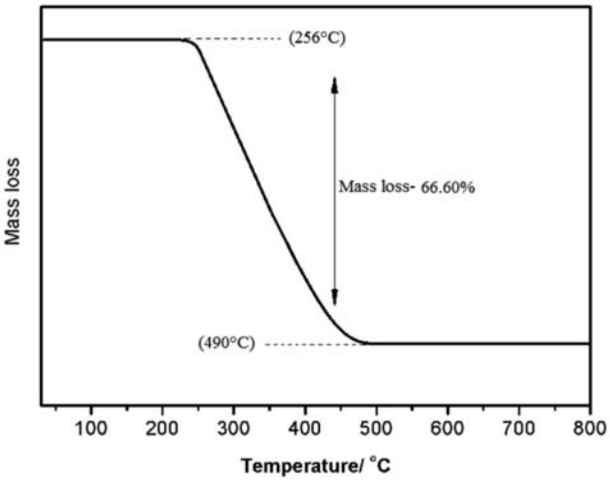


Figure S4. Thermogravimetric analysis (TGA) curve of **1**