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One-Pot Synthesis, Crystal Structure, and Fluorescence Property of a Cadmium(II) Complex Based on Mono Salicylaldehyde Schiff Base Ligand[1]

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Abstract—A new cadmium(II) complex [Cd(NO_2-Salen)$_2$] containing Schiff base ligand (NO_2-Salen = *N*-mono-5-nitro-salicylideneamino ethanato) has been prepared through facile condensation reaction of substituted salicylaldehyde with ethylene-diamine and has been structurally characterized by elemental analysis, IR spectra and X-ray diffraction. It is formulated as $C_{18}H_{20}CdN_6O_6$ crystallizes in the orthorhombic system, space group of *Pccn*. The ligand of 5-nitrosalicylaldehyde-ethylene-diamine exhibits unusual mono asymmetry tridentate mode. The Cd^{2+} ion has a coordination number of six and assumes a distorted octahedral geometry. It exhibits an offset π–π stacking interaction between the substituted benzene ligands of adjacent mononuclear complexes. The neutral monomeric units of [Cd(NO_2-Salen)$_2$] are linked into a one-dimensional (1D) array via the intermolecular hydrogen bonds and π–π stacking interactions. The complex exhibits strong emission in visible region with the maximum wavelength of 428 nm, which is tentatively assigned to the $\pi \to \pi^*$ intraligand fluorescence.

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INTRODUCTION

More recently the design, synthesis and characterization of transitional metal complexes with Schiff-base ligands play a relevant role in the coordination chemistry, due to their importance as synthetic models for the functional materials [1, 2]. In particular, the complexes containing Schiff base ligands have increased the interest in field of synthetic, biological and magneto chemistry due to their key roles in many applications, such as antibacterial, antiviral and antifungal agents [3–5]. Diamino tetradentate Schiff bases compounds have been used as biological models to understand the structures of biomolecules and biological processes [6], and when administered as their metal complexes the anticancer activity of such complexes is enhanced in comparison to the free ligand [7]. Meanwhile, synthesis of mono- and polynuclear coordination compounds of group 12 metal ions [8–10] continues unabated for the accesses of functional materials by exploiting the veracity of the coordination geometry around metal ion templates and varied organic blockers. There also has been growing interest in the coordination chemistry of cadmium complexes due to the increased recognition of its role in biological organisms [11], and due to its rich structural chemistry. However, among which, the cadmium atom is commonly seven-coordinated, linked to the nitrogen and oxygen atoms of the Schiff base, or is further ligated by the nitrogen, sulphur and oxygen atoms from the second ligand, and most of them are reluctant to form crystals suitable for X-ray analysis. As part of our continuing work on Schiff base complexes [12], and in order to further study on the influence of coordinating behavior by the electron withdrawing specie and photo luminescence property in the facile self-assembly processes for Schiff base complex. In this work, synthesis and crystal structure of a new Cd(II) complex [Cd(NO_2-Salen)$_2$] (**I**) containing asymmetry substituted salicylaldehyde Schiff base, together with its properties have been reported. The NO_2-Salen ligand presents mono deprotonated fashion in complex, and to our best knowledge, such coordination mode is seldom reported.

EXPERIMENTAL

Materials and physicalm measurements. All chemicals and solvents commercially purchased were of reagent grade and used without further purification. Elemental analyses for carbon, hydrogen and nitrogen were carried out on a Model 240 PerkinElmer elemental analyzer. The infrared spectrum was performed on an Avatar^{TM} 360 E.S.P. IR spectrometer in the 4000–400 cm^{-1} region with KBr pellets. The powder X-ray diffraction (PXRD) pattern was measured using a Bruker D8 Advance powder diffractometer at 40 kV,

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40 mA for CuK_α radiation ($\lambda = 1.5418$ Å). Liquid state luminescence spectra in the visible ranges were measured at room temperature with an Edinburgh instrument FLS920 fluorescence spectrometer.

Synthesis of complex I. The mixture of $CdCl_2 \cdot H_2O$ (1 mmol, 0.231 g) and $Na(CN)_2$ (0.153 g, 2 mmol) was refluxed in anhydrous methanol (10 mL) for 50 min, decanted off, and filtered. The resulting colorless solution was added to 10 mL methanol solution of freshly distilled 5-nitrosalicylaldehyde and 10 mL methanol solution of ethylene–diamine at molar ratio 1 : 1 simultaneously, and mixture was stirring condensation for 3 h. The resulting light yellow solution was diffused with diethyl ether vapor at room temperature for two weeks. The colorless block crystal were formed and collected by filtration and dried in air. The yield was 27 mg (54%).

For $C_{18}H_{20}N_6O_6Cd$

anal. calcd., %:	C, 40.86;	H, 3.81;	N, 15.89.
Found, %:	C, 40.76;	H, 3.47;	N, 15.57.

IR (KBr; ν, cm^{-1}): 3432 s, 3352 s, 3036 m, 2934 s, 1649 s, 1628 m, 1604 s, 1562 s, 876 s, 841 s, 514 m, 465 m.

X-ray structure determination. A single crystal of the title complex (0.25 × 0.21 × 0.17 mm) was mounted on a Bruker SMART APEX II CCD diffractometer equipped with a graphite-monochromatized MoK_α radiation ($\lambda = 0.71073$ Å) by using a φ/ω scan mode at room temperature in the range of $2.35° \le \theta \le 25.49°$. Corrections for Lp factors were applied and all non-hydrogen atoms were refined with anisotropic thermal parameters. The structure was solved by direct methods with SHELXS-97 [13]. The hydrogen atoms were assigned with common isotropic displacement factors and included in the final refinement by use of geometrical restrains. A full-matrix least-squares refinement on F^2 was carried out using SHELXL-97 [14]. The final $R_1 = 0.0362$, $wR_2 = 0.1246$, ($w = 1/[\sigma^2(F_o^2) + (0.1255P^2) + 0.7500P]$, where $P = (F_o^2 + 2F_c^2)/3$), $S = 1.028$, $(\Delta\rho)_{max} = 0.715$ and $(\Delta\rho)_{mix} = -0.974$ e/Å^3. Crystallographic and experimental details are summarized in Table 1. Moreover, the selected bond lengths and bond angles are listed in Table 2.

Supplementary material for structure **I** has been deposited with the Cambridge Crystallographic Data Centre (no. 961103; deposit@ccdc.cam.ac.uk or http://www.ccdc.cam.ac.uk).

Table 1. Crystal data and structure refinements for complexes **I**

Parameter	Value
Crystal shape/color	Block/colorless
Formula weight	528.80
Temperature	293(2)
Crystal system	Orthorhombic
Space group	*Pccn*
Unit cell dimensions:	
a, Å	21.239(7)
b, Å	9.513(3)
c, Å	10.568(4)
V, Å^3	2135.4(13)
Z	4
ρ, g cm^{-3}	1.645
F(000)	1064
μ, mm^{-1}	1.070
θ Range for data collection, deg	2.35–25.49
Limiting indices ranges	$-25 \le h \le 25$, $-9 \le k \le 11$, $-12 \le l \le 12$
Max. and min. transmissions	0.8390 and 0.7758
Data/restraints/parameters	1982/0/141
GOOF	1.028
R_1, wR_2 ($I > 2\sigma(I)$)	0.0362, 0.1246
R_1, wR_2, all data	0.0643, 0.1784
Largest diff. peak and hole, e/Å	0.715 and –0.974

$R = [\Sigma||F_o| - |F_c||/\Sigma|F_o|]$, $R_W = \Sigma_W[||F_o^2 - F_c^2|^2/\Sigma_W(|F_w|^2)^2]^{1/2}$.

RESULTS AND DISCUSSION

The principal perspective view of title complex with atomic labeling scheme is illustrated in Fig. 1. Unfortunately, the diocyanate anion does not present in the final product. The mononuclear unit is composed of six-coordinated cadmium ion, two NO_2-Salen ligands. The coordination polyhedron around the Cd^{2+} ion can be visualized as a slightly distorted octahedral geometry with a novel CdO_2N_4 mode. Among the donor set, the ligand NO_2-Salen affords four N atoms and two O atoms to coordinate with central ion. Interestingly, the asymmetric coordination pattern of the ligand results in the final crystal belongs to a centric space group. The bond distance of Cd(1)–O(1) is 2.292(4), of Cd(1)–N(1) is 2.329(5), of Cd(1)–N(2) is 2.317(5) Å giving the slightly distorted octahedral coordination geometry, mainly due to the coordination of the deprotonated N, O donor Schiff base ligand [15]. The bond parameters are within the reasonable ranges for other six-coordinated Cd(II)

Table 2. Selected bond lengths (Å) and angles (deg) for complex **I***

Bond	d, Å	Bond	d, Å
Cd(1)–O(1)	2.292(4)	Cd(1)–N(1)	2.329(5)
Cd(1)–N(2)	2.317(5)		
Angle	**ω, deg**	**Angle**	**ω, deg**
O(1)Cd(1)O(1)$^{\#1}$	97.4(2)	N(2)Cd(1)N(1)	74.15(17)
O(1)Cd(1)N(2)	149.63(17)	O(1)Cd(1)N(1)$^{\#1}$	93.18(18)
O(1)Cd(1)N(2)$^{\#1}$	91.21(18)	N(2)Cd(1)N(1)$^{\#1}$	117.17(18)
N(2)Cd(1)N(2)$^{\#1}$	95.9(3)	N(1)Cd(1)N(1)$^{\#1}$	164.3(3)
O(1)Cd(1)N(1)	76.34(18)		

* Symmetry transformations used to generate the equivalent atoms: $^{\#1}$ $-y + 2/3, -x + 1/3, z - 1/6$.

complexes with oxygen and nitrogen donating ligands [16].

Among the donor atoms, the equatorial plane in polyhedron of octahedron is comprised of one oxygen atom of the monodentate deprotonated hydroxyl group and three iminic nitrogen atoms atom from the diaminoethane moiety. Whereas, the hydroxyl oxygen atom and another iminic nitrogen atom are located at axial positions of the octahedron. Interestingly, just one iminic functional group of diaminoethane molecule was deprotonated, giving rising to a mono acetalization asymmetry Schiff base in this case, and mono deprotonated substituted Salen type Schiff base ligand as this case has been less well investigated. The characteristic feature of the observed bridging mode is the use of single oxygen hetero-ring nitrogen atom to coordinate with the metal ion on one side, two nitrogen atoms both bridging and chelate donated by a same tridentate ligand on the other two sides, respectively, with the O,O,N,N,N,N bonding moiety. Another significant feature of structure is that there are no coordinated or crystallization water molecules, which proves that it is crystallized from a non aqueous medium. Presumably the abundance of coordination sites and chelating ability of the ligand preclude the possibility of water binding to central cation.

Chelation of Cd^{2+} ion leads to coplanarity of the two fragments sharing a common central ion including nitro group, and makes a dihedral angle of 77.74° between the adjacent benzene ring planes. NO_2-Salen ligand coordinates to the Cd^{2+} ion to form two six-membered chelate ring Cd(1)–C–C–C–N–O and two five-membered ring Cd(1)–N–C–C–N. This coordination fashion is compared to that of reported nickel(II) complex with analogous Schiff base ligand and water coligand [17]. For the equatorial ligands in polyhedron, the average deviation from the least-square planes is calculated to be only 0.029(1) Å, indicating the high planarity of the unit in **I**. The small distortion of the coordination geometry around the metal

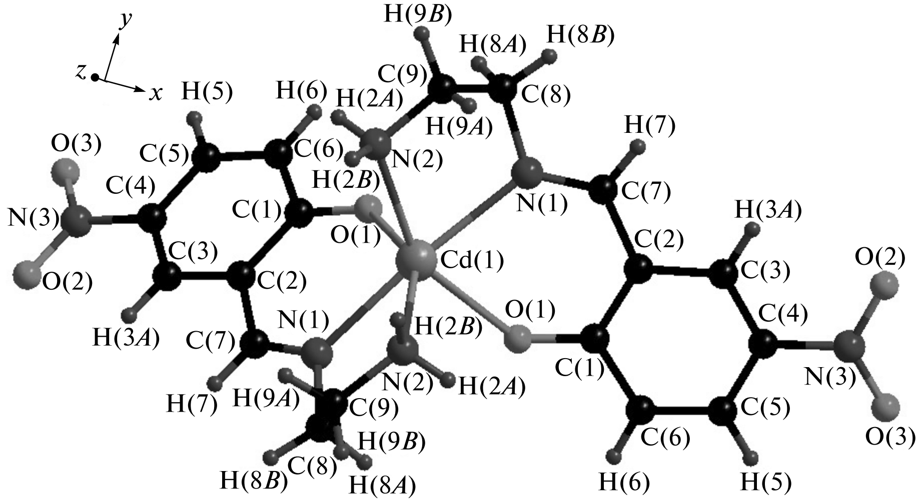

Fig. 1. The coordination environment of Cd^{2+} ion in the symmetry unit of **I** viewed along xz plane. Displacement ellipsoids are drawn at the 30% probability level and H atoms are shown as small spheres of arbitrary radii.

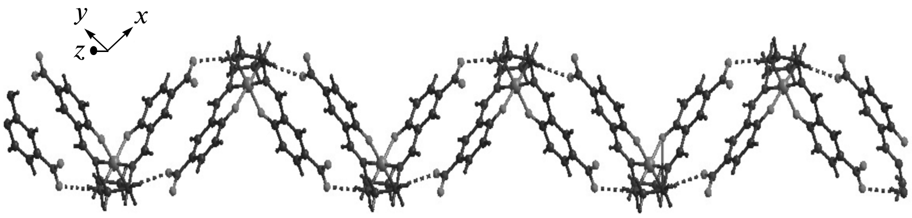

Fig. 2. Schematic illustration of the 1D zigzag chains aggregate through hydrogen bonding.

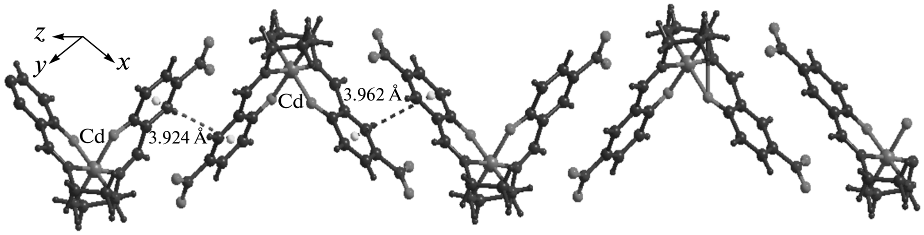

Fig. 3. Schematic representation of offset π–π stacking interactions between adjacent mononuclear complex units along *xy* plane.

atoms is attributed to the rigid effects of the chelate Schiff base ligand.

Two nitro groups are nearly coplanar with the benzene planes, and the dihedral angle between which is 6.2(9)°, and the mean benzene ring is inclined at 3.8(9)° to six-membered chelate ring each other, respectively. Strangely, this coordination is essential similar to that in a previous reported *o*-vanillin Schiff base complex [18]. But it is essentially cannot be compared with 2D network based on cadmium(II)–Schiff base units [19].

For the equatorial ligands in each polyhedron, the average deviation from their least-square planes is calculated to be only 0.043(3) Å for **I**, indicating the high planarity of each unit. Figure 2 shows the alignment of a one-dimensional alternating chain viewed along the *xy* plane, in which the cadmium ions are bridged by NO_2-Salen ligand to maintain charge balance. It is noteworthy that there are obvious strong hydrogen bondings between the adjacent monomeric units. The hydrogen bonding parameters involving nitrogen and oxygen atoms are listed in Table 3. Within chain, the parallel benzene plane intervals vary from 3.924 to 3.962 Å, and the distance between the two benzene ring planes indicates the evident π–π stacking, as illustrated in Fig. 3. The hydrogen bondings and weak π–π stacking interactions further connect the chains into a 3D supramolecular architecture. Thereby, the complex can also be viewed as 3D supramolecular architecture via intermolecular weak interaction. In the framework, one-dimensional channels present along the *z* axis.

Infrared spectrum of complex **I** displays a broad strong absorption peak at 3432 cm^{-1}, which is assigned to the C–H stretching vibration from benzene moiety. It exhibits a strong band at 3036 and 2934 cm^{-1}, corresponding to $\nu(NH_2)$ stretch of imino group from the ethane-diamine moiet [20]. This band shifts slightly to higher wave number side relative to the free ligand indicating coordination of metal ion due to reduction of electron density of the amine linker [21], as previously reported [8], and this is consistent with the structure analysis above. The observation of peaks at 1649 and 1627 cm^{-1} assigned to ν(C=O), 1604 and 1561 cm^{-1} to ν(C=N) stretching vibration, and a band in the 841–882 cm^{-1} range are assigned to that of C=C–H from benzene ring. The new weak non-ligand bands at about 514 and 465 cm^{-1} in spectra of the complexes are assigned to stretching frequencies of ν(Cd–O) and ν(Cd–N) bonds.

The powder XRD patterns of compound **I** shows strong peaks where 2θ are 10.2, 14.1, 16.0, 23.6 degrees, which are well matched with the simulation ones based on single crystal data analysis, and it indicates that the bulk sample of **I** obtained is in a pure phase.

Table 3. Geometric parameters of hydrogen bonds for complex **I***

D–H···A	Distance, Å			Angle DHA, deg
	D–H	H···A	D···A	
N(2)–H(2*B*)···O(1)$^{\#2}$	0.90	2.39	3.195(7)	150
N(2)–H(2*A*)···O(2)$^{\#1}$	0.90	2.21	3.043(7)	170

* Symmetry transformations used to generate the equivalent atoms: $^{\#1}$ $-y + 2/3, -x + 1/3, z - 1/6$; $^{\#2}$ $-y + 1/3, -x + 2/3, z + 1/6$.

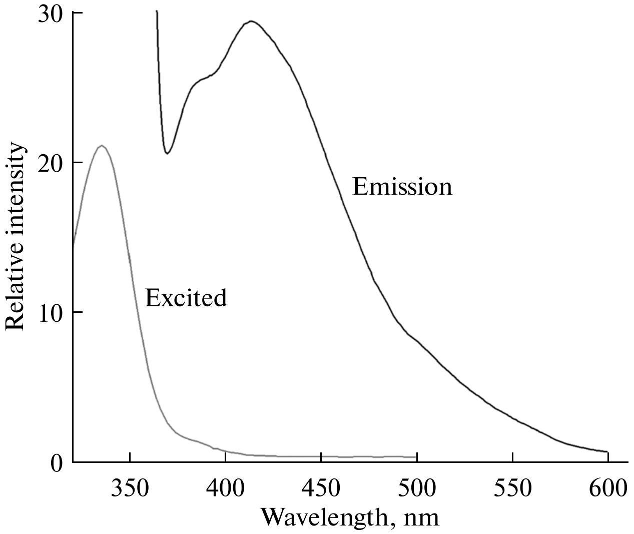

Fig. 4. The emission spectra of crystalline **I** in methanol suspension sample at room temperature.

Taking into accounting the luminescent properties of cadmium complexes, photoluminescence properties of the ethanol suspension samples (~0.001 mol/L) of **I** were investigated at room temperature, it shows excitation luminescence maximum at wavelength of 324 nm, which is attributed to $\pi \rightarrow \pi^*$ and/or $n \rightarrow \pi^*$ transition. As illuminated in Fig. 4, upon photoexcitation with 348 nm, the title complex shows no emission originating from metal-centered MLCT/LMCT under excited states, as are expected. It exhibited emission spectra in the region from 420 to 450 nm (in visible region) with the maximum wavelength of 428 nm, and the emission observed in this complex is tentatively assigned to the $\pi \rightarrow \pi^*$ intraligand fluorescence [22]. As well known, the d^{10} ion is electrochemically stable, and thus, when coordinate to ligand, is not significantly contributive to the ligand-field effect [23]. Thus, the emission observed in the complexes is tentatively assigned to the intraligand fluorescence [24]. It is interesting that the Cd(II) complexes show a higher intensity than that of free ligand. Metal ions can enhance the fluorescence emission of some Schiff base ligands containing an aromatic ring.

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