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Cd(II) Dithiocarbamate Complexes: Synthesis, Spectral Studies, Thermogravimetric Analysis and Semiconducting Behaviour

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Five new homoleptic Cd(II) dithiocarbamate complexes (**1-5**) have been synthesized and characterized by IR, NMR, UV-visible spectroscopic and thermogravimetric analysis. Single-crystal X-ray diffraction study of complex **1** revealed a triclinic system with space group *P*-1 and possesses a centrosymmetric dimeric structure. In this complex, both C–H···S and C–H·π intermolecular interactions are playing a crucial role in the stabilization of the dithiocarbamate complex. Complexes (**1-5**) show weak conductivity at ambient temperature ($\sigma_\pi = 10^{-9}$-10^{-10} S·cm^{-1}) because of the absence of M···S/S···S intermolecular stacking. Plot of logσ *versus* T^{-1} in the 303-363 K range indicates their semiconducting behaviour. However, their electrical conductivities gradually increase with increasing temperature and ideally decrease with decreasing temperature range showing their semiconducting nature. TGA showed thermal decomposition of complexes into CdS as the final product with grain size of 1-10 nm.

Keywords: Cd(II) dithiocarbamate complexes, Luminescent emission, Conductivity, Thermogravimetric studies.

INTRODUCTION

Dithiocarbamates are a group of organic compounds, which belongs to 1,1- dithiolate family and are formed by an exothermic reaction between CS_2 and primary (1º) or secondary (2º) amine in presence of a strong base like NaOH/KOH. These compounds are precious due to their interesting chemistry and multiple uses in diverse applications, for example, it is applicable in the area of medicine [1,2], industry [3,4], agriculture [5], vulcanization of rubber [6,7] and their significance in biological systems and catalyst [8-10] and also be used to separate different metal ions by HPLC [11-14] and capillary gas chromatography [15]. The most important interesting aspect of dithiocarbamates is their applications in coordination chemistry [16]. Dithiocarbamate complexes have attracted the attention of researchers due to their capability to stabilize transition metals in different oxidation states and increasing interest in this area is the functionalization of N-atom by different substituents.

Besides, their complexes show improved conductivity profiles in the solid-state due to extended delocalized S···S/M···S intermolecular distorted structures. Interestingly, group 12 metal dithiocarbamates [17-20] continue to attract attention because of their diversity of structures, improved optical properties and their property to act as molecular precursors for the formation of semiconductors [21-24]. Besides some apparent similarities, the dithiocarbamate ligands differ considerably in coordinating capacity and properties. Generally, dithiocarbamates occur in three different dominant resonance forms as shown in Fig. 1. The resonance form I and II bearing mononegative charge favours stabilization of lower oxidation state *i.e.* +2 of the metal ions, whereas resonance form III bearing mono negative charge on each sulfur atom stabilizes higher oxidation state of the metal ion and is referred to as the thioureide form, this form occurs with the delocalization of the nitrogen lone pairs *via* the sulfur atom [25,26]. Their complexation ability finds its use as structural motifs in supramolecular chemistry.

In Cd(II) complexes, the functionalization of the ligands often induces important covalent and non-covalent interactions such as π··π, C–H··π, O···H and N···H to construct the supramolecular networks by tuning their physical and chemical properties that are generally not achieved by the individual components [27-30]. Recently, these metal-dithiocarbamate complexes have received considerable attention because of their diverse applicability in various fields especially in medi-

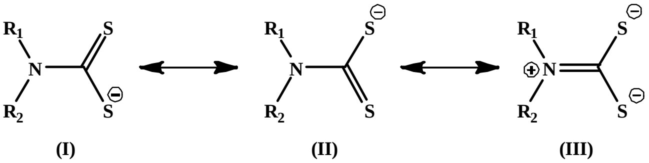


Fig. 1. Resonance structures representation of the dithiocarbamate ligands

cine as anti-parasitic and antibacterial agents [31]. Based on the above considerations to discover the better physico-chemical properties, this study includes the synthesis, spectroscopic characterization and pressed pellet electrical conductivity as well as thermogravimetric analysis of five new Cd(II) dithiocarbamate complexes (**1-5**) of formulae [Cd(L_1-L_5)$_2$] [L_1 = potassium-*N*-(benzyl)-*N*-(4-methyl benzyl)dithiocarbamate], [L_2 = potassium-*N*-(ethyl)-*N*-(4-methyl benzyl)dithiocarbamate], [L_3 = potassium-*N*-(cyclohexyl)-*N*(4-methyl benzyl)dithiocarbamate], [L_4 = potassium-*N*-(benzyl)-*N*-(2-hydroxy benzyl)-dithiocarbamate] and [L_5 = potassium-*N*-(benzyl)-*N*-(ethyl)-dithiocarbamate]. Single crystal X-ray diffraction (SCXRD) revealed the structure of complex **1** indicating both C–H···S and C–H··π intermolecular interactions, which played an important role in the stabilization of the dithiocarbamate complex.

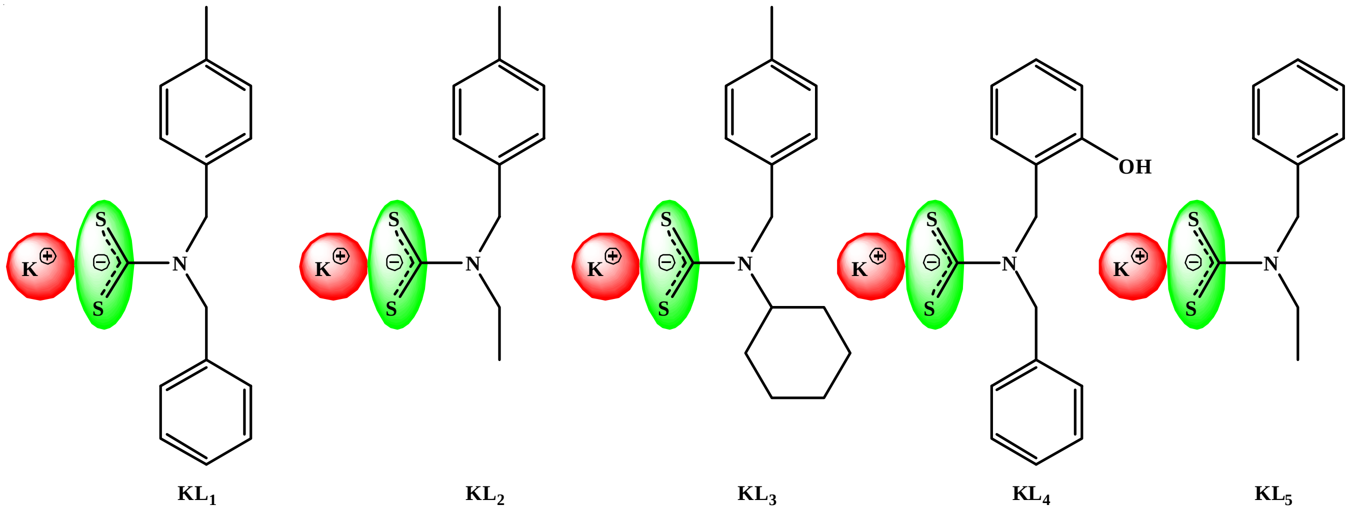
EXPERIMENTAL

Reagent grade chemicals Cd($OOCCH_3$)$_2$·$2H_2O$, 4-methylbenzaldehyde, salicylaldehyde, benzylamine, benzaldehyde, cyclohexylamine, ethylamine (Sigma-Aldrich) and CS_2 (SRL Mumbai) were used as received. All reactions were carried out under ambient conditions. The dithiocarbamate ligands (**Scheme-I**) [potassium-*N*-(benzyl)-*N*-(4-methyl benzyl)dithiocarbamate (KL_1)], [potassium-*N*-(ethyl)-*N*-(4-methyl benzyl)-dithiocarbamate (KL_2)], [potassium-*N*-(cyclohexyl)-*N*(4-methyl benzyl)dithiocarbamate (KL_3)], [potassium-*N*-(benzyl)-*N*-(2-hydroxy benzyl)-dithiocarbamate (KL_4)] and [potassium-*N*-(benzyl)-*N*-(ethyl)dithiocarbamate (KL_5)] were synthesized as described earlier [32-34] by the reaction of CS_2 and KOH with appropriate 2°-amines and characterized *via* spectroscopy techniques (IR, ^{1}H and ^{13}C NMR). Element analyzer (Exeter CE-440) was used for the analysis of C, H and N; Gallenkamp's apparatus was used for determination of the melting point. The spectra of IR were recorded using KBr pellets on Varian Excalibur 3100-FT IR spectrophotometer and ^{1}H and ^{13}C NMR spectra were measured on JEOLAL 300 FT NMR spectrometer. UV-visible absorption was recorded in 200-800 nm region on Shimadzu UV-1800 spectrometer. Under a nitrogen atmosphere, thermogravimetric analyses were carried out in the temperature range of 20-800 ºC at a heating rate of 10 ºC min^{-1}. Transmission electron microscopy (TEM) images were recorded by electron diffraction using a JEOL 2000FX transmission electron microscope (TEM) operational at 200 kV whereas EDX measurements were performed using a Philips ESEM XL30 equipped with an energy-dispersive X-ray diffractometer. Solid-state electrical conductivity was measured using the conventional two-probe technique on a Keithly 236 source measure unit.

Synthesis of the complexes

Complex 1: To a 15 mL methanol/water solution of ligand KL_1 (0.32g, 1 mmol), 10 mL aqueous methanolic solution of cadmium acetate dihydrate (0.5 mmol, 0.13 g) was added dropwise and stirred for 3-4 h at room temperature, which resulted a light-yellow precipitate. The precipitate was filtered off and washed with the same solvent mixture several times along with diethyl ether to get a good yield of the final solid product and was recrystallized in dichloromethane. Yield: 0.27 g, 79%, m.p.: 197 ºC. Anal. calcd. (found) % for $C_{32}H_{32}N_2S_4Cd$: C, 60.03 (58.90); H, 5.35 (5.08); N, 4.38 (4.22); S, 20.03 (19.92). IR (KBr, ν_{max}, cm^{-1}): 1002 (C-S); 1409 (C-N); ^{1}H NMR (500 MHz, $CDCl_3$, δ, ppm): 7.39-7.34 (m, 5H, aromatic protons of -C_6H_5), 7.25-7.19 (m, 4H, aromatic protons of -$C_6H_4CH_3$), 5.04 (s, 2H, methylene protons of –$CH_2C_6H_5$), 5.01 (s, 2H, methylene protons of -$CH_2C_6H_4CH_3$), 2.37 (s, 3H, methyl protons); ^{13}C {^{1}H} NMR (125 MHz, $CDCl_3$, δ, ppm): 205.81 (-CS_2), 138.05, 134.57, 131.45, 129.60, 128.92, 128.97, 128.08, 128.05 (aromatic carbons), 55.52 (methylene carbon of -$CH_2C_6H_4CH_3$), 55.47 (methylene carbon of -$CH_2C_6H_5$), 21.17 (methyl carbon).

Complex 2: This complex was synthesized using ligand KL_2 (0.26 g, 1 mmol) by adopting the same method described for complex **1**. Yield: 0.24 g, 81%, m.p.: 194 ºC. Anal. calcd. (found) % for $C_{22}H_{28}N_2S_4Cd$: C, 47.69 (47.57); H, 5.92 (5.83);



Scheme-I: DTCs Ligands (KL_1-KL_5) were used in this work

N, 4.08 (3.97); S, 22.14 (22.09). IR (KBr, ν_{max}, cm^{-1}): 1001 (C-S); 1436 (C-N); ^{1}H NMR (500 MHz, DMSO-d_6, δ, ppm): 7.15-7.06 (m, 4H, aromatic protons), 5.27 (s, 2H, -methylene protons of -$CH_2C_6H_4CH_3$), 3.42 (q, 2H, methylene protons of -CH_2CH_3), 2.21 (t, 3H, -ArCH_3), 1.09 (t, 3H, methyl protons); ^{13}C {^{1}H} NMR (125 MHz, DMSO-d_6, δ, ppm): 202.39 (-CS_2), 137.51, 133.32, 129.8, 127.44 (aromatic carbons of -$C_6H_4CH_3$), 56.85 (methylene carbons of -$CH_2C_6H_4CH_3$), 50.52 (methylene carbons of -CH_2CH_3), 21.23 (-ArCH_3), 12.68 (methyl carbon).

Complex 3: Light yellow colour complex **3** was synthesized by adopting the previously mentioned method for complex **1** using ligand KL_3 (0.32 g, 1 mmol). Yield: 0.29 g, 83%, m.p.: 196 ºC. Anal. calcd. (found) % for $C_{30}H_{40}N_2S_4Cd$: C, 54.17 (54.06); H, 6.75 (6.60); N, 4.08 (3.98); S, 18.66 (18.52). IR (KBr, ν_{max}, cm^{-1}): 1011 (C-S); 1412 (C-N); ^{1}H NMR (500 MHz, DMSO-d_6, δ, ppm): 7.29-7.17 (m, 4H, aromatic), 5.14 (s, 2H, methylene protons of -$CH_2C_6H_4CH_3$), 3.29 (d, 2H, methylene protons of -$CH_2C_6H_{11}$), 2.46 (s, 3H, methyl protons), 1.6-1.17 (m, 11H, cyclohexyl ring protons); ^{13}C {^{1}H} NMR (125 MHz, DMSO-d_6, δ, ppm): 207.69 (-CS_2), 138.40-127.05 (aromatic carbons), 65.26 (methylene carbon of -$CH_2C_6H_4CH_3$), 53.16 (methylene carbon of -$CH_2C_6H_{11}$) 39.72- 25.89 (carbon of cyclohexyl ring), 25.26 (methyl).

Complex 4: Light yellow colour complex **4** was obtained using ligand KL_4 (0.33 g, 1 mmol) choosing the same method as described for complex **1**. Yield: 0.28 g, 81%, m.p.: 195 ºC. Anal. calcd. (found) % for $C_{30}H_{28}O_2N_2S_4Cd$: C, 52.13 (52.08); H, 4.37 (4.37); N, 4.05 (3.96); S, 18.55 (18.48). IR (KBr, ν_{max}, cm^{-1}): 972 (C-S), 1453 (C-N); ^{1}H NMR (500 MHz, $CDCl_3$, δ, ppm): 7.28-7.19 (m, 5H, aromatic protons of -C_6H_5), 7.13-6.73 (m, 4H, aromatic protons of -C_6H_4OH), 5.21 (s, 1H, alcoholic proton), 4.66 (s, 2H, methylene protons of -$CH_2C_6H_5$), 4.65 (s, 2H, methylene protons of -$CH_2C_6H_4OH$); ^{13}C {^{1}H} NMR (125 MHz, $CDCl_3$, δ, ppm): 208.34 (-CS_2), 154.40, 134.04, 129.98, 129.74, 128.96, 128.86, 128.50, 120.86, 119.82, 116.60 (aromatic carbons), 51.50 (methylene carbon of -$CH_2C_6H_5$), 50.79 (methylene carbon of -$CH_2C_6H_4OH$).

Complex 5: Using the same approach as for complex **1**, but with ligand KL_5 (0.25 g, 1 mmol), a light-yellow colour complex **5** was synthesized and separated. Yield: 0.27 g, 84%, m.p.: 198 ºC. Anal. calcd. (found) % for $C_{20}H_{24}N_2S_4Cd$: C, 49.22 (49.13); H, 5.37 (5.18); N, 5.74 (5.53); S, 26.28 (26.15). IR (KBr, ν_{max}, cm^{-1}): 1000 (C-S), 1421 (C-N); ^{1}H NMR (500 MHz, DMSO-d_6, δ, ppm): 7.37-7.25 (m, 5H, aromatic), 5.15 (s, 2H, methylene protons of -$CH_2C_6H_5$), 3.77 (q, 2H, methylene protons of -CH_2CH_3), 1.14 (t, 3H, methyl protons); ^{13}C {^{1}H} NMR (125 MHz, DMSO-d_6, δ, ppm): 202.00 (-CS_2); 137.34, 128.98, 128.04, 127.88 (aromatic); 57.97 (methylene carbons of -$CH_2C_6H_5$); 49.71 (methylene carbons of -CH_2CH_3), 12.26 (methyl carbon).

X-ray crystallography: SCXRD data of complex **1** was recorded on Oxford Diffraction X-caliber CCD diffractometer [Mo*K*α radiation (λ = 0.71073 Å)] with a dimension of 0.22 × 0.22 × 0.17 mm^3. Determination of unit cell data, data collection and reductions were performed using the CrysAlis pro software [35]. The structure of complex **1** was solved and refined by a direct method applying SHELXS-97 [36].

RESULTS AND DISCUSSION

The synthesized Cd(II) complexes **1-5** were synthesized in a good yield *via* reaction of cadmium acetate with a methanolic solution of the respective ligand (**Scheme-II**) in 1:2 molar ratios and are air-stable melt or decompose in the temperature range 188-198 ºC and are soluble in most of the organic solvents. As anticipated, all the cadmium complexes are diamagnetic and characterized by C, H, N, ^{1}H, ^{13}C, IR, UV-vis and complex **1** has been elucidated by SCXRD.

$$2KL + Cd(CH_3COO)_2{\cdot}2H_2O \xrightarrow[\text{Stir., 3-4 h}]{\text{Methanol/RT}} [Cd(L)_2] + 2CH_3COOK + 4H_2O$$

Scheme-II: A general methodology for the preparation of the complexes (**1-5**)

^{1}H NMR studies: D_2O, DMSO-d_6 and $CDCl_3$ solvents were used for recording the ^{1}H NMR spectra of the ligands (KL_1-KL_5) and their Cd(II) complexes (**1-5**). For different types of protons present in ligands, the chemical shift values of ^{1}H NMR signals were carefully compared with that of its Cd(II) complexes. Protons of aromatic rings, methylene and methyl groups were detected between the ranges 7.43-6.83, 5.29-5.02, 3.34-2.05 ppm, respectively in the ^{1}H NMR spectra of ligands KL_1-KL_5. The methylene protons of the alkyl chain (adjoining to nitrogen atom) were detected between δ 3.91-3.61 ppm and methyl protons of the alkyl chain were observed between δ 1.09-1.10 ppm. It was observed that the δ values of benzene, methyl, aromatic and aliphatic methylene protons showed no consi-derable shift upon complexation, which indicates that these groups did not participate in complexation.

^{13}C NMR spectroscopy: The ^{13}C NMR spectra of dithiocarbamate compounds show the chemical shift value for carbon present in NCS_2 moiety above δ 190 ppm. In ^{13}C NMR spectra of the free ligands signals for S_2C–N moieties were observed between δ 215.45-209.36 ppm, subsequently upon the complexation δ values were obtained between δ 208.34-202.00 ppm for all cadmium metal complexes [29,37,38]. For NCS_2 carbon in cadmium metal complexes, δ values for the chemical shift were observed 7 ppm downfield than that of their corresponding ligands indicating Cd-S bonding. The peaks of –CH_2 (linking with N-atom) of benzene derivative groups were observed between δ 56.49-50.09 ppm. In case of KL_2 and KL_5 ligands, these peaks were observed between around δ 50.52-49.15 ppm of the alkyl chain while signals for methyl carbon of the alkyl chain were observed around δ 12.68-11.31 ppm. In case of KL_1, KL_2 and KL_3 ligands, signals for methyl groups present at the *para* position of benzene units were observed around δ 25.74-20.29 ppm. After complexation, the chemical shift values of benzene rings carbons, methyl carbon and aromatic and aliphatic methylene carbon showed the light upfield and downfield shifts in comparison to that of their respective ligands.

FTIR studies: The IR spectral data of the dithiocarbamate ligands and their Cd(II) complexes are given in Table-1. The bands for ν(C-N) are observed 1453-1409 cm^{-1} region in all The

TABLE-1
SELECTED IR BANDS (cm^{-1}) OF THE DITHIOCARBAMATES AND THEIR Cd(II) COMPLEXES

Complex	ν(C–N)	ν(C–S)
$C_{16}H_{16}NS_2K$ (KL$_1$)	1353	1027
$C_{11}H_{14}NS_2K$ (KL$_2$)	1352	1040
$C_{15}H_{20}NS_2K$ (KL$_3$)	1384	1013
$C_{15}H_{14}ONS_2K$ (KL$_4$)	1351	1029
$C_{10}H_{12}NS_2K$ (KL$_5$)	1354	1077
$C_{32}H_{32}N_2S_4Cd$ (**1**)	1409	1002
$C_{22}H_{28}N_2S_4Cd$ (**2**)	1436	1001
$C_{30}H_{40}N_2S_4Cd$ (**3**)	1412	1011
$C_{30}H_{28}O_2N_2S_4Cd$ (**4**)	1453	972
$C_{20}H_{24}N_2S_4Cd$ (**5**)	1421	1000

Cd(II) complexes while these bands are observed at lower frequencies in the ligand 1384-1351 cm^{-1}, which indicates a partial double bond character in the C-N bond of the S_2C-NR_2. The presence of only a single and strong brand in the region 1077-972 cm^{-1}are attributed to ν(S-C-S) asymmetric mode and is supposed to indicate a symmetrical bonding of the dithiocarbamate moiety. In all Cd(II) complexes sharp bands are observed in the range 465-422 cm^{-1} for Cd-S moiety [39-41].

UV-vis absorption and photoluminescence studies: To acquire some helpful information regarding the coordination characteristics of cadmium ions, the UV-vis absorption spectra of cadmium dithiocarbamate complexes (**1-5**) were taken in 200-800 nm ranges by preparing solutions of complexes in CH_2Cl_2. The absorption spectra of complexes **1-5** showed similar absorption bands near 220 and 225 nm that were distinguished by metal perturbed π-π* ILCT transition of cadmium complexes. The metal to ligand charge transfer (MLCT) band appeared in the range of 266-285 nm (Fig. 2). Complexes (**1-5**) showed emission bands around 375 nm with a Stokes shift of 90-109 nm upon excitation at 266-285 nm (Fig. 3) in dichloromethane solution at room temperature, arising from the metal perturb charge transfer transition of the ligand.

Crystal structure of [$C_{64}H_{64}N_4Cd_2S_8$] (1): The single crystal of cadmium complex **1** was accumulated from CH_2Cl_2 solution in 21 days. The crystal lattice details including important bond lengths and angles are listed in Tables 2 and 3. Complex **1** crystallizes in a triclinic system of *P*-1 space groups, passes centrosymmetric dimeric structure as shown in Fig. 4 and are centro-symmetric dinuclear molecule where four benzyl-(4-methyl-benzyl)-dithiocarbamate ligands are asymmetrically bonded by two cadmium atoms as S,S-chelating bridging and S,S-chelating fashion. The Cd1 atoms reside in square pyramidal environments shown in Fig. 4 and are asymmetrically S,S-chelated through two ligands benzyl-(4-methyl-benzyl)-dithiocarbamate of bond length Cd1-S13 and Cd1-S11 are 2.567(10) Å and 2.577(9) Å, while Cd1-S43 and Cd1-S41 are 2.876(9) Å and 2.544(10) Å, respectively. The geometry just about the Cd1 atom is mainly presumed as for tremendously distorted square pyramid as the value of τ is 0.30 in comparison to 0.0 for a principal square pyramid while for a trigonal bipyramid the value is 1.0 [37]. The S43 atom, occupies an axial position bond length is 2.876(9) Å and acts as a bridging atom to the Cd1 atom. Thus, the DTCs are bonded to a S,S-chelating-bridging manner, with Cd1 and other Cd1 atoms, thereby enormously forming a dinuclear structure.

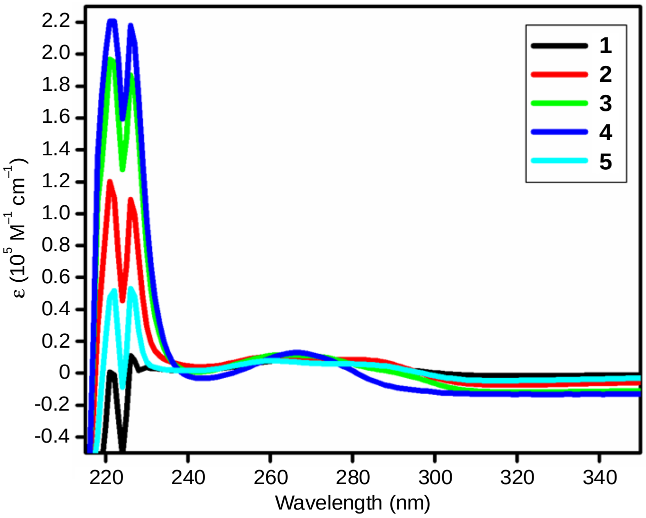


Fig. 2. UV-visible absorption spectra of complex (**1-5**) in CH_2Cl_2 solution

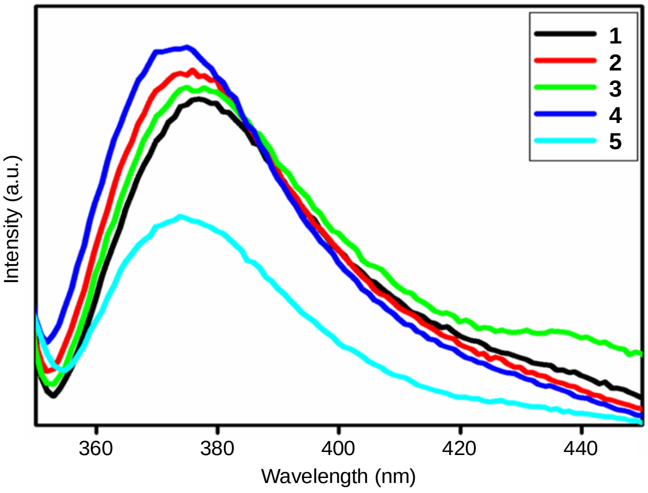


Fig. 3. Emission spectra of complex **1-5** in CH_2Cl_2 solution

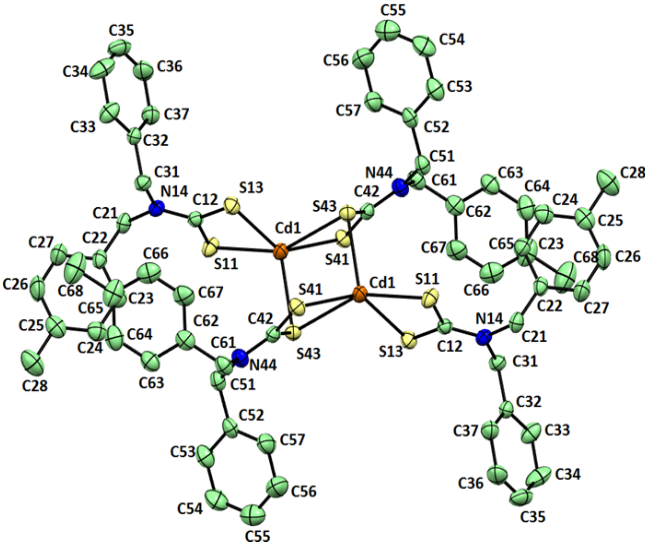


Fig. 4. Representation of atomic number scheme of complex **1** by ORTEP Diagram

TABLE-2
CRYSTAL LATTICE PARAMETERS OF COMPLEX **1**

Chemical formula	$C_{64}H_{64}N_4S_8Cd_2$
FW (g mol^{-1})	1370.47
Crystal system	Triclinic
Space group	*P*-1
a (Å)	10.1623(7)
b (Å)	13.0805(11)
c (Å)	13.7950(13)
V (Å^3)	1531.5(2)
β (deg)	93.648(6)
Z	1
T (K)	150(2)
ρ_{calc} (gram cm^{-1})	1.486
μ (Mo Kα) (mm^{-1})	1.010
F (000)	700
Crystal size (mm^3)	0.22 × 0.22 × 0.17
Index ranges	$-14 \le h \le 8$; $-18 \le k \le 18$; $-16 \le l \le 19$
Reflns collected	10804
Independent reflns	8538
No. of parameters	354
Refln with I > 2σ(I)	6271
R_1^a, wR_2^b [I > 2σ(I)]	0.0494
R_1^a, wR_2^b (all data)	0.0764,0.1290
GOF^c	0.927
Residual electron density, e Å^{-3}	1.355, -0.815

$^aR_1 = \Sigma||Fo|-|Fc||/\Sigma|Fo|$; $^bwR2 = \{[\Sigma w(Fo^2 - Fc^2)/\Sigma w(Fo^2)^2]\}^{1/2}$; $w = 1/[\sigma^2(Fo^2) + (xP)^2]$, where $P = (Fo^2 + 2Fc^2)/3$; ^{c}GOF = $S = \{[\Sigma w(Fo^2 - Fc^2)^2]/(n-p)\}^{1/2}$, where n = number of reflections and p = number of the refined parameters.

TABLE-3
SELECTED BOND DISTANCES (Å) AND ANGLES (°)
BY X-RAY DIFFRACTION IN COMPLEX **1**

Bond length (Å)		Bond angle (°)	
Cd1-S41	2.544(10)	S41-Cd1-S13	137.3(3)
Cd1-S13	2.567(10)	S41-Cd1-S11	117.6(3)
Cd1-S11	2.577(9)	S13-Cd1-S11	70.2(3)
Cd1-S43	2.876(9)	S41-Cd1-S43	98.9(3)
S11-C12	1.724(3)	S13-Cd1-S43	119.6(3)
S13-C12	1.339(3)	S11-Cd1-S43	107.0(3)
S41-C42	1.715(3)	S41-Cd1-S43	66.6(3)
S43-C42	1.735(4)	S13-Cd1-S43	88.6(3)
N14-C12	1.339(4)	S11-Cd1-S43	152.3(3)
N44-C42	1.331(4)	S43-Cd1-S43	98.9(2)

The Cd-S bond lengths were found between 2.544 to 2.876 Å. The bite angle for S41-Cd-S43 is 66.6º while for S11-Cd-S13 is 70.2º. The bond lengths of the N44-C42 and N14-C12 are 1.331 Å and 1.339 Å, respectively. This bond is shorter than the expected distance of 1.47 Å for C-N bond but similar to that reported in the literature [37]. Complex **1** shows a slightly shorter C=N bond (1.28Å) as compared to the expected C=N bond of about 1.35Å confirming the complexation and successful contribution of the resonance form (Fig. 1). It is noticeable that in the dithiocarbamate complexes, the C-S bond lengths 1.339 to 1.735 Å are appreciably smaller than those of the C-S single bond length (1.81 Å) because of the NCS_2 backbone π conjugation.

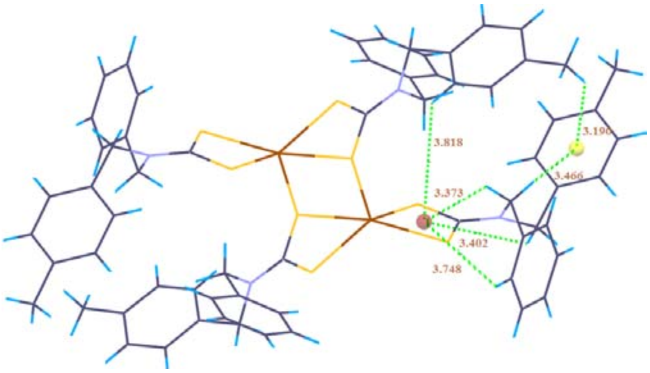


Fig. 5. Complex **1** shows many intermolecular C–H··π interactions

From viewpoint of different types of intramolecular interaction (Fig. 5) complex **1** has furthermore become stable by a weak interaction of C-H···π (3.190 Å) among *para*-methyl hydrogen atom to a phenyl as well as π electrons of another phenyl ring. Interaction of C-H··π (3.466 Å) is observed for aromatic methylene protons while methylene protons (adjacent to N atom) interaction is recorded (3.373 Å, 3.748 Å) with four member's π conjugation sulfur and Cd metal center.

Weak interactions C–H···S (Fig. 6 and Table-4) can be seen among the H atoms of the benzyl ring and methyl group with the coordinated sulfur atom of the ligands. The extent of the specific C–H···S interactions can be explained by unequal downfield shifts of the signals from the associated protons. The S···H–C bond angles are observed to be 118.9º and 151.2º, respectively and the S···H distances are seen consistent with the same geometry for S11···H23 and S41···H35 with bond lengths of 2.944 and 2.877 Å, respectively (Table-4), are shorter than the sum of the van der Waals radii of H and S atoms.

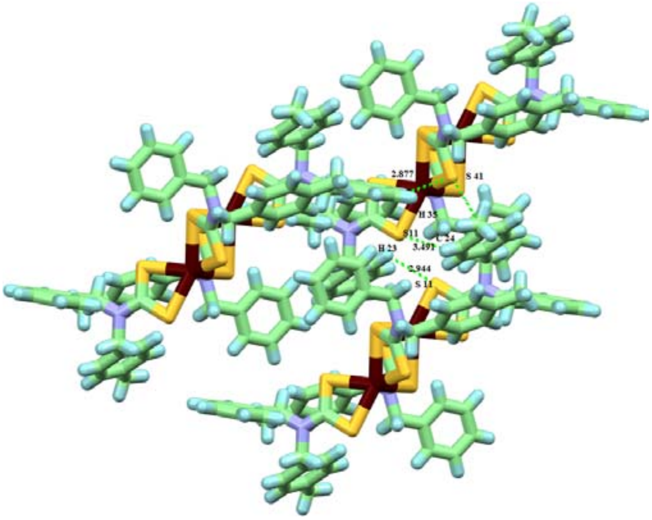


Fig. 6. C–H···S and S···H interaction in complex**1**

TABLE-4
BOND LENGTH (Å) AND BOND ANGLE (°) ASSOCIATED WITH WEAK INTERMOLECULAR INTERACTIONS IN COMPLEX **1**

D–H···A	d(D-H)	d(H···A)	d(D···A)	∠(DHA)
C23-H23···S11	0.930	2.944	3.491	118.98
C35-H35···S41	0.930	2.877	3.719	151.22

Pressed pellet electrical conductivities: Cadmium(II) dithiocarbamate complexes show electrical conductivities arising from metal-sulfur, sulfur-sulfur and metal-metal intermolecular interactions [42]. The conventional two-probe method was applied to record the electrical conductivities of complexes **1-5** with the help of Keithly 236 source measure unit. The pellets were prepared at a load of 15 kN and the contacts on the pellet's surfaces were made using silver paste (diameter: 11.5 mm for complexes **1** and **5**, 11.4 mm for complexes **2**, **3** and **4**; and the thickness of 1.3 mm, 1.6 mm, 1.5 mm, 1.2 mm and 1.4 mm for complexes **1-5**, respectively). All the complexes show weak conductivity at room temperature ($\sigma_{rt} = 10^{-9}$-10^{-10} S cm^{-1}). A plot of log σ *versus* T^{-1} in the 303-363 K range indicates their semiconducting behaviour. However, their electrical conductivities gradually increase with increasing temperature (Fig. 7) and ideally decreases with decreasing temperature range showing their semiconducting nature. The band gaps calculated from the graph were found to be 0.77, 0.88, 0.76, 0.78 and 0.74 eV of the Cd(II)complexes **1-5**, respectively.

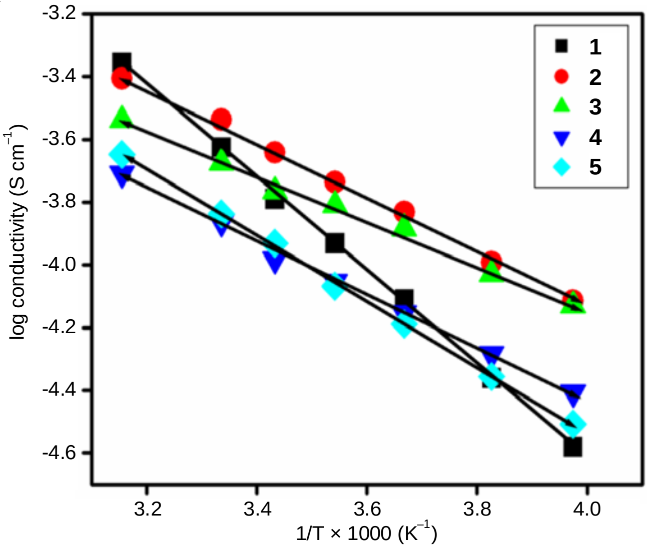


Fig. 7. Temperature-dependent electrical conductivities of complexes

Thermogravimetric analysis: Thermal decomposition of the synthesized cadmium(II) complexes (**1-5**) was studied by thermogravimetric analysis (TGA). The samples were placed in an alumina cup and heated at a temperature ranging from 20-800 ºC with a heating rate of 10 ºC/min in the presence of a nitrogen atmosphere. The TGA plots (Fig. 8) of all the complexes (**1-5**) show that they lost their weigh-in two-step decomposition. The thermal decomposition of the complexes started at a lower temperature (100 ºC) with the loss of water molecules in the first decomposition step. The second and final step of the decomposition started at 350 ºC and metal sulfide residues were obtained around 545 ºC, indicating that the cadmium(II) complexes may be used as a single source precursor for the utilization of metal sulfide nanoparticles [43]. These products were further characterized by EDAX and TEM to confirm the cadmium sulfide nanoparticles.

TEM studies: The morphology and particle size of the cadmium(II) complexes (**1-5**) were confirmed by TEM analysis (Fig. 9). TEM image of the cadmium sulfide nanoparticles shows the spherical morphology with approximately uniform size distribution. It was observed from the image that some of the particles are elongated while some are agglomerated and other are spherical in the shape with grain size between 1-10 nm. The small size has been attributed to changes in their decomposition due to the different functional groups in the complexes.

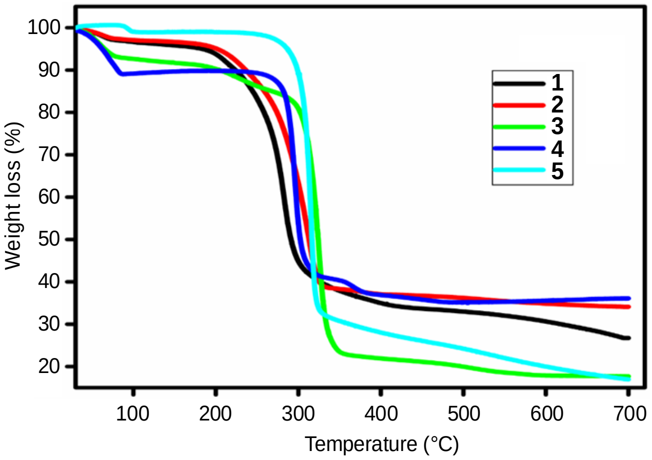


Fig. 8. Thermogravimetric curves of complexes **1-5**

EDAX studies: The cadmium sulfide nanoparticles formations were further established by performing the EDAX studies. EDX spectra of cadmium sulfide nanoparticles are presented in Fig. 10 to confirm the elemental compositions of cadmium sulfide nanoparticles. However, for all the complexes, strong signals were observed with the ratio of Cd and S approximately in 1:1 ratio, revealing the presence of CdS residue, while other additional weak signals for elements such as C, O and K were also found in traces.

Conclusion

Five new cadmium dithiocarbamate complexes (**1-5**) with the general formula $[Cd(L)_2]$ have been synthesized and characterized by different spectroscopic techniques (IR, NMR, UV-vis, SCXRD, *etc.*), elemental analysis, thermal characterization and electrical conductivity. Only the crystal of complex **1** was obtained by slow evaporation in dichloromethane solution and possess centro-symmetric dimeric structure and stabilized by weakly C–H··π and C–H···S intermolecular interactions. The absorption spectral data of the Cd(II) complexes (**1-5**) shows very similar absorption bands near 220 and 225 nm and were assigned to π-π*, intra ligand charge transfer (ILCT) transition. Spectral bands near 266-285 nm were attributed to metal to ligand charge transfer (MLCT) transition. Complexes (**1-5**) show emission bands around 375 nm with a Stokes shift of 90-109 nm upon excitation at 266-285 nm in dichloromethane solution at room temperature, arising due to the MLCT transition. The synthesized cadmium complexes (**1-5**) show weak conductivities at room temperature and exhibit semiconducting behaviour. As temperature increases, electrical conductivity increases and as temperature decreases, conductivity decreases, indicating the semi-conductivity of the Cd(II) complexes. Thermal analysis shows that Cd(II) complexes **1-5** have similar nature and are decomposed in two steps resulting in the formation of cadmium sulfide as the ultimate product of the thermal decomposition process.

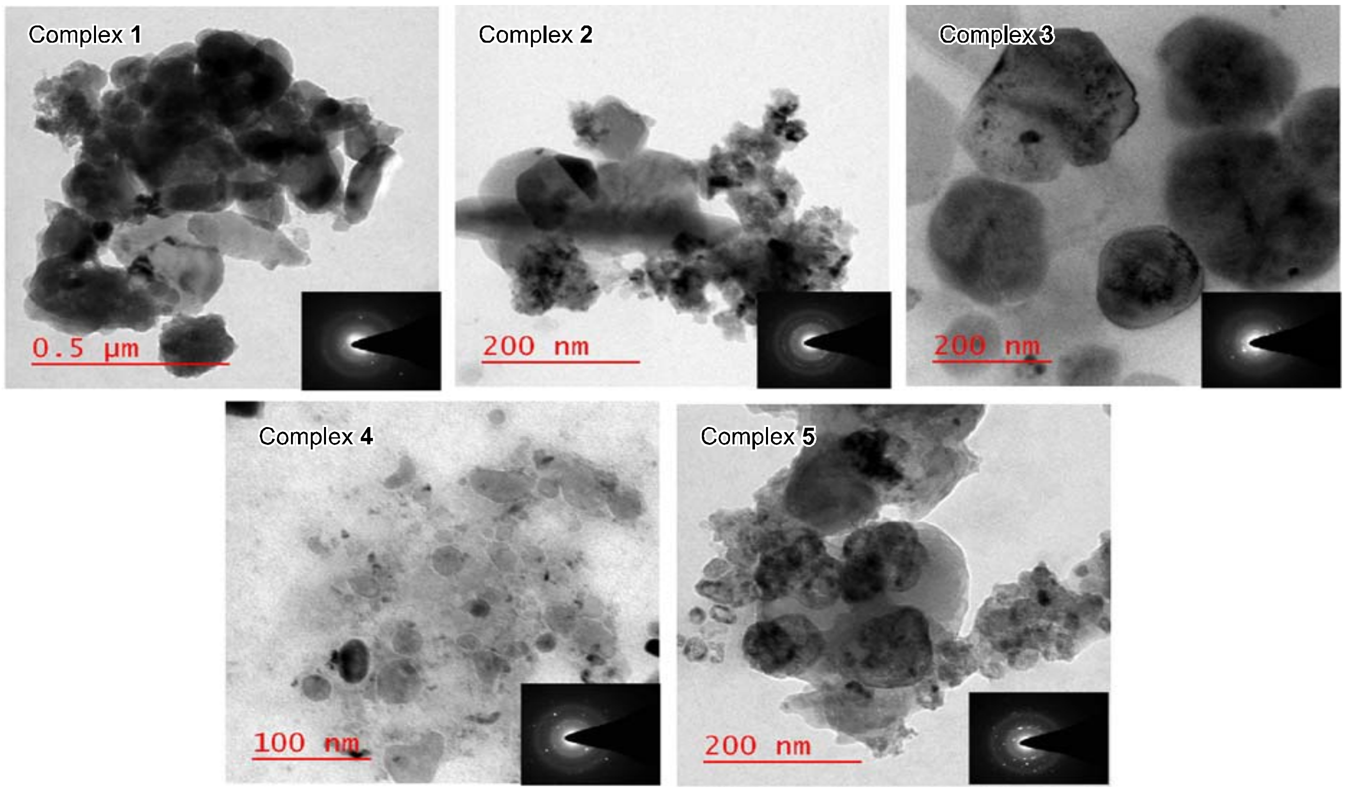


Fig. 9. Transmission electron microscopy images of complexes (**1-5**), the inset in the images shows the SAED pattern

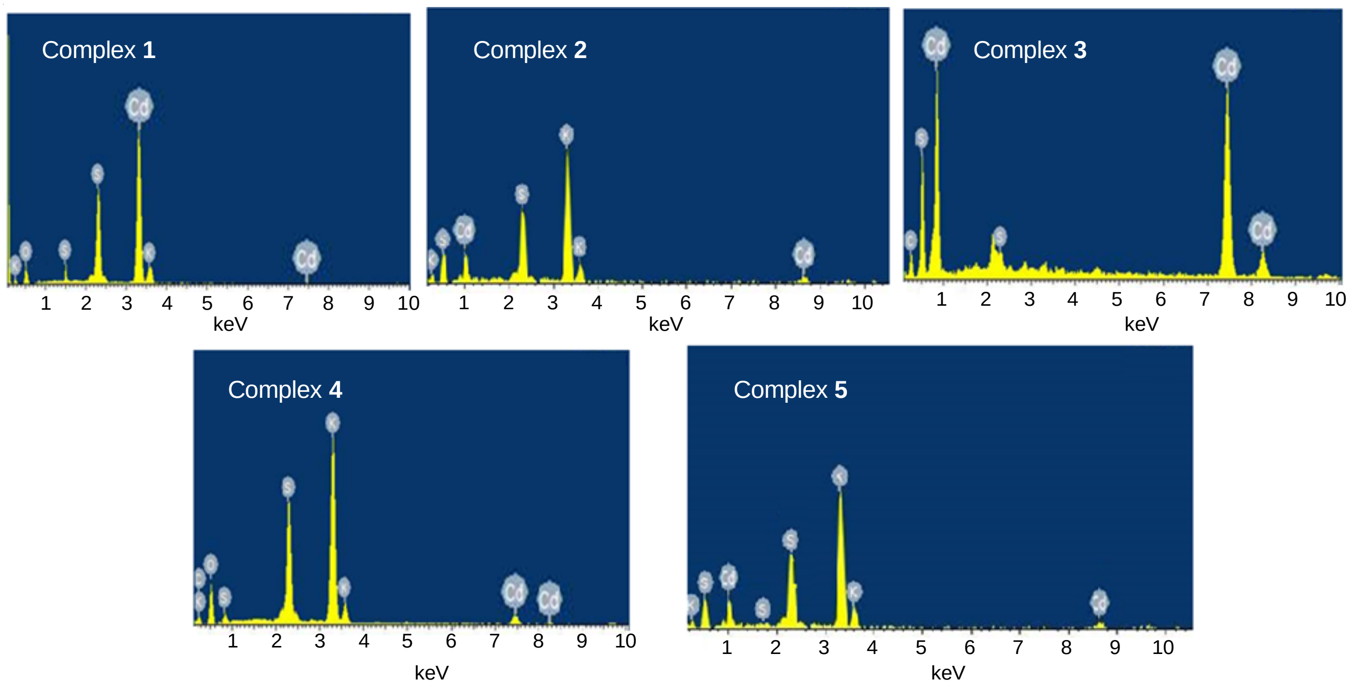


Fig. 10. EDS micrographs for the metal sulfide obtained from the precursor complexes **(1-5)** respectively

Supplementary data: CCDC 1869927 contains the supplementary crystallographic data for [N-benzyl-(4-methyl-benzyl)-dithiocarbamate] (**1**). These data can be obtained free of charge *via* http://www.ccdc.cam.ac.uk/conts/retrieving.html or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; Fax :(+44) 1223-336-033 or e-mail: deposit@ccdc.cam.ac.uk

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CONFLICT OF INTEREST

The authors declare that there is no conflict of interests regarding the publication of this article.

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