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Three novel Cd(II) dithiocarbamate complexes: synthesis, structural diversity and fluorescence properties

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Abstract

Three new homoleptic cadmium (II) dithiocarbamate complexes having molecular formula $[Cd(KL)_2]$, $(KL1=C_{15}H_{13}N_1F_1S_2)$ (1); $(L2=C_{13}H_{11}N_1F_1S_2)$ (2); $(L3=C_{11}H_{14}N_1O_1S_2)$ (3), have been synthesized and characterized by elemental analysis, spectroscopy (IR, ¹H and ¹³CNMR and UV–Vis). Single crystal X-ray studies confirm that the complex 1 crystallises in Orthorhombic with space group *P*na21 and holding dimeric structure. In this complex Cd²⁺ having distorted octahedral geometry about the metal centre forms 1D coordination polymeric structures. The dimeric form of complex 2 and 3 crystallizes in triclinic crystal lattice with space group P-1.

Keywords Cd-dithiocarbamate complexes · C-H...S interactions · Fluorescence properties

Introduction

The coordination chemistry of dithiocarbamate ligands is of peculiar interest, as it can form complexes with most of the transition and main group metal ions [1–6]. The intermolecular interactions of dithiocarbamate ligands with metals form homoleptic $[M(L)_2]^{2-}$ anions, in monodentate, bidentate (chelate or bridging), tridentate and even tetradentate fashion, yielding exciting coordination properties and unusual bonding behavior which are responsible for structural diversity and properties of complexes. Such abilities bring in several keystone features which can be implemented in various fields like industry, agriculture and in biomedical fields (cancer, neurogenerative diseases). Recently the dithiocarbamate and iron chelators moieties can be considered as

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² Department of Chemistry, National Institute of Technology Raipur, G. E. Road, Raipur, Chhattisgarh 492010, India fruitful way in the treatment of abnormalities of AIDS and neurodegenerative diseases as the dithiocarbamate have the potential to block the activation of nuclear factor KB (NF-KB), a transcription factor involved in inflammatory processes and human immunodeficiency virus type 1 (HIV-1) expression and signaling events regarding to type of cancer (Scheme 1).

In contrast to a plethora of examples of Zn(II) dithiocarbamates [2,3b] showing structural diversity, the number and structural types of cadmium dithiocarbamate complexes reported to date are extremely limited [7–16]. Here we have reported three new homoleptic Cd-complexes of having formula [Cd(KL)₂], (KL1 = $C_{15}H_{13}N_1F_1S_2$) (1); (L2 = $C_{13}H_{11}N_1F_1S_2$) (2); (L3 = $C_{11}H_{14}N_1O_1S_2$) (3), based on dithiocarbamate.

Experimental

Materials and methods

All the chemicals like acetaldehyde, benzaldehyde, 2-thiophenecarboxaldehyde, 4-methoxybenzylamine, 4-flourobenzylamine, CS_2 and NaOH were purchased from Sigma Aldrich and used as such.



Scheme 1 Delocalization of electron in dithiocarbamate ligands



Scheme 2 Structure of ligands used in this work

Synthesis of dithiocarbamate ligands

Potassium salt of the dithiocarbamate ligands viz. [(KL1 = $C_{15}H_{13}N_1F_1S_2$ (*N*-Ethyl-*N*-4-flourobenzyl dithiocarbamate); KL2 = $C_{13}H_{11}N_1F_1S_2$ (*N*-4-flourobenzyl- *N*-thiophene dithiocarbamate); KL3 = $C_{11}H_{14}N_1O_1S_2$ (*N*-ethyl-*N*-4-methoxybenzyl dithiocarbamate)] were prepared according to literature procedures [17–19] by the reaction of the appropriate secondary amine with KOH in CS₂ (Scheme 2).

Synthesis of complexes

The homoleptic complexes **1–3** are prepared by known process [20–25] in good yield by the reaction of cadmium metal and their corresponding ligand in 1:2 molar ratios in methanolic solution (Scheme 3). The complexes are air-stable and melt in the 142–210 °C temperature range. The complexes have been characterized by elemental analyses and spectroscopy (IR, ¹H and ¹³CNMR, UV–Vis). Single crystal X-ray studies show that all complexes are having Cd⁺⁺ with different molecular geometry and space group (Scheme 4).

Results and discussion

Synthesis

The complexes **1–3** were synthesized by the reaction of $Cd(CH_3COO)_2$ with their corresponding ligand in 1:2 molar ratio in the methanolic solution. All the complexes are stable at room temperature and soluble in organic solvent like $CHCl_3$, DMSO and DMF. The C, H, N analysis of complexes is, Found (calcd.) for $C_{30}H_{26}CdF_2N_2S_4(1)$: C, 51.83 (51.80); H, 4.06 (3.91); N, 4.03 (3.96) (yield: 0.51 g, 73%); $C_{52}H_{44}CdF_4N_4S_{12}(2)$: C, 44.15 (44.11); H, 3.42 (3.27); N, 3.96 (3.91) (yield: 0.49 g, 69%); $C_{20}H_{24}CdN_2S_4(3)$: C, 44.89 (44.80); H, 4.90 (4.81); N, 5.25 (5.18) (yield: 0.54 g, 72%).

NMR spectra

The ¹³CNMRof complexes **1–3** showed a low field resonance associated with the NCS₂ carbons of the dithiocarbamates moieties in the range $\delta = 203-208$ ppm due to dominant contribution of $R_2N^+ = CS_2^{-2-}$ resonance form in the dithiocarbamate complexes as compare to free ligand



Scheme 3 Schematic representation of synthesis of complexes



Scheme 4 Schematic representation of complexes 1-3

Table 1	NMR	data	(δ,	ppm)	of	ligands	(1-3)
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Compound	Nucleus	$-C_{6}H_{4}$	-CH	$_{2}C_{6}H_{4}F$	$-CH_2C_6H_5$	_	OCH ₃	CS_2			$-C_4H_3S$	-CH ₃
$\overline{C_{15}H_{13}N_{1}F_{1}S_{2}^{-}(KL1)}$	$^{1}\mathrm{H}$	6.93–7.34(m)	3.82((s)	3.80(s)	_		_			_	_
	¹³ C	114-138	53.30)	52.55	_		216.32			_	_
$C_{13}H_{11}N_1F_1S_2^{-}$ (KL2)	1 H	6.79–7.18(m)	3.68((s)	-	_		_	6.72-7.1	8(d,s)		_
	¹³ C	114-135	55.35	5	_	_		216.38			158-159	_
$C_{11}H_{14}N_1O_1S_2^{-}$ (KL3)	$^{1}\mathrm{H}$	6.80-7.30(m)	_		3.87(s)	3	.69(s)	_			_	1.18(t)
	¹³ C	113–129	_		56.30	5	3.24	210.31				20.06
Table 2 NMR chemical shifts (δ, ppm) of Complexes $(1-3)$		Compound		Nucleus	-C ₆ H ₄		-CH ₂	C ₆ H ₄ F	CH ₂ C ₆ H ₅	CS ₂	–CH ₂	-CH ₃
(o, FF) (-	- /	$\overline{C_{30}H_{26}N_2CdF_2S}$	4 (1)	¹ H	6.91–7.30(m)	3.66(s)	3.58(s)	-	_	_
		$C_{26}H_{22}N_2CdF_2S$	4 (2)	¹ H	6.56–7.20(i	m)	3.66(s	s)	-	207	_	_
				¹³ C	114–129		54.91		-	205.18	-	_
		$C_{20}H_{24}CdN_2S_4$ (3)	$^{1}\mathrm{H}$	6.80-7.20(1	m)	-		3.69(s)	_	2.34(q)	1.16(t)
				¹³ C	105–137		-		51.41	203.01	40.05	12.19



Fig. 1 UV–Vis spectra of 1-3 in CH_2Cl_2 solution

 $(\delta = 209-219 \text{ ppm})$. In ¹H NMR spectra of the complexes **1–3**, shows characteristic of the ligand functionalities and participate well to the corresponding hydrogen atoms. There is no perceptible shift in the proton NMR spectra of the complexes in comparison to potassium salt of the ligands (Tables 1, 2).

FTIR Spectra

In the IR spectra of complexes 1–3 the strong v(C-N) bands was observed in the range of 1426–1477 cm⁻¹. This stretching vibration may be ascribed to an increase in the carbon–nitrogen double bond character due to delocalization of electron towards the metal atoms in each of the dithiocarbamate complexes [26–28].In the dithiocarbamate ligands two types of v(C-S) bands, the $v(CS_2)_{asym.}$ and $v(CS_2)_{sym}$ are appear at around 1020 cm⁻¹ and 975 cm⁻¹, respectively.



Fig. 2 Emission spectra of 1-3 in CH₂Cl₂ solution

These absorption are replaced by a strong singlet at approximately 1000 cm⁻¹ in all the complexes, indicates a symmetrical coordination of the dithiocarbamate moiety to the metal ions [29, 30].

Absorption and emission spectra

The absorption and emission spectra of dithiocarbamate complexes are measure in CH₂Cl₂ solution and predicted in Figs. 1 and 2. The absorptions in the range between 200 and 800 nm all the complexes due to ligand centered intra ligand charge transfer (ILCT) and metal perturbed intra ligand charge transfer (ILCT) transitions, respectively. The excitation of 270 nm for complex 1, 265 nm for complex 2 and 267 nm for complex 3 we observed the emission peaks at 332 nm, 334 nm and 351 nm, respectively, for complexes 1, 2 and 3. The stokes shift of 62 nm, 69 nm and 84 nm was observed for these complexes. The closed shell d¹⁰ cadmium(II) compounds are very important because of their luminescence properties. When excited at 270 nm in the liquid state a strong broad bands at 315-320 nm arises from the metal perturbed intra ligands charge transfer state (Figs. 1, 2).

Crystal structures

Single crystals of complexes 1-3 were grown by slow evaporation of solutions of the compounds in CH_2Cl_2 -methanol [31–34] and the molecular structures of complexes are determined by X-ray crystallography. Crystal data and refinement details are listed Table 3 and selected bond lengths and bond angles are given in Table 4. The Cd²⁺ ions shows no stereo-chemical preferences arising from ligand field stabilization effects due to this reason it can show diversity of coordination numbers, viz. 4, 5 and 6, and geometries.

Complex 1 crystallizes in orthorhombic crystal system with space group Pna21 and holding dimeric structure. In this complex, Cd^{2+} is having distorted octahedral geometry and forms 1D coordination polymeric structures (Figs. 3, 4) in which sulphur atoms S13, S43 are bridging with two Cd²⁺ atoms. The bond length between

Table 3 Crystallographic	Compound	1	2	3	
parameters for complexes 1–3	Formula	C ₃₀ H ₂₆ Cd F ₂ N ₂ S ₄	C ₅₂ H ₄₄ Cd ₂ F ₄ N ₄ S ₁₂	C ₂₀ H ₂₄ Cd N ₂ S ₄	
	Formula weight	693.17	1410.43	533.05	
	Crystal system	Orthorhombic	Triclinic	Triclinic	
	Space group	Pna21	P -1	P -1	
	a (Å)	8.1758(4)	9.8027(4)	8.664(3)	
	b (Å)	11.5717(5)	11.9846(4)	11.4196(4)	
	c (Å)	29.699(18)	12.1569(4)	11.7088(4)	
	α (Å)	90	74.478(1)	74.932(1)	
	β (Å)	90	81.903(1)	87.279(1)	
	δ (Å)	90	88.069(1)	77.417(1)	
	$V(\text{\AA}^3)$	2809.8(3)	1362.39(8)	1091.71(7)	
	Ζ	4	1	2	
	$p_{calc}(g \text{ cm}-3)$	1.639	1.719	1.622	
	T(K)	150(2)	100(2)	100(2)	
	μ (Mo K α) (mm ⁻¹)	1.112	1.296	1.391	
	F (000)	1400	708	540	
	Independent refins	7585	6764	4061	
	Reflections with $I > 2_{\sigma}(I)$	6553	5844	3817	
	Final indices $[I > 2 \text{ s}(I)] R1^{a}$, wR ₂ ^b	0.0526	0.0403	0.0737	
	$R1^{a}$, wR2 ^b [all data]	0.0636,0.1311	0.0510, 0.0896	0.0255, 0.0737	
	Goodness of Fit	1.007	1.085	1.226	

 ${}^{a}R_{1} = \sum ||Fo| - |Fc|| / \sum |Fo|$

 ${}^{b}R_{2} = \{ [\sum w (F0^{2} - Fc^{2}) / \sum w (Fo^{2})^{2}] \}^{1/2}, w = 1 / [\sigma^{2}(Fo^{2}) + (xP)^{2}], where P = (Fo^{2} + 2Fc^{2}) / 3.$

1	
Bond lengths (Å)	
Cd(1)–S(11)	2.549(2)
Cd(1)–S(13)	2.7524(13)
Cd(1)–S(41)	2.549(2)
Cd(1)–S(43)	2.7458(13)
C(42)–N(44)	1.34(7)
Bond angles (°)	
S(11)-Cd(1)-S(13)	96.31(6)
S(11)-Cd(1)-S(43)	100(5)
S(13)-Cd(1)-S(43)	107.23(3)
2	
Bond lengths (Å)	
Cd(01)–S(002)	2.6115(8)
Cd(01)–S(003)	2.6081(9)
Cd(01)–S(004)	2.5784(9)
Cd(01)-S(005)	2.5723(9)
Bond angles (°)	
S(002)-Cd(01)-S(002)	89.28(3)
S(003)-Cd(01)-S(002)	109.73(3)
S(004)-Cd(01)-S(002)	105.77(3)
S(004)-Cd(01)-S(003)	70.28(3)
3	
Bond lengths (Å)	
Cd(1)–S(1)	2.5515(7)
Cd(1)–S(2)	2.6036(7)
Cd(1)–S(3)	2.5566(6)
Cd(1)–S(4)	2.5999(6)
Bond angles (°)	
S(1)-Cd(1)-S(3)	145.32(2)
S(1)-Cd(1)-S(4)	103.443(19)
S(2)-Cd(1)-S(4)	160.16(2)
S(3)-Cd(1)-S(2)	105.79(2)
S(4)-Cd(1)-S(2)	110.23(2)

Table 4 Table for selected bond lengths and bond angle of complexes1-3

Cd(1)–S(41),Cd(1)–S(11) is 2.549(2)Å and the bond lengths of S(13)–Cd(1), S(43)–Cd(1) are 2.7524 Å and 2.8265(13) Å, respectively, confirming that S(13), S(43) are *S*,*S*-chelating-bridging as well as *S*,*S*-chelating fashion. The bite angle S(43)–Cd(1)–(13) is 87.09°, while the angle S(41)–Cd(1)–S(13) is 98.85°. The N44–C42 and N14–C12 bond lengths are 1.340 and 1.335 Å, respectively. These values are midway between C–N (1.47 Å) and C=N (1.28 Å) indicating the partial double bond character in the N–C bond of the ligand.

Complex 1 is stabilized by several non-covalent interactions in which C–H^{...}F interaction form a six member ring having F(58)–H21(B) and F(58)–H(23) bond lengths are 2.288 and 2.530, respectively (Fig. 5), and the bond length of F(28)–H(56) is 2.486 Å. In C–H^{...}S interaction the H^{...}S distance is 2.579 Å and C–H^{...}S angle is 111.05°.

The dimeric form of complex **2** crystallizes in triclinic crystal lattice with space group P-1. In this complex Cd^{2+} are in square pyramidal environments in whichS(002) atoms are bridging with two Cd atoms. The bond length between Cd(01)–S(003) and Cd(01)–S(005) are 2.608 Å 2.572 Å, respectively (Figs. 6, 7, 8, 9).

The bond lengths of S(002)–Cd(01) is 2.787 Å confirming that S(002) is bonding with Cd(01) in *S*,*S*-chelating-bridging as well as *S*,*S*-chelating manner. The bite angle S(002)–Cd(01)–S(002) is 89.28°, while the angle Cd(01)–S(002)–Cd(01) is 90.72°. The N(00B)–C(00D) and N(00A)–C(00C) bond lengths are 1.332 and 1.337 Å indicating the partial double bond character in the N–C bond of the ligand. In complex **2** C–H···S, C–H···π, π ···π and S···S non-covalent interactions are observed in which C–H···S interactions having C–H···S interaction distance of 2.918 Å and angle of 92.19° (Figs. 10, 11, 12, 13).

The complex **3** crystallizes in triclinic with space group P-1. In this complex Cd^{2+} are in square pyramidal environmentsabout the metal centre in which S(4) atoms are bridging with two Cd atoms. The bond length of Cd(1)–S(4) 2.7867(6)Å is longer than other Cd–S bond length. The C–H··· π interaction in this complex having bond length 3.334 Å and the length between H(9A)–H(9B) is 2.287 Å (Figs. 14, 15).

3.6.Thermogravimetric analysis of complexes 1–3

Thermal decompositions of complexes have been investigated in temperature range 30–800 °C with a flow rate of 10.00 °C/min under N₂ atmosphere. The TGA graph shows that all complexes begin to loss their weight in two steps [35–39]. In first step all the dithiocarbamate complexes loss their weight around 100 °C which corresponds to the loss of water molecule present within the crystal lattice. The second weight loss starts at around 270 °C and leads to the formation of CdS phases around 620 °C. In complexes 1 the higher residual weights were obtained, which indicate the higher percentage of oxygen and sulfur giving in decomposition products. These products probably containing mixed metal oxide-sulphides and CdS residue [40–43] (Fig. 16).

Conclusion

We have successfully synthesized homoleptic Cd(II) complexes based on [(KL1 = $C_{15}H_{13}N_1F_1S_2$ (*N*-ethyl-*N*-4-flourobenzyl dithiocarbamate); KL2 = $C_{13}H_{11}N_1F_1S_2$ (*N*-4-flourobenzyl-*N*-thiophene dithiocarbamate); KL3 = $C_{11}H_{14}N_1O_{12}$ (*N*-ethyl-*N*-4-methoxybenzyl





Fig. 4 Polymeric structure of complex 1

dithiocarbamate)] ligands. Complex 1 crystallises in Orthorhombic with space group *P*na21 and holding dimeric structure. In this complex Cd²⁺ having distorted octahedral geometry about the metal centre forms 1D coordination polymeric structures. The dimeric form of complex 2 and 3 crystallizes in triclinic crystal lattice with space group P-1. The TGA analysis of the complexes begin to loss their weight in two steps leads to the formation of CdS phases around 620 °C. In complexes 1 the higher residual weights probably containing mixed metal oxide-sulphides and CdS residue.



Fig. 6 C–H^{...}F interaction of complex **1**

Fig. 7 C–H^{...}S and C–H^{...} π interaction of complex 1



Fig. 8 Flower like structure of complex 1





Fig. 12 $\pi^{...}\pi$ interaction in complex 2

Fig. 9 Crystal structure of complex 2



Fig. 10 C–H^{...}S interaction of complex 2



Fig. 13 S^{...}S interaction in complex 2





Fig. 14 C–H^{...} π interaction of complex 3

Fig. 11 C–H^{...} π chelate in complex 2



Fig. 15 C-H^{...}S and H^{...}H interaction of complex 3



Fig. 16 TGA plot of complexes

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