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Synthesis, spectral, electrochemical, thermal and biological studies of benzyl/tolylxanthates of cadmium(II)

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Abstract : New dithiocarbonates of cadmium(II) corresponding to $[(ArOCS_2)_2Cd]$, $[(ArOCS_2)M\{S_2\overline{POCH_2C(CH_3)_2CH_2O}\}]$ and $[(ArOCS_2)_2Cd.nL]$ (Ar = *o*-, *m*-, *p*-$CH_3C_6H_4/C_6H_5CH_2$), L = $N_2C_{12}H_8$, $N_2C_{10}H_8$; *n* = 2, L = NC_5H_5, $P(C_6H_5)_3$ have been isolated by the reaction of sodium salt of dithiocarbonates with cadmium dichloride in 1 : 2 molar ratio, mixed ligand complex in 1 : 1 : 1 molar ratio by the reaction of dithiocarbonate, alkylene dithiophosphate and metal salt in aqueous medium and their adducts with phosphorous and nitrogen donor ligand in 1 : 1 and 1 : 2 molar ratio. These complexes have been characterized by elemental analyses, mass, IR and heteronuclear NMR (^1H, ^{31}P and ^{13}C) spectroscopic analysis. Thermal and redox properties of complexes were studied by thermogravimetric analysis and cyclic voltammetry. These studies confirm that in the nitrogen and phosphorous donor complexes the geometry around the cadmium metal centre is distorted octahedral, and in the parent cadmium dithiocarbonate complex it is distorted tetrahedral. The dithiocarbonate ligands and some selected complexes were screened against *Fusarium oxysporum* shows that the free ligands reveal significantly less activity compared to the corresponding cadmium complexes.

Keywords : Xanthate, dithiocarbonate, alkali metal, cyclic voltammetry, antimicrobial, tolyl, thermogravimetrical analysis, spectroscopy.

Introduction

Alkyldithiocarbonates have engrossed ample consideration in academia particular for providing various bonding aspects with metals and metalloids[1–7]. Various bonding modes of these ligands with several metals have been established in which these behaved as monodentate[8,9], bidentate[10] and chelating ligands[11,12]. These are known to form chelate complexes with virtually all the transition elements and have proved to be a versatile chelating agents for the separation and extraction of metals in the analytical chemistry and mineral floating[13,14]. Subsequently, transition metal dithiolate complexes exhibited a rich and interesting chemistry that has been studied extensively. It is relevant to mention that these dithiocarbonato derivatives have attracted increasing attention owing to their versatile applications as vulcanizers[15,16], pesticides[17], fungicides[18], flotation reagents in metallurgy[19,20], corrosion inhibitors[21], agricultural reagents[22–24] and recently in treatment of various infections[25–28] have been described in literature. The alkyldithiocarbonate chemistry of the cadmium is well developed and as expected, their chemistry is constrained to the +2 oxidation state. The ease and stability of the complexation reaction is on the fact that cadmium act as strong Lewis acids and hence readily complex to electron-rich sulfur containing ligands in the principle of Hard Soft [Lewis] Acid Base, HSAB[29]. These complexes have been found to be good air-stable precursors for CdS nanocrystals used as semiconductors, have been the focus of considerable attention because of the ability to fine-tune their electronic and optical properties for possible applications[30]. Although, in recent years, owing to toxicity of cadmium and the introduction of regulations the use of cadmium has declined. Cadmium and its compounds are a substan-

tial industrial and environmental pollutant[31] which seriously impairs erythropoiesis. Cadmium accumulates in humans throughout their lives[32], with a negative effect on human beings and also to soil micro-organisms[33–36]. The development of the efficient antidotes for cadmium intoxication has proven to be a task of considerable difficulty. The affinity of 1,1-dithiolate ligands for cadmium was indicated by the fact that the ligands can be employed as scavengers for this toxic element in biological media. Compared to the well developed chemistry of alkyldithiocarbonate derivatives of the main group and transition metals, much less attention has been paid to aryl derivatives of cadmium. A literature survey revealed wide range of literature allied to alkyldithiocarbonates but no such report or patent is available on tolyl/benzyl-dithiocarbonates derivatives with cadmium. The versatile bonding, structural features and fascinating chemical as well as electrochemical reactivity of cadmium alkyldithiocarbonate complexes prompted us to make a systematic study of cadmium tolyl/benzyldithiocarbonates and continuing our studies[37–41]. It was thought worthy to synthesize and characterize new complexes of cadmium and also to find out the comparative study of biological activity of dithiocarbonate ligand and its cadmium complexes.

Experimental

Materials and methods :

Solvents were distilled and dried over sodium before use. Chloroform (Thomas Baker) was dried over P_2O_5. $CdCl_2$ (Merck) was used as received. Sodium salts of tolyl/benzyl dithiocarbonates were synthesized according to a literature procedure[37]. Moisture was carefully excluded during the experimental manipulations for the synthesis of ligands by using standard Schlenk techniques. Cadmium was estimated gravimetrically as $[Cd(C_5H_5N)_2](SCN)_2$ and sulphur by Messenger's method[42]. Elemental analyses (C, H, N, S) were conducted using the Elemental Analyser Vario EL-III and Mass spectra of the compounds were recorded on ESQUIRE3000_00037 spectrophotometer. Infrared spectra were recorded from 4000 to 200 cm^{-1} on a Perkin-Elmer spectrum RX1 FT-IR spectrophotometer. ^1H, ^{13}C and ^{31}P (proton-decoupled) NMR spectra were recorded in $CDCl_3$ and DMSO-d_6 using TMS as internal reference and H_3PO_4 (85%) as external reference on a Bruker Avance III 400 MHz. All chemical shifts are reported in δ units downfield from TMS. The thermogram was analyzed by using Perkin-Elmer, diamond TG/DTA instrument. The thermogram was recorded in the temperature range from 30 °C to 1000 °C under nitrogen atmosphere. The cyclic voltammograms were recorded on Autolab (Metrohm). The potential is applied between the reference electrode (Ag/AgCl) and the working electrode (Gold electrode) and the current is measured between the working electrode and the counter electrode (Platinum wire). 0.1 *M* Phosphate buffer solution (pH 7.0) was used. The antifungal activity was tested under laboratory condition using classical poison food technique method.

Synthesis of $[(o\text{-}CH_3C_6H_4OCS_2)_2Cd]$ (**1**) :

To a solution of cadmium(II) chloride (0.44 g, 2.42 mmol) was added a solution of sodium salt of *o*-tolyldithiocarbonate (1.00 g, 4.84 mmol) in 20 mL distilled water was added dropwise with constant stirring at room temperature. A white precipitate was formed immediately and the mixture was stirred for further 30 min. The precipitated white complex was filtered off by G-4 sintered funnel. The precipitates were washed first with water followed by petroleum ether three times followed by drying under *in vacuo* over P_2O_5, which yielded the complex (**1**) as white solid in 82% (0.68 g) yield.

Synthesis of $[(o\text{-}CH_3C_6H_4OCS_2)Cd\text{-}\{S_2POCH_2C(CH_3)_2CH_2O\}]$ (**5**) :

To an aqueous solution (~20 mL) of sodium salt of *o*-tolyldithiocarbonate (1.00 g, 4.84 mmol) was added aqueous solution of neopentylene ligand (1.06 g, 4.84 mmol). Now an aqueous solution of cadmium chloride (0.88 g, 4.84 mmol) was added to this mixture with constant at room temperature. Formation of white precipitates was observed immediately. The precipitated white complex was filtered off by G-4 sintered funnel. The precipitates were washed first with water followed by petroleum ether three times followed by drying under *in vacuo* over P_2O_5, which yielded the desired product **5** as pale yellow solid in 69% (1.65 g) yield.

Synthesis of [(o-$CH_3C_6H_4OCS_2)_2Cd.2NC_5H_5$] (**9**) :

To a chloroform solution of [(*o*-$CH_3C_6H_4OCS_2)_2Cd$] **(1)** (0.50 g, 1.04 mmol), chloroform solution of pyridine (0.16 g, 2.08 mmol) was added dropwise with constant stirring at room temperature. Colorless solution changes to pale yellow within 15 min. The contents were stirred for a further 30 min at room temperature. The solvent was then evaporated under vacuum, which results in **9** as yellow solid in 82% (0.74 g) yield.

Synthesis of [(o-$CH_3C_6H_4OCS_2)_2Cd.2P(C_6H_5)_3$] (**21**) :

To a methanolic solution (30 mL) of 0.50 g of [(*o*-$CH_3C_6H_4OCS_2]_2Cd$] **(1)** (1.04 mmol) was added dropwise to a methanolic solution (30 mL) of 0.55 g of triphenylphosphine (2.08 mmol) was added with constant stirring at room temperature. The reaction mixture was stirred for 1 h. The solvent was evaporated *in vacuo*, which resulted in the formation of the complex [(*o*-$CH_3C_6H_4OCS_2]_2Cd.2P(C_6H_5)_3$] **(21)** as white solid in 87% (0.94 g) yield.

The compounds **2-4**, **6-8**, **10-20** and **21-24** reported herein were synthesized by using similar methodology and required stoichiometric weights as per the compounds **1, 5, 9** and **20**, respectively. The relevant synthetic and analytical data are given in Table 1.

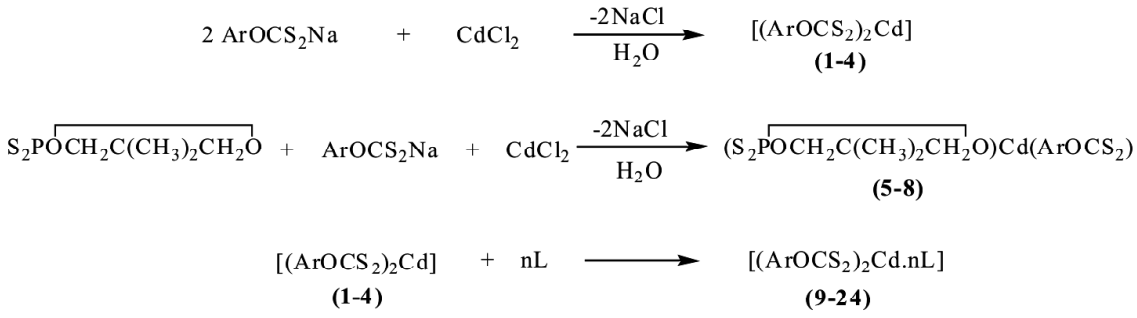
Antifungal activity :

The antifungal activities of the complexes were evaluated by the poisoned food technique against pathogenic strain of fungus *Fusarium oxysporium*[43]. Potato dextrose medium (PDA) was prepared in a flask and sterilized; 100 mm of each sample was added to the PDA medium and poured into each sterilized petri plate. Mycelial discs taken from the standard culture (*Fusarium oxysporum)* of fungi were grown on PDA medium for 7 days. These cultures were used for aseptic inoculation in the sterilized petri dish. Standard cultures, inoculated at 28 ± 1 °C, were used as the control. The efficacy of each sample was determined by measuring the radial fungal growth. The radial growth of the colony was measured in two directions at right angles to each other, and the average of two replicates was recorded in each case. Data were expressed as percent inhibition over the control from the size of the colonies. The percent inhibition was calculated using the formula % Inhibition = $[(C - T)/C]\times100$, where C is the diameter of the fungus colony in the control plate after 96 h incubation and T is the diameter of the fungus colony in the tested plate after the same incubation period. Both antifungal activities were tested in the Bio-assay Laboratory, Department of Chemistry, University of Jammu, Jammu.

Results and discussion

Bis-(*o-, m-, p*-tolyl)/dibenzyldithiocarbonates of cadmium(II) **(1-4)** were prepared as white solids in fairly good yield by reaction of cadmium chloride with sodium (*o-, m-, p*-tolyl)/benzyldithiocarbonates in 1 : 2 molar ratio in aqueous medium. Mixed ligand complexes of cadmium were synthesized as white solids by the reaction of sodium tolyl/benzyldithiocarbonate and sodium *O,O′*-neopentylenephosphorodithionate with cadmium chloride in 1 : 1 : 1 molar ratio in aqueous medium yielded tetrameric entities [$(ArOCS_2)Cd(\overline{POGO})$] **(5-8)**. The compounds **1-4** were reacted with the nitrogen and phosphorous donor ligands, like triphenylphosphine, pyridine, 2,2′-bipyridine and 1,10-phenanthroline, in methanol in appropriate stoichiometric. These reactions were quite facile and yielded hexacoordinated monomeric entities [$(ArOCS_2)_2Cd.nL$] and Ar = *o-, m-, p*-$CH_3C_6H_4$ and $C_6H_5CH_2$; L = $C_{10}H_8N_2$, $C_{12}H_8N_2$ for n = 1 and $P(C_6H_5)_3$, C_5H_5N for n = 2. Adducts with pyridine **(9-12)** were yellow solids while adducts with triphenylphosphine **(21-24)** were white solids, 2,2′-bipyridine **(13-16)**, and 1,10-phenanthroline **(17-20)** were obtained as pale yellow solids respectively.

These are soluble in common organic solvents like benzene, toluene, chloroform, acetone and also in coordinating solvents like DMSO and DMF but sparingly soluble in the non-polar organic solvents viz. carbon tetrachloride and *n*-hexane. These non-volatile complexes, however, can be kept unchanged under anhydrous atmosphere. The compounds obtained were sufficiently pure but these were further washed with distilled water followed by petroleum ether three times for the sake of extra purity. The elemental analyses (C, H, N, S, and Cd) were found consistent with the molecular formulae of the complexes (Scheme 1).



Scheme 1

IR :

IR spectral assignment of the complexes **1**-**24** is done on the basis of relevant literature reports[38–39, 44–50]. The comparison of IR spectra of these complexes with starting materials has also shown seminal information. Dithiocarbonates can be easily detected by the presence of three main regions of concern : one is associated with the stretching of C-O-C of $ROCS_2$ (1250–1200 cm^{-1}); second is associated with stretching of S-C-S of CS_2 (1050–950 cm^{-1}) which is found to be reliable for determining the chelating mode of the ligand and last one linked with Cd-S i.e. metal sulphur stretching (420–250 cm^{-1}). Bonati *et al.*[45] authenticate that presence of only one strong bond in the 1044–1019 cm^{-1} region, which is associated with ν(C=S) stretching vibrations, indicates complete symmetric bidentate bonding by dithiocarbonate ligand. Thus in complexes **(1**-**4)**, the sharp bands were observed in the range 1040–1022 cm^{-1} indicates the bidentate mode of bonding by the dithiocarbonate ligand to the cadmium metal centre. The strong bands of the ν(C-O-C) asymmetric stretching for bidentate coordinated dithiocarbonate ligands appear at 1250–1218 cm^{-1}. The broad band for ν(C=C) (tolyl and benzyl ring stretching) were presented in the range 1613–1591 cm^{-1}. In the far region, an additional new band of weak to medium intensity (absent in the spectra of ligands) was observed in the region 356–335 cm^{-1} for dithiocarbonate complexes **(1**-**4)** which is ascribed to ν(Cd-S) stretching vibration. The appearance of new band for ν(Cd-S) indicates the coordination of the dithiocarbonate ligand with the metal as expected. In case of mixed ligand complexes appearance of two new bands in the region 629–621 and 551–540 cm^{-1} ascribed to $\nu(P\text{-}S)_{asym}$ and $\nu(P\text{-}S)_{sym}$, respectively and two strong intensity bands were observed in the region 949–935 and 841–834 cm^{-1}, which may be ascribed to the ν(P)-O-C and νP-O-(C) vibrations of the alkylene dithiophosphate moiety, respectively. The shift of νP-S and νC=S vibrations compared to the parent ligands is due to the bidentate mode of bonding by the dithio ligands with metal. This supports the coordination of dithiophosphate ligand with the metal centre **(5**-**8)**. The comparison of IR data of the complexes and donor stabilised complexes with preliminary materials has shown some significant and characteristic changes like shifting of bands i.e. Cd-S vibrations are shift towards higher frequency, a small shift to lower frequency of C-S vibrations and surprisingly comparatively large shift to lower frequency of the C-O-C vibrations. All these changes resulted because of change of coordination number from four to six[51,52] and due to decrease in electron flow in consonance with increase in electron charge donated by donor ligands like pyridine, triphenylphosphine, 1,10-phenanthroline and 2,2′-bipyridyl. The IR spectra of these compounds showed all the bands observed in the parent metal(II)-bis(dithiocarbonate) moiety (**1**-**4**) and bands characteristic of the donor ligands like pyridine (**9**-**12**), triphenylphosphine (**13**-**16**), 1,10-phenanthroline (**17**-**20**) and 2,2′-bipyridyl **(20**-**24)**. Infra red spectrum of free pyridine, 2,2′-bipyridyl and 1,10-phenanthroline have shown bands at 1620–1510, 1615–1502 cm^{-1} and at 1595–1500 cm^{-1} due to interactions between

Table 1. Synthetic and analytical data of Cd^{II} dithiocarbonates

Sr. No.	Reactants g (mmol) [*$ArOS_2Na$]/$CdCl_2$ [*$ArOS_2]_2Cd$/L′		A	Molar ratio	Product (Physical state)	M.W. Found (Calcd.)	Yield (%)	M.p. (°C) (Dec.)	Analyses (%) : Found (Calcd.) C	H	M	S	N
1	1.00	0.44	–	2 : 1	[(*o*-$CH_3C_6H_4OCS_2)_2Cd$]	478.83	82	180	40.11	2.56	23.30	26.55	–
	(4.84)	(2.42)			(White solid)	(478.95)			(40.12)	(2.95)	(23.47)	(26.78)	
2	1.00	0.44	–	2 : 1	[(*m*-$CH_3C_6H_4OCS_2)_2Cd$]	478.78	76	182	40.09	2.36	23.37	26.46	–
	(4.84)	(2.42)			(White solid)	(478.95)			(40.12)	(2.95)	(23.47)	(26.78)	
3	1.00	0.44	–	2 : 1	[(*p*-$CH_3C_6H_4OCS_2)_2Cd$]	478.82	79	179	40.06	2.62	23.39	26.56	–
	(4.84)	(2.42)			(White solid)	(478.95)			(40.12)	(2.95)	(23.47)	(26.78)	
4	1.00	0.44	–	2 : 1	[($C_6H_5CH_2OCS_2)_2Cd$]	478.81	84	182	40.01	2.46	23.45	26.65	–
	(4.84)	(2.42)			(White solid)	(478.95)			(40.12)	(2.95)	(23.47)	(26.78)	
5	1.00	0.88	1.06	1 : 1 : 1	[(*o*-$ArOCS_2$)Cd(S_2POGO)]	493.82	69	179	31.62	3.35	22.67	25.99	–
	(4.84)	(4.84)	(4.84)		(Pale yellow solid)	(493.88)			(31.68)	(3.48)	(22.81)	(26.02)	
6	1.00	0.88	1.06	1 : 1 : 1	[(*m*-$ArOCS_2$)Cd(S_2POGO)]	493.83	71	177	31.60	3.45	22.77	25.94	–
	(4.84)	(4.84)	(4.84)		(Pale yellow solid)	(493.88)			(31.68)	(3.48)	(22.81)	(26.02)	
7	1.00	0.88	1.06	1 : 1 : 1	[(*p*-$ArOCS_2$)Cd(S_2POGO)]	493.80	70	179	31.62	3.35	22.67	25.99	–
	(4.84)	(4.84)	(4.84)		(Pale yellow solid)	(493.88)			(31.68)	(3.48)	(22.81)	(26.02)	
8	1.00	0.88	1.06	1 : 1 : 1	[($C_6H_5CH_2OCS_2$)Cd(S_2POGO)]	493.79	72	174	31.65	3.45	22.70	25.90	–
	(4.84)	(4.84)	(4.84)		(Pale yellow solid)	(493.88)			(31.68)	(3.48)	(22.81)	(26.02)	
9	0.50	0.16)	–	1 : 2	[(*o*-$CH_3C_6H_4OCS_2)_2Cd$.2py]	665.14	82	180	46.75	3.61	16.59	19.20	8.40
	(1.04)	(2.08)			(Yellow solid)	(665.16)			(46.95)	(3.64)	(16.90)	(19.28)	(8.42)
10	0.50	0.16	–	1 : 2	[(*m*-$CH_3C_6H_4OCS_2)_2Cd$.2py]	665.12	87	179	46.65	3.60	16.62	19.10	8.30
	(1.04)	(2.08)			(Yellow solid)	(665.16)			(46.95)	(3.64)	(16.90)	(19.28)	(8.42)
11	0.50	0.16	–	1 : 2	[(*p*-$CH_3C_6H_4OCS_2)_2Cd$.2py]	665.11	80	167	46.69	3.59	16.69	19.25	8.39
	(1.04)	(2.08)			(Yellow solid)	(665.16)			(46.95)	(3.64)	(16.90)	(19.28)	(8.42)
12	0.50	0.16	–	1 : 2	[($C_6H_5CH_2OCS_2)_2Cd$.2py]	665.14	82	178	46.70	3.58	16.58	19.19	8.39
	(1.04)	(2.08)			(Yellow solid)	(665.16)			(46.95)	(3.64)	(16.90)	(19.28)	(8.42)
13	0.50	0.16	–	1 : 1	[(*o*-$CH_3C_6H_4OCS_2)_2Cd$.bipy]	635.10	79	189	49.10	3.40	17.69	20.17	4.39
	(1.02)	(1.02)			(Yellow solid)	(635.13)			(49.17)	(3.49)	(17.70)	(20.19)	(4.41)
14	0.50	0.16	–	1 : 1	[(*m*-$CH_3C_6H_4OCS_2)_2Cd$.bipy]	635.10	77	186	49.10	3.40	17.66	20.12	4.37
	(1.02)	(1.02)			(Yellow solid)	(635.13)			(49.17)	(3.49)	(17.70)	(20.19)	(4.41)
15	0.50	0.16	–	1 : 1	[(*p*-$CH_3C_6H_4OCS_2)_2Cd$.bipy]	635.10	80	187	49.11	3.44	17.68	20.16	4.36
	(1.02)	(1.02)			(Yellow solid)	(635.13)			(49.17)	(3.49)	(17.70)	(20.19)	(4.41)

Table 1 (contd.)

16	0.50	0.16	–	1 : 1	$[(C_6H_5CH_2OCS_2)_2Cd.bipy]$	635.10	78	188	49.12	3.42	17.62	20.15	4.40
	(1.02)	(1.02)			(Yellow solid)	(635.13)			(49.17)	(3.49)	(17.70)	(20.19)	(4.41)
17	0.50	0.22	–	1 : 1	$[(o\text{-}CH_3C_6H_4OCS_2)_2Cd.phen]$	661.14	85	184	50.80	3.62	16.99	19.31	4.20
	(1.15)	(1.15)			(Yellow solid)	(661.17)			(50.86)	(3.66)	(17.00)	(19.40)	(4.24)
18	0.50	0.22	–	1 : 1	$[(m\text{-}CH_3C_6H_4OCS_2)_2Cd.phen]$	661.15	80	179	50.82	3.61	16.98	19.32	4.21
	(1.15)	(1.15)			(Yellow solid)	(661.17)			(50.86)	(3.66)	(17.00)	(19.40)	(4.24)
19	0.50	0.22	–	1 : 1	$[(p\text{-}CH_3C_6H_4OCS_2)_2Cd.phen]$	661.10	81	180	50.80	3.62	16.95	19.29	4.19
	(1.15)	(1.15)			(Yellow solid)	(661.17)			(50.86)	(3.66)	(17.00)	(19.40)	(4.24)
20	0.50	0.22	–	1 : 1	$[(C_6H_5CH_2OCS_2)_2Cd.phen]$	661.13	86	181	50.85	3.62	16.99	19.30	4.21
	(1.15)	(1.15)			(Yellow solid)	(661.17)			(50.86)	(3.66)	(17.00)	(19.40)	(4.24)
21	0.50	0.55	–	1 : 2	$[(o\text{-}CH_3C_6H_4OCS_2)_2Cd.2PPh_3]$	1009.50	87	189	61.82	4.70	11.09	12.40	–
	(1.04)	(2.08)			(White solid)	(1009.57)			(61.86)	(4.99)	(11.13)	(12.70)	
22	0.50	0.55	–	1 : 2	$[(m\text{-}CH_3C_6H_4OCS_2)_2Cd.2PPh_3]$	1009.53	89	190	61.82	4.71	11.11	12.41	–
	(1.04)	(2.08)			(White solid)	(1009.57)			(61.86)	(4.99)	(11.13)	(12.70)	
23	0.50	0.55	–	1 : 2	$[(p\text{-}CH_3C_6H_4OCS_2)_2Cd.2PPh_3]$	1009.49	82	191	61.81	4.69	11.08	12.48	–
	(1.04)	(2.08)			(White solid)	(1009.57)			(61.86)	(4.99)	(11.13)	(12.70)	
24	0.50	0.55	–	1 : 2	$[(C_6H_5CH_2OCS_2)_2Cd.2PPh_3]$	1009.51	86	192	61.80	4.71	11.10	12.46	–
	(1.04)	(2.08)			(White solid)	(1009.57)			(61.86)	(4.99)	(11.13)	(12.70)	

where, *Ar = (*o*-, *m*- and *p*-$CH_3C_6H_4$-) and $C_6H_5CH_2$-; G = $CH_2C(CH_3)_2CH_2$; A = OGOPS$_2$Na; L′ = py (**9**-**12**), bipy (**13**-**16**), 1-10-phen (**17**-**20**), PPh_3 (**21**-**24**); Sr. No. **1**-**8** = $CdCl_2$, **9**-**24** = L′.

ν(C=C) and ν(C=N) symmetric ring stretching and in-plane antisymmetric ring vibrations. These bands are found to be separated about 100 cm^{-1} apart[45,46]. The characteristic ν(C=C) aromatic stretching bands were observed in the range 1597–1591 cm^{-1} for the complexes (**9**-**20**). The band for ν(C=N) in the range 1451–1440 cm^{-1} for complexes (**9**-**12**), 1452–1440 cm^{-1} for complexes (**13**-**16**) and 1452–1441 cm^{-1} for complexes (**17**-**20**) due to the coordinated donor ligands like pyridine, 2,2′-bipyridyl and 1,10-phenanthroline depict a shift toward lower frequencies. Similar is the case observed for triphenylphosphine moiety where assignment of strong band due to ν(P-C) stretching vibrations in the region 1432–1415 cm^{-1} in the derivatives (**20**-**24**) thus indicates the presence of triphenylphosphine as the coordinated ligand. These observations and kinds of negative shifts are suggestive of binding of donor ligands like pyridine, bipyridyl, phenanthroline and triphenylphosphine to the central metal ion. This shift occurs due to maintenance of a ring current arising out of π-electron delocalization in the chelate formation i.e. upon coordination. This confirms the involvement of nitrogen and phosphorous atom of donor ligands in the metal centre[45–52]. The presence of direct bond of donor ligands to metal via the nitrogen atom in complexes (**9**-**20**) and phosphorous atom in complexes (**20**-**24**) can be supported by the existence of band at 752–740 cm^{-1} and 555–525 cm^{-1} which may be assigned to ν(Cd-N) and ν(Cd-P) vibrations respectively. The medium intensity bands in the range of 353–335 cm^{-1} are typically assigned to the ν(Cd-S) vibrations in all the complexes. The strong intensity bands that were present in the region 1239–1230 cm^{-1} were assigned to ν(C-O-C) stretching vibrations. Sharp bands due to ν(C=S) in the range 1044–1019 cm^{-1} without any shoulder confirms the bidentate chelation of dithiocarbonate ligands with the cadmium in complexes (**1**-**24**). The ν(CS_2) stretching vibrations appeared at 1145–1140 cm^{-1} and 1008–1002 cm^{-1} in the parent dithiocarbonate ligand is replaced by a strong intensity band which remains unsplitted in all the cases. This shifting and arising of single sharp band due to ν(CS_2) vibrations in the complexes are quite diagnostic to propose isobidentate mode of bonding of the dithio moiety with cadmium as the appearance of only one band without any splitting in the same region is attributed to the bidentate mode of binding of the dithiocarbonate ligand[38–40]. The νC-H vibrations (due to tolyl and benzyl ring) were observed in their characteristic region. The IR spectral values are given in Table 2.

^1H NMR :

The ^1H NMR spectra of these complexes show the characteristic proton resonances of the corresponding tolyl and benzyl protons. The chemical shift for the methyl protons of the tolyldithiocarbonate moiety in the complexes **1**-**3** appeared as singlet at 2.18–2.32 ppm where as the methylene protons of the benzyldithiocarbonato moiety in the complexes **4** resonated at 4.47 ppm as singlet. The protons of the C_6H_4 (tolyl ring) and C_6H_5 (benzyl ring) gave signals in the range 6.73–7.14 and 7.12–7.24 ppm with their usual splitting pattern. There is a negligible upfield shift of *ca.* 0.03–0.20 ppm as compared with their position in the free ligand, presumably, as a consequence of coordination. There were two resonances for the ring protons of *para* complexes whereas four resonances were observed for *ortho* and *meta* derivatives. The splitting pattern and intensities of peaks in the spectra of all these complexes are found to be consistent with their structures. The chemical shift for the protons of the -CH_3 attached to the neopentylene moiety was observed at 0.90–1.12 ppm as a singlet and protons of -OCH_2 appear at 3.21–3.45 ppm as a singlet. The values of the chemical shifts are found to be in similar range to those of the ligands from which these were prepared. Hence, there is no significant changes were observed as a result of being linked to cadmium. The chemical shifts for the tolyl and benzyl ring protons in these complexes were observed in the region 6.52–7.14 and 7.09–7.34 ppm, respectively with their usual splitting pattern. The aryl protons of the free heteroaromatic nitrogen and phosphorous donor bases viz. pyridine, triphenylphosphine, 1,10-phenanthroline and 2,2′-bipyridyl exhibited signals with different multiplicities because of the aromatic methyne -CH= protons. For pyridine, three signals were observed at 8.59, 7.38 and 7.75 ppm as doublet, triplet and triplet for proton at position (2′,6′), (3′,5′) and (4′), respectively and for triphenylphosphine moiety multiplet was observed in the region 7.19–7.34 ppm for protons (2′-6′) of the

Table 2. IR spectral data of cadmium(II) dithiocarbonates complexes (in cm^{-1})

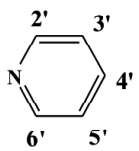
#Sr. No.	ν(C-O-C)	ν(C=S)	ν(C-C)	ν(M-S)	ν(P)-O-C	νP-O-(C)	νP=S	νP-S	ν(N-C)	ν(P-C)	ν(M-N)	ν(M-P)
1	1238s	1032s	1597b	351m	–	–	–	–	–	–	–	–
2	1239s	1040s	1594b	347m	–	–	–	–	–	–	–	–
3	1247s	1038s	1613b	356m	–	–	–	–	–	–	–	–
4	1250s	1022s	1596b	340m	–	–	–	–	–	–	–	–
5	1238s	1038s	1596s	349m	935s	834s	621s	549m	–	–	–	–
6	1224s	1044s	1594s	356m	937s	837s	629s	551m	–	–	–	–
7	1218s	1042s	1595s	344m	946s	839s	624s	545m	–	–	–	–
8	1241s	1038s	1592s	341m	949s	841s	623s	540m	–	–	–	–
9	1234s	1030s	1592b	353m	–	–	–	–	1447s	–	750m	–
10	1232s	1036s	1591b	348m	–	–	–	–	1450s	–	749m	–
11	1234s	1033s	1596b	352m	–	–	–	–	1451s	–	752m	–
12	1230s	1020s	1591b	343m	–	–	–	–	1450s	–	747m	–
13	1231s	1031s	1593b	352m	–	–	–	–	1449s	–	740m	–
14	1232s	1035s	1594b	350m	–	–	–	–	1441s	–	742m	–
15	1230s	1034s	1595b	349m	–	–	–	–	1452s	–	749m	–
16	1229s	1021s	1591b	340m	–	–	–	–	1450s	–	741m	–
17	1236s	1031s	1593b	350m	–	–	–	–	1442s	–	750m	–
18	1233s	1035s	1597b	345m	–	–	–	–	1452s	–	749m	–
19	1236s	1034s	1592b	350m	–	–	–	–	1440s	–	750m	–
20	1238s	1021s	1594b	340m	–	–	–	–	1451s	–	748m	–
21	1230s	1023s	1591b	350m	–	–	–	–	–	1415s	–	555m
22	1231s	1030s	1592b	347m	–	–	–	–	–	1432s	–	536m
23	1239s	1030s	1595b	349m	–	–	–	–	–	1431s	–	525m
24	1230s	1019s	1593b	335m	–	–	–	–	–	1423s	–	539m

Where, s = sharp, b = broad, m = medium, w = weak.

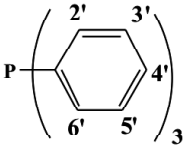
#Sr. No. of the complexes is according to Table 1.

aromatic ring. Similar case was observed for 1,10-phenanthroline and 2,2′-bipyridyl moieties. Where four signals were observed for 1,10-phenanthroline at 8.81 ppm (2′,9′ proton, doublet), 7.26 ppm (3′,8′ proton, triplet), 8.00 ppm (4′,7′ proton, doublet) and 7.52 ppm (5′,6′ proton, triplet). For 2,2′-bipyridyl these signals were indicative of 6,6′ proton as doublet at 8.59 ppm, 3,3′ proton as doublet at 8.14 ppm, 4,4′ proton as triplet at 7.66 ppm and 5,5′ proton as triplet at 7.12 ppm.

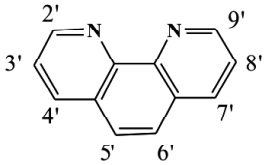
The mixed ligand complexes of cadmium of present investigation show very little downfield shift of signals due to the diamagnetic character of this metal ions. The protons 2′ and 6′ of pyridine and triphenylphosphine, 2′ and 9′ of 1,10-phenanthroline and 6 and 6′ of 2,2′-bipyridyl exhibit maximum shift (0.30–0.41 ppm) to lower field due to deshielding and hence gave their characteristic chemical shift in the range 7.18–7.50, 7.20–7.64, 7.41–7.65 and 7.14–7.36 ppm. This deshielding of protons thus indicates the



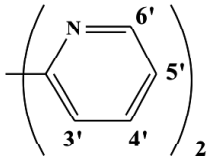
pyridine



Triphenylphosphine



1,10-Phenanthroline



2,2′-Bipyridyl

Table 3. ^{1}H NMR and ^{31}P NMR spectral data of cadmium(II) dithiocarbonates complexes in $CDCl_3$ (in ppm)

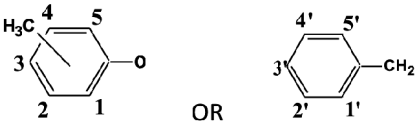
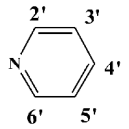
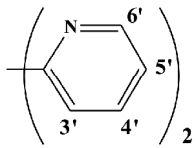
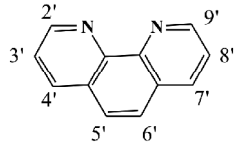
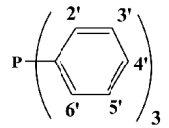
Sr. No.	Tolyl/Benzyl moiety		Neopentylene moiety		Donor moiety	^{31}P NMR
	-CH_3/ -CH_2	 OR	-CH_3	–OCH_2		
1	2.28, s, 6H	7.06, d, 2H [$H_{(2)}$]; 6.74, t, 2H [$H_{(3)}$]; 6.99, t, 2H [$H_{(4)}$]; 6.78, d, 2H [$H_{(5)}$]	–	–	–	–
2	2.32, s, 6H	6.89, s, 2H [$H_{(1)}$]; 6.97, d, 2H [$H_{(3)}$]; 7.14, t, 2H [$H_{(4)}$]; 6.73, d, 2H [$H_{(5)}$]	–	–	–	–
3	2.18, s, 6H	6.78, d, 4H [$H_{(1,5)}$]; 7.13, d, 4H [$H_{(2,4)}$]	–	–	–	-
4	4.47, s, 4H	7.12–7.24, m, 10H [$H_{(1'-5')}$]	–	–	–	–
5	2.34, s, 3H	7.10, d, H [$H_{(2)}$]; 6.73, t, H [$H_{(3)}$]; 6.95, t, H [$H_{(4)}$]; 6.76, d, H [$H_{(5)}$]	1.10, s, 6H	3.42, s, 4H	–	85.43, s
6	2.25, s, 3H	6.74, s, H [$H_{(1)}$]; 6.84, d, H [$H_{(3)}$]; 7.09, t, H [$H_{(4)}$]; 6.77, d, H [$H_{(5)}$]	1.12, s, 6H	3.23, s, 4H	–	85.03, s
7	2.31, s, 3H	6.75, d, 2H [$H_{(1,5)}$]; 7.03, d, 2H [$H_{(2,4)}$]	0.90, s, 6H	3.21, s, 4H	–	85.45, s
8	4.41, s, 2H	7.09–7.25, m, 5H [$H_{(1'-5')}$]	1.11, s, 6H	3.45, s, 4H	–	86.01, s
9	2.24, s, 6H	7.00, d, 2H, [$H_{(2)}$]; 6.80, t, 2H, [$H_{(3)}$]; 6.95, t, 2H, [$H_{(4)}$]; 6.70, d, 2H, [$H_{(5)}$]	–	–	 7.18, d, 4H, [$H_{(2',6')}$]; 7.94, t, 4H, [$H_{(3',5')}$]; 8.50, t, 2H, [$H_{(4')}$]	–
10	2.27, s, 6H	6.74, s, 2H, [$H_{(1)}$]; 6.60, d, 2H, [$H_{(3)}$]; 7.11, t, 2H, [H(4)]; 6.25, d, 2H, [H(5)]	–	–	7.44, d, 4H, [$H_{(2',6')}$]; 8.00, t, 4H, [$H_{(3',5')}$]; 8.40, t, 2H, [$H_{(4')}$]	–
11	2.20, s, 6H	6.60, d, 4H, [$H_{(1,5)}$]; 7.00, d, 4H, [$H_{(2,4)}$]	–	–	7.50, d, 4H, [$H_{(2',6')}$]; 8.01, t, 4H, [$H_{(3',5')}$]; 8.43, t, 2H, [$H_{(4')}$]	–
12	4.31, s, 4H	7.20–7.30, m, 10H [$H_{(1'-5')}$]	-	-	 7.30, d, 4H, [$H_{(2',6')}$]; 8.20, t, 4H, [$H_{(3',5')}$]; 8.90, t, 2H, [$H_{(4')}$]	–

Table 3 (contd.)

13	2.27, s, 6H	7.01, d, 2H, [$H_{(2)}$]; 6.83, t, 2H, [$H_{(3)}$]; 6.92, t, 2H, [$H_{(4)}$]; 6.72, d, 2H, [$H_{(5)}$]	–	–	7.09, d, 2H, [$H_{(6',6')}$]; 7.64, t, 2H, [$H_{(5',5')}$]; 8.01, t, 2H, [$H_{(4',4')}$]; 8.53, d, 2H, [$H_{(3',3')}$]	–
14	2.21, s, 6H	6.81, s, 2H, [$H_{(1)}$]; 6.91, d, 2H, [$H_{(3)}$]; 7.09, t, 2H, [$H_{(4)}$]; 6.82, d, 2H, [$H_{(5)}$]	–	–	7.09, d, 2H, [$H_{(6',6')}$]; 7.64, t, 2H, [$H_{(5',5')}$]; 8.01, t, 2H, [$H_{(4',4')}$]; 8.53, d, 2H, [$H_{(3',3')}$]	–
15	2.14, s, 6H	6.74, d, 4H, [$H_{(1,5)}$]; 7.03, d, 4H, [$H_{(2,4)}$]	–	–	7.12, d, 2H, [$H_{(6',6')}$]; 7.66, t, 2H, [$H_{(5',5')}$]; 8.36, t, 2H, [$H_{(4',4')}$]; 8.59, d, 2H, [$H_{(3',3')}$]	–
16	4.29, s, 4H	7.27–7.32, m, 10H [$H_{(1'-5')}$]	–	–	7.12, d, 2H, [$H_{(6',6')}$]; 7.60, t, 2H, [$H_{(5',5')}$]; 8.01, t, 2H, [$H_{(4',4')}$]; 8.49, d, 2H, [$H_{(3',3')}$]	–
						
17	2.24, s, 6H	7.00, d, 2H, [$H_{(2)}$]; 6.80, t, 2H, [$H_{(3)}$]; 6.95, t, 2H, [$H_{(4)}$]; 6.70, d, 2H, [$H_{(5)}$]	–	–	7.41, d, 2H, [$H_{(2',9')}$]; 7.84, t, 2H, [$H_{(3',8')}$]; 8.63, d, 2H, [$H_{(4',7')}$]; 9.20, d, 2H, [$H_{(5',6')}$]	–
18	2.27, s, 6H	6.74, s, 2H, [$H_{(1)}$]; 6.90, d, 2H, [$H_{(3)}$]; 7.01, t, 2H, [$H_{(4)}$]; 6.52, d, 2H, [$H_{(5)}$]	–	–	7.65, d, 2H, [$H_{(2',9')}$]; 7.85, t, 2H, [$H_{(3',8')}$]; 8.01, d, 2H, [$H_{(4',7')}$]; 8.97, d, 2H, [$H_{(5',6')}$]	–
19	2.20, s, 6H	6.60, d, 4H, [$H_{(1,5)}$]; 7.00, d, 4H, [$H_{(2,4)}$]	–	–	7.52, d, 2H, [$H_{(2',9')}$]; 7.93, t, 2H, [$H_{(3',8')}$]; 8.43, d, 2H, [$H_{(4',7')}$]; 9.10, d, 2H, [$H_{(5',6')}$]	–
20	4.31, s, 4H	7.20–7.30, m, 10H [$H_{(1'-5')}$]	–	–	7.54, d, 2H, [$H_{(2',9')}$]; 7.92, t, 2H, [$H_{(3',8')}$]; 8.50, d, 2H, [$H_{(4',7')}$]; 8.99, d, 2H, [$H_{(5',6')}$]	–
						
21	2.28, s, 6H	7.06, d, 2H [$H_{(2)}$]; 6.74, t, 2H [$H_{(3)}$]; 6.99, t, 2H [$H_{(4)}$]; 6.78, d, 2H [$H_{(5)}$]	–	–	7.20–7.38, bs, 30H, [$H_{(2'-6')}$]	28.15
22	2.32, s, 6H	6.89, s, 2H [$H_{(1)}$]; 6.97, d, 2H [$H_{(3)}$]; 7.14, t, 2H [$H_{(4)}$]; 6.73, d, 2H [$H_{(5)}$]	–	–	7.24–7.64, bs, 30H, [$H_{(2'-6')}$]	26.12
23	2.18, s, 6H	6.78, d, 4H [$H_{(1,5)}$]; 7.13, d, 4H [$H_{(2,4)}$]	–	–	7.21–7.64, bs, 30H, [$H_{(2'-6')}$]	25.05
24	4.47, s, 4H	7.12–7.23, m, 10H [$H_{(1'-5')}$]	–	–	7.38–7.64, bs, 30H, [$H_{(2'-6')}$]	28.89

Where, s = singlet, d = doublet, bs = broad singlet, t = triplet.

[#]Sr. No. of the complexes is according to Table 1.

coordination of the base to the metal centre which is similar to the shift found in the analogous adducts[51,53]. The ^{1}H NMR values are given in Table 3.

^{13}C NMR :

The ^{13}C NMR spectra of these complexes showed chemical shifts for all carbon nuclei in their characteristic regions. The signals for methyl ($-CH_3$) and methylene ($-CH_2$) carbon occurred in the ranges 19.52–21.32 and 64.01–72.21 ppm, respectively. The carbon nuclei of phenyl groups ($-C_6H_5$ and $-C_6H_4$) displayed their resonance in the region 112.20–134.64 ppm. The carbon attached to the methyl and methylene group appeared at 121.90–136.82 and 135.61–142.81 ppm, respectively. The signal in the region 150.10–153.77 ppm was due to the carbon attached to the oxygen in the tolyl derivatives. The chemical shift for the dithiocarbonate carbon ($-OCS_2$) appeared at 167.87–183.62 ppm with an upfield shift (30–36 ppm) compared to the parent ligands[30]. Presumably, this reflects the fact that environment around the CS_2 carbon is the one most affected by the formation of the Cd-S bond. The chemical shifts for C-O carbon of the dithiophosphate moieties (**5**-**8**) were found in the region 72.78–73.01 ppm, respectively. The -C- and $-CH_3$ carbon nuclei of the neopentylene moiety have shown their chemical shifts at 30.98–31.18 and 21.11–21.23 ppm, respectively. The position of $-CS_2$ carbon moved to a higher field (2–3 ppm) as compared to the parent metal-dithiocarbonate **(1**-**4)** moiety and was at 171.45–188.02 ppm, indicating the participation of the donor groups in coordination with the metal. The signal of the substituent on the phenyl ring of the ligand is absorbed at the value that is expected, according to the nature of the substituent. The ^{13}C NMR spectra of the complexes (**9**-**24**) have exhibited the chemical shifts of the carbon nuclei of the donor moieties. There were three resonances for the aryl carbon nuclei of the pyridine in the region 124.20–149.89 ppm, four for the triphenylphosphine in the region 124.70–136.64 ppm, four for 2,2′-bipyridyl in the region 124.40–149.63 ppm and six for 1,10-phenanthroline moiety in the region 120.01–149.68 ppm, respectively.

^{31}P NMR :

The phosphorus atom of the dithiophosphate moiety in these complexes (**5**-**8)** appears as a singlet in the region 85.03–86.01 ppm with an upfield shift compared to corresponding free ligand in the ^{31}P NMR spectra. The occurrence of singlet is indicating its equivalent nature in the molecule. It has been proposed that the difference in the phosphorus chemical shift values between the corresponding ligand and the complex is a strong indicator of bidentate mode of bonding of cadmium with the alkylenedithiophosphate ligand. This singlet also signifies the symmetric nature of the phosphorus atom. The range observed for ^{31}P nucleus present in these complexes is consistent with bidentate behavior of dithiophosphate moiety according to Glidewell[54]. The appearance of a singlet was observed for each complex may be considered as an authentication of the formation of the compounds. A phosphorus signal in the range 25.05–28.89 ppm was observed in the complexes **(21**-**24)** for the triphenylphosphine i.e. deshielded with respect to uncoordinated triphenylphosphine moiety (–6.03 ppm). This authenticates the coordination of triphenylphosphine with metal in complexes **(21**-**24)**. The ^{13}C NMR values are given in Table 4.

Mass :

Two important peaks were observed in the mass spectrum : the molecular ion peak and the base peak. The molecular ion peak indicates the molecular mass of the complex, which is very weak in the case of the complexes investigated and the base peak is the strongest peak. The electron impact mass data show the presence of molecular ion peaks $[Cd(S_2COAr)_2]$ centered at *m/z* 478 **(2**, **3)** in the isotopic cluster of respective metal atom, in addition to some other peaks of different fragments, which were formed after consecutive dismissal of different groups. The occurrence of molecular ion peak in the complexes is supporting the monomeric nature of the complexes. In general, mixed sulfur donor ligand complexes 493 **(6)** do not show a very strong molecular ion peak, which may be due to a pyrolytic decomposition because of the relatively high temperature or due to the fragmentation of molecular ion in the ionization chamber. We observe weak molecular ion peaks surrounded by isotopic cluster of their respective metal for the representative com-

Table 4. ^{13}C NMR spectral data of cadmium(II) dithiocarbonates complexes in $CDCl_3$ (in ppm)

#Sr. No.	CH_n ($n = 2$ or 3)	$C(CH_n)$ ($n = 2$ or 3)	-C-O	Tolyl/Benzyl moiety			(O)-C-S	Neopentylene moiety			Donor moiety
				C_{ortho}	C_{meta}	C_{para}		-CO-	-C-	$-CH_3$	
1	20.80	125.93	153.77	115.51	127.61, 129.86	119.25	169.29	–	–	–	–
2	21.32	134.01	153.14	113.91, 117.32	130.32	122.33	168.56	–	–	–	–
3	21.13	134.11	151.63	120.83	128.33	–	167.87	–	–	–	–
4	71.29	135.61	–	126.61	127.40	128.96	182.90	–	–	–	–
5	20.81	121.90	150.41	121.51	125.61, 126.81	122.22	168.29	72.90	31.10	21.12	–
6	20.22	136.82	150.81	120.61, 124.23	134.64	131.88	168.56	72.91	31.18	21.17	–
7	19.52	130.12	150.61	120.81	128.30	–	169.87	72.78	30.98	21.23	–
8	64.01	142.81	–	125.31	130.41	126.21	183.62	73.01	31.01	21.11	–
											py
9	20.81	121.90	150.41	121.51	125.61, 126.81	122.22	174.29	–	–	–	125.20, 131.80, 148.60
10	20.32	123.02	150.10	119.91, 126.31	130.30	123.32	171.96	–	–	–	124.20, 131.06, 149.38
11	19.52	130.12	150.61	120.81	128.30	–	171.87	–	–	–	129.45, 136.02, 149.89
12	69.98	142.81	–	125.31	130.41	126.21	187.62	–	–	–	129.81, 136.27, 149.05
											bipy
13	21.08	124.79	152.90	113.32	132.75, 132.98	120.11	172.98	–	–	–	125.01, 126.05, 135.05, 147.09
14	20.05	134.64	150.81	112.20, 115.84	131.04	120.61	173.81	–	–	–	124.40, 136.82, 142.88, 149.63
15	20.43	130.09	150.11	115.64	127.12	–	175.04	–	–	–	136.12, 142.32, 143.09, 148.54
16	71.09	136.70	–	126.61	127.00	128.69	188.02	–	–	–	130.08, 130.83, 147.61, 147.90
											1,10-phen
17	20.62	127.89	150.81	114.70	129.97, 129.98	122.61	172.63	–	–	–	120.61, 124.23, 136.64, 138.64, 142.88, 149.63
18	20.01	134.65	150.82	112.20, 115.84	131.86	120.62	171.45	–	–	–	121.61, 124.23, 136.60, 138.64, 142.88, 149.68
19	20.21	129.80	151.01	114.32	127.91	–	174.54	–	–	–	120.53, 124.13, 136.10, 139.94, 142.43, 149.60
20	72.21	138.40	–	127.79	127.01	128.60	186.12	–	–	–	120.01, 127.40, 127.06, 129.02, 134.71, 139.15
											PPh_3
21	20.05	127.01	152.02	114.20	122.23, 124.40	120.21	174.29	–	–	–	124.70, 129.47, 136.62, 141.88
22	20.32	123.02	150.10	119.91, 126.31	130.30	123.32	171.96	–	–	–	125.12, 127.01, 135.64, 141.08
23	19.52	130.12	150.61	120.81	128.30	–	171.87	–	–	–	126.21, 127.91, 136.64, 140.41
24	69.01	142.81	–	125.31	130.41	126.21	187.62	–	–	–	126.30, 129.92, 134.14, 139.54

#Sr. No. of the complexes is according to Table 1.

plex. In the mass spectrum of the [(*m*-$CH_3C_6H_4OCS_2$)Cd($S_2\overline{POCH_2C(CH_3)_2CH_2O}$)], molecular ion peak was observed at *m/z* 493 (**6**), which is surrounded by isotopic cluster and a peak for dithiocarbonate moiety [(*m*-$CH_3C_6H_4OCS_2$)Cd)] at 296 (40). From this scheme we conclude that a dithiophosphate ligand is lost and its peaks are observed at *m/z* 197 (32). The base peak, which was observed at *m/z* 107 in the complexes due to [*m*-$CH_3C_6H_4O$], indicates the relative abundance of the respective group. The presence of the dithiocarbonate moiety in the fragmentation pattern shows that dithiocarbonates are stronger chelating agents as compared to alkylenedithiophosphate ligand.

The mass spectra of the addition complexes of cadmium with pyridine, triphenylphosphine, 2,2′-bipyridyl and 1,10-phenanthroline shows weak molecular ion peak in all the cases centered at *m/z* 665, 635, 661 and 1009 which is surrounded by isotopic envelop of their representative metal, in complexes (**9**, **15**, **19** and **22**). Peaks corresponding to higher *m/z* values can be regarded as direct fragmentation of the molecular ion, while peaks corresponding to lower *m/z* values can be considered as daughter fragments. The Mass spectral values of some complexes are given in Table 5.

Thermogravimetric analysis :

The thermal behaviors of the complexes were studied under inert atmosphere in the range of 30–1000 °C and displays weight losses in steps with different time intervals and at different temperatures. These losses indicate decomposition and evaporation of the volatile part of the sample. The curved portion indicates weight loss during process of heating. The thermal behavior of bis(*o*-tolyldithiocarbonato)cadmium(II) complex **(1)** has also been followed up to 1000 °C. In our study, the first thermolytic cleavage (endothermic) starts at 145 °C with 6.5% loss of weight, corresponding to methyl group (Obsd. 6.5%). The second stage ranges between 150 and 685 °C, corresponding to the formation of intermediate [$(OCS_2)_2Cd$] having 38.1% weight loss (38.9% Obsd.), which decomposes at higher temperatures to give CdS at 930 °C (69.9% Calcd., 69.7% Obsd.), after which a straight line is observed, indicating no change above this temperature range. The experimental mass losses of the compounds are in very good agreement with the calculated values. The thermal behavior of the complex [(*p*-$CH_3C_6H_4OCS_2$)Cd{$S_2POC(CH_3)_2C(CH_3)_2O$}] **(7)** was

Table 5. Mass spectral data of some cadmium(II) dithiocarbonates

#Sr. No.	M.W.	*m/z*, relative intensities of the ions and assignment
2	478.9	[M^+] 478 (21) [(*m*-$CH_3C_6H_4OCS_2)_2Cd$]; [M^+] 448 (15) [$(C_6H_4OCS_2)_2Cd$]; [M^+] 328 (14) [(*m*-$CH_3C_6H_4OCS_2$)CdS]; [M^+] 183 (30) [*o*-$CH_3C_6H_4OCS_2$]; [M^+] 107 (100) [*o*-$CH_3C_6H_4O$]; [M^+] 144 (21) [CdS]; [M^+] 76 (46) [CS_2]
3	478.9	[M^+] 478 (21) [$(C_6H_5CH_2OCS_2)_2Cd$]; [M^+] 328 (14) [$(C_6H_5CH_2OCS_2)$CdS]; [M^+] 183 (30) [$C_6H_5CH_2OCS_2$]; [M^+] 107 (100) [$C_6H_5CH_2O$]; [M^+] 144(20) [CdS]; [M^+] 76 (70) [CS_2]
6	493.8	[M^+] 493 (17) [(*m*-$CH_3C_6H_4OCS_2$)Cd($S_2\overline{POCH_2C(CH_3)_2CH_2O}$)]; [$M^+$] 197 (32) [($S_2\overline{POCH_2C(CH_3)_2CH_2O}$)]; [$M^+$] 296 (40) [(*m*-$CH_3C_6H_4OCS_2$)Cd]; [$M^+$] 165 (11) [$S\overline{POCH_2C(CH_3)_2CH_2O}$]; [$M^+$] 144 (40) [CdS]; [$M^+$] 107 (100) [*m*-$CH_3C_6H_4O$]; [$M^+$] 76 (60) [$CS_2$]
9	665.1	[M^+] 665 (17) [(*o*-$CH_3C_6H_4OCS_2)_2Cd.2NC_5H_5$]; [$M^+$] 478 (8) [(*o*-$CH_3C_6H_4OCS_2)_2Cd$]; [$M^+$] 328 (9) [(*o*-$CH_3C_6H_4OCS_2$)CdS]; [$M^+$] 183 (9) [*o*-$CH_3C_6H_4OCS_2$]; [$M^+$] 107 (100) [*o*-$CH_3C_6H_4O$]; [$M^+$] 79 (16) [$NC_5H_5$]; [$M^+$] 144 (27) [CdS]; [$M^+$] 76 (46) [$CS_2$]
16	635.1	[M^+] 635 (13) [$(C_6H_5CH_2OCS_2)_2Cd.N_2C_{10}H_8$]; [$M^+$] 478 (8) [$(C_6H_5CH_2OCS_2)_2Cd$]; [$M^+$] 328 (10) [$(C_6H_5CH_2OCS_2)$CdS]; [$M^+$] 183 (12) [$C_6H_5CH_2OCS_2$]; [$M^+$] 156 (21) [$N_2C_{10}H_8$]; [$M^+$] 107 (100) [$C_6H_5CH_2O$]; [$M^+$] 76 (49) [$CS_2$]; [$M^+$] 144 (40) [CdS]
19	661.1	[M^+] 661 (11) [(*p*-$CH_3C_6H_4OCS_2)_2Cd.N_2C_{12}H_8$]; [$M^+$] 478 (8) [(*p*-$CH_3C_6H_4OCS_2)_2Cd$]; [$M^+$] 328 (8) [(*p*-$CH_3C_6H_4OCS_2CdS$]; [$M^+$] 183 (9) [*p*-$CH_3C_6H_4OCS_2$]; [$M^+$] 182(19) [$N_2C_{12}H_8$]; [$M^+$] 107 (100) [*p*-$CH_3C_6H_4O$]; [$M^+$] 76 (39) [$CS_2$]; [$M^+$] 144(48) [CdS]
22	1009.5	[M^+] 1009 (9) [(*m*-$CH_3C_6H_4OCS_2)_2Cd.2P(C_6H_5)_3$]; [$M^+$] 478 (8) [(*m*-$CH_3C_6H_4OCS_2)_2Cd$]; [$M^+$] 328 (8) [(*m*-$CH_3C_6H_4OCS_2CdS$]; [$M^+$] 183 (10) [*m*-$CH_3C_6H_4OCS_2$]; [$M^+$] 265(29) [$P(C_6H_5)_3$]; [$M^+$] 107 (100) [*m*-$CH_3C_6H_4O$]; [$M^+$] 76 (50) [$CS_2$]; [$M^+$] 144 (40) [CdS]

#Sr. No. of the complexes is according to Table 1.

studied under inert atmosphere in the range of 25–1000 °C that displays weight losses in three steps with different time intervals and at different temperatures. In thermal analysis of the complex there are different temperature ranges visible, in which decomposition of the sample occurs. In the first decomposition step, there is a weight loss of 32.9% (Calcd.), 32.8% (Obsd.) which lead to the formation of fragment $[(OCS_2)Cd(S_2PO_2)]$ at 222 °C. In the second step of decomposition, there is a weight loss of 58.6% at 622.7 °C leading to the formation intermediate product $[Cd(OCS_2)]$. In the final decomposition step, the total weight loss of 70.8% Calcd. (70.6% Obsd.) strongly supports CdS as the final product after complete decomposition. The above observations indicate the formation of the cadmium sulfide as the final decomposition product of the complex **7**.

The TG curve reflects a multistage process caused by thermolysis of cadmium(II) adduct with 1,10-phenanthroline **(20)**. The first stage in the TG curve shows the most intense weight loss in the range of 100–270 °C, the weight loss (27.6% Obsd., 27.3% Calcd.) leads to thermolysis of compound and approximately corresponds to the removal of phenanthroline group (the calculated mass loss is 27.6%) and lead to the formation of parent compound $[(C_6H_5CH_2OCS_2)_2Cd]$. The 55.2% (Calcd.), 55.4% (Obsd.) weight loss attests the formation of major fragment $[(OCS_2)_2Cd]$ at 840 °C. This is confirmed by steep curve after 750 °C. The weight loss continued upto 980 °C with the formation of the final residue with a theoretical weight loss 78.2% (79.3% Obsd.) at 966 °C corresponding to CdS as the end product of thermolysis products.

Redox behaviour :

The complex $[(m\text{-}CH_3C_6H_4OCS_2)_2Cd]$ (**2**) is electroactive with respect to the metal center. The cyclic voltammogram of the complex in the potential range of +2.0 to –0.8 V at a scan rate of 100 mV/s recorded in methanol exhibited two redox processes; each reduction is associated with a single-electron transfer process. Two well-defined one-electron cyclic responses were observed. The cyclic voltagram of the complex depicts a cathodic peak at E_{pc} = –0.56 V for Cd^{II}/Cd^{I} couple and anodic peak is E_{pa} = 1.3 V for Cd^{I}/Cd^{II}. The corresponding anodic and cathodic currents are $i_c = -8.4\times10^{-7}$ and $i_a = 1.0\times10^{-6}$ A. The ratio to anodic and cathodic current is found to be $i_c/i_a = 0.8$ which is close to unity corresponding to simple one-electron process as shown in Fig. 1.

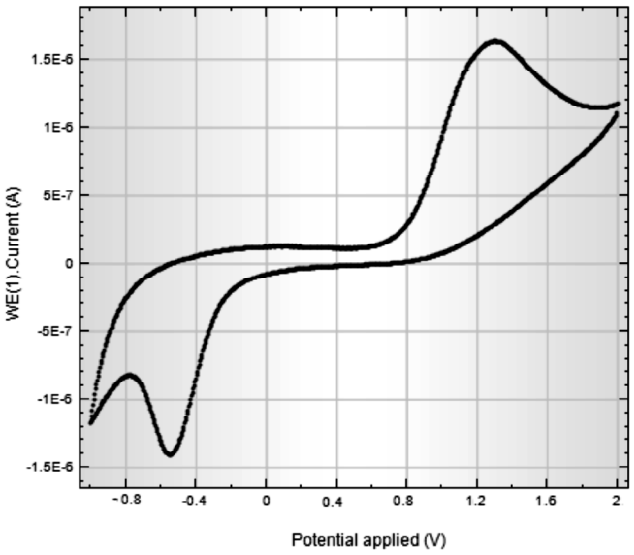


Fig. 1. Cyclic voltammetric curve of $[(m\text{-}CH_3C_6H_4OCS_2)_2Cd]$ (**2**).

The outcome of the above results confirms the formation of the cadmium(II) dithiocarbonate complexes and a probable geometry may be assigned to these compounds. The formation of the mixed ligand complexes is supported by the ^{31}P NMR spectra which exhibited the signal due to neopentyl dithiophosphate moiety with a downfield shift. The ν(P=S) and ν(P-S) bands in comparison to the parent dithiophosphate ligands indicates the formation of these complexes. Occurrence of a singlet with deshielding for the phosphorus atom of the dithiophosphato moiety indicates the bidentate mode of chelation by the dithiophosphate ligand and also the equivalent nature of the phosphorus atom in these complexes. Further appearance of new bands in the IR spectra confirms the formation of new metal complexes (**1**-**24**). It is evident from the ^{13}C NMR spectra of all compounds the C of the CS_2 group shows an up field shift as compared with the free ligand. Moreover, the C–S band is shifted to higher frequencies in the IR spectra of the complexes (**9**-**24**)

which substantiate the coordination of donor atoms with cadmium complexes. Bidentate mode of bonding by dithiocarbonate ligands as shown by IR would lead to distorted tetrahedral and octahedral geometry around cadmium in bis-dithiocarbonates (**1**-**8**) and donor stabilized complexes (**9**-**24**), respectively (Fig. 2(a-c)).

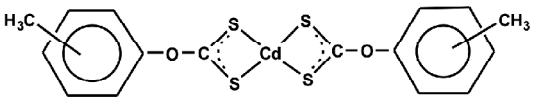


Fig. 2(a). Proposed distorted tetrahedral geometry for the complexes $[(ArOCS_2)_2Cd]$ (Ar= *o*-, *m*- and *p*-$CH_3C_6H_4$).

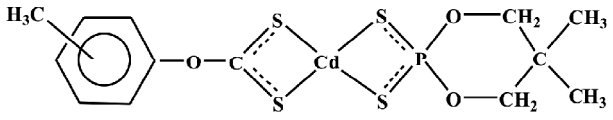


Fig. 2(b). Proposed distorted tetrahedral structure for $[(ArOCS_2)Cd(S_2\overline{POGO})]$ (Ar = *o*-, *m*- and *p*-$CH_3C_6H_4$).

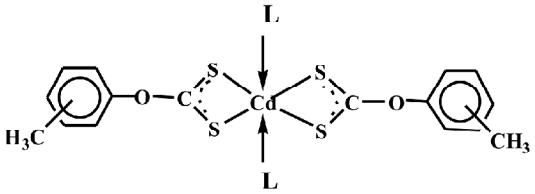


Fig. 2(c). Proposed distorted octahedral structure for $[(ArCS_2)_2Cd.nL]$ (Ar = *o*-, *m*- and *p*-$CH_3C_6H_4$), *n* = 1, L = $N_2C_{10}H_8$ (**13-15**), $N_2C_{12}H_8$ (**17-19**); *n* = 2, L = NC_5H_5 (**9-11**), $P(C_6H_5)_3$ (**21-23**).

Antifungal activity :

The antifungal activity of a few representative cadmium complexes was studied against *Fusarium oxysporum*. Antifungal activities of sodium salt of (*o*-, *m*- and *p*-tolyl)/benzyl dithiocarbonate and derivatives of cadmium **(2**, **6**, **11**, **16**, **17**, **24)** dithiocarbonate ligand have been measured and summarized in Table 6. Our results show that parent compounds and the corresponding adducts of the parent compounds both exhibit potent antifungal activities against *Fusarium*. The impact of the metal was found in the antimicrobial activity against the tested fungal species. The results obtained by the poison food method indicated that the coordination compounds have enhanced activity compared with the ligands. The values obtained

Table 6. *In vitro* evaluation of cadmium(II) dithiocarbonates complexes against the fungus *Fusarium oxysporium* f. Sp. *Capsici;* Control (C) = 4.5 cm

#Sr. No.	Conc. (ppm)	Colony diameter (mm)	%Inhibition $I = [(C - T)/C] \times 100$
o-$CH_3C_6H_3OCS_2Na$	50	4.5	0
	100	4.1	8.8
	150	3.9	13.3
	200	3.7	17.7
	250	3.6	20.0
$CdCl_2$	50	1.5	66.6
	100	1.0	77.7
	150	0.8	82.2
	200	0.6	86.6
	250	0.5	89.0
2	50	4.0	11.1
	100	3.5	22.2
	150	2.0	55.5
	200	1.5	66.6
	250	1.2	73.3
6	50	2.5	44.4
	100	2.0	55.5
	150	1.5	66.6
	200	0.7	84.4
	250	0.6	86.6
10	50	1.0	77.7
	100	0.8	82.2
	150	0.5	89.0
	200	0.5	89.0
	250	0.5	89.0
16	50	2.2	51.1
	100	2.0	55.5
	150	0.7	84.0
	200	0.6	86.6
	250	0.5	89.0
17	50	2.3	48.8
	100	2.0	55.5
	150	0.8	82.2
	200	0.6	87.0
	250	0.5	89.0
24	50	2.0	55.5
	100	1.5	66.6
	150	1.0	77.8
	200	0.7	84.4
	250	0.5	89.0

#Sr. No. of the complexes is according to Table 1.

suggest that aryl dithiocarbonate derivatives of cadmium are more fungitoxic than their parent ligands. This shows that metal derivatives are more fungitoxic than the chelating agent (Ligand) itself. The dithiocarbonates, represented by the general structure -O-C(=S)-S-Ar, have no hydrophilic group. On the contrary, these compounds are considered to be lipophilic. The enhanced activity of the metal derivatives may be ascribed to the increased lipophilic nature of these derivatives arising due to the chelation and toxicity of the metal chelates increases with increasing concentration of the complexes, the inhibitory effect on the mycelial growth of the fungus also increases, which can be explained on the basis of Overtone's concept and Tweedy's Chelation theory[55]. Metal ions are adsorbed on the cell walls of the microorganisms, disturbing the respiration processes of the cells and thus blocking the protein synthesis that is required for further growth of the organisms. Hence, metal ions are essential for the growth-inhibitory effects[56]. According to Overtone's concept of cell permeability, the lipid membrane that surrounds the cell favors the passage of only lipid-soluble materials, so lipophilicity is an important factor controlling the antifungal activity. Upon chelation, the polarity of the metal ion will be reduced due to the overlap of the ligand orbitals and partial sharing of the positive charge of the metal ion with donor groups. In addition, chelation allows for the delocalization of π-electrons over the entire chelate ring and enhances the lipophilicity of the complexes. This increased lipophilicity facilitates the penetration of the complexes into lipid membranes, further restricting proliferation of the microorganisms. All of the metal complexes possess higher antifungal activity than the ligand. All the complexes showed promising result in inhibiting the mycelial growth of the fungus at a concentration of 250 ppm. The comparison of antifungal activity of the ligand and some of the complexes is described diagrammatically in Fig. 3 and their comparison with the biocidal activities of free ligands and newly formed complexes are summarized as follows :

(1) All the aryl dithiocarbonate ligands possess a pronounced antifungal effect against the fungus at higher concentration and less activity at low concentration.

(2) Mixed dithiophosphato-dithiocarbonato complexes are proved to be more potent antifungal agents as compared to simple bis-dithiocarbonato complexes.

(3) In some cases complexes with diverse concentrations also showed equal activities against fungal species. By comparison of antifungal behavior of these synthesized complexes with their corresponding free ligands, we found that these complexes exhibited greater antifungal effects over free ligands used due to increase in lipo-

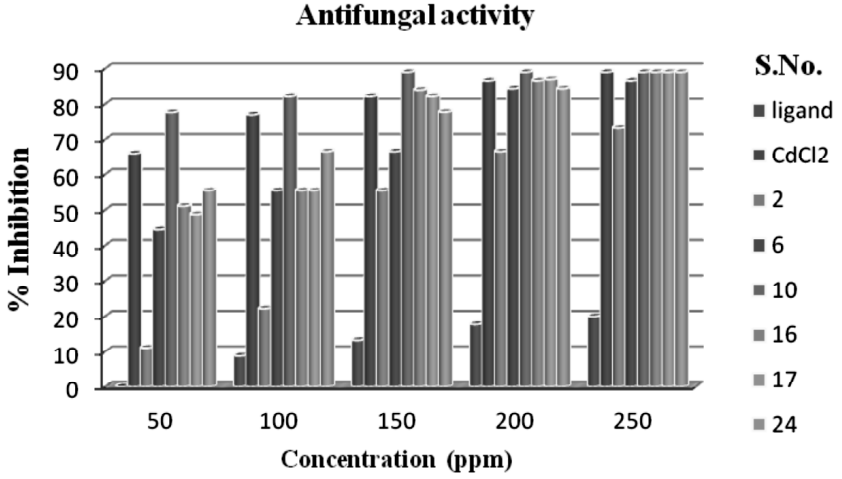


Fig. 3. Graph showing comparative result of antifungal activity of ligand, cadmium salt and cadmium complexes.

philic character of the metal complexes.

(4) Due to the known effects (poisonous nature) of cadmium salts we herein compare the antifungal activity of metal salts (cadmium chloride) with that of newly synthesized complexes of cadmium. The results shows that cadmium chloride has higher antifungal effects when it is used individually compared to ligand itself and complexes (**2**, **6**, **11**, **16**, **17**, **24**). This is due to the presence of chloride ion which enhanced microbial activity due to the formation of hypochlorous acid when free chloride upon oxidation resulting into chlorine (most plausibly, in the cells of microorganism the oxidized form of NAD^+ or $NADP^+$ can acquire two electron and get reduced to and as a result of this two chloride as counter ion get oxidized) that react with water[57].

(5) However the cadmium complex show high antifungal activity against fungus compared to cadmium chloride and free ligand. So it can be concluded that even though cadmium chloride has higher antifungal effects and this combination reduce its activity, the complexes still show significant activity that may in part be associated with the presence of cadmium, ligand and specially anions[58].

On conclusion it has been found that adducts of cadmium show pronounced antifungal activity as compared to the parent cadmium dithiocarbonate complexes. Due to the presence of anions (strong donors) like pyridine, triphenylphosphine, 1,10-phenanthroline and 2,2′-bipyridyl. Maximum inhibition is seen at higher concentration i.e. at 250 ppm in case representative complexes of cadmium. Mixed ligand complexes of dithiocarbonates with alkylene dithiophosphate of cadmium are found to show distinct activity against the fungus *Fusarium oxysporium.* As it is evident from the antifungal screening data, adducts of nitrogen and phosphorous donor ligands are more potent than the parent complex which are in turn more potent than the dithiocarbonate ligands. Adducts by means of nitrogen donor bases are prove to be more fungicidal as compared to phosphorous donor bases.

Conclusions

We have reported synthesis and characterization of some new metal complexes of cadmium with dithiocarbonates, neopentylenedithiophosphates and nitrogen and phosphorous donor ligands, having distorted tetrahedral and octahedral geometry. Further, electrochemical study depicted one electron redox process of the metal. TGA studies shows that final stable product of these complexes is metal sulphides i.e. these complexes can act as good precursors for CdS. Antimicrobial screening data show that cadmium complexes with nitrogen donor atoms are more potential compared to phosphorous complexes.

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