Bis(di(2-hydroxyethyl)dithiocarbamato) Cadmium(II) with N- donor ligands: Synthesis, Spectral, Thermal studies and Bond Valence Sum(BVS) Analysis

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Abstract: $[Cd(deadtc)_2]_2$ **(1)**, $[Cd(deadtc)_2(2,2'-bipy)]$ **(2)**, $[Cd(deadtc)_2(1,10-phen))]$ **(3)**, $[Cd_2(deadtc)_4(4,4'-bipy)]$ **(4)**, $[Cd(deadtc)_2(TMED)]$ **(5)** and $[Cd(deadtc)_2(py)]$ **(6)** ($deadtc^-$ = di(2-hydroxyethyl)dithiocarbamate anion, 2,2'-bipy = 2,2'-bipyridine, 4,4'-bipy = 4,4'-bipyridine, 1,10-phen = 1,10-phenanthroline, TMED = Tetramethylethylenediamine, py = pyridine) have been synthesized and characterized by IR and electronic spectroscopy, elemental analysis and thermogravimetry. IR spectra of the complexes show that the thioureide (C-N) band values are lower than the values observed for the parent dithiocarbamate. A reduction in the thioureide stretching frequency is due to the increase in coordination around the cadmium ion and the resultant increase in electron density. Thermal studies indicate that 1,10-phenanthroline adduct is more stable than other adducts. The charge transfer transitions are observed in the region 310 – 340 nm. Bond valence sum (BVS) values close to 2.00 in all the cadmium complexes support the correctness of the crystal structures.
 Key words: dithiocarbamate, thioureide, cadmium, X-ray structure, bipyridine and BVS analysis.

INTRODUCTION

Dithiocarbamates have numerous applications in chemical, agriculture, and pharmaceutical industries owing to their metal-binding and antioxidant properties[1,2]. Dithiocarbamates of zinc and cadmium have continued to attract attention in recent years on account of their industrial applications [3,4] and biological profiles [5,6].

Cadmium dithiocarbamate complexes have been used as a precursor for the synthesis of CdS nanoparticles [7,8].

Tetrahedral zinc and cadmium dithiocarbamate complexes are known to expand their coordination numbers by adding neutral nitrogenous ligands. The crystal structures on mixed ligand complexes involving cadmium dithiocarbamates and nitrogenous bases such as 2,2'-bipyridine, 1,10-

phenanthroline and Tetramethylethylenediamine were reported [9-22]. All the adducts contain discrete molecular units with CdS_4N_2 chromophore in a distorted octahedral geometry. X-ray photoelectron spectral, NMR, cyclicvoltammteric and thermal studies were carried out on zinc and cadmium dithiocarbamates and their 2,2'-bipyridine, 1,10-phenanthroline, 4,4'-bipyridine adducts [23-27]. XPS studies showed a significant reduction in binding energy values of $S2_p$ electrons in bipyridine and phenanthroline adducts compared to the parent dithiocarbamates. The increased electron density on metal centre on adduct formation is shown by the reduction in $Cd2p_{3/2}$ binding energy. ^{1}H and ^{13}C NMR spectra of the complexes show the drift of electrons from the nitrogen of the substituents forcing a high electron density towards sulfur via the thioureide -system. The cyclic voltammetric studies show clearly the presence of excess electron density on the metal ions in all the adducts compared to the parent dithiocarbamates.

Single crystal x-ray structures of $[Cd(S_2CN(C_6H_5CH_2))_2(C_5H_5N)][28]$ and $[Cd(C_5H_5N)\{S_2CN \quad (i-C_4H_9)_2\}_2$ [29] show that metal ion center is five-coordinated with pyramidal environment and bound to four sulfur atoms from two bidentate dithiocarbamate ligands and to one nitrogen atom from pyridine . The structure of $[Cd_2(dedtc)_4 \quad (trans-NC_5H_4C(H) = C(H)C_5H_4N)]$ ($dedtc^-$ = diethyldithiocarbamate anion) has been reported[30]. The linear polymeric structure shows bidentate coordination by the dithiocarbamate ligand and a distorted octahedral geometry for cadmium defined by a trans $-N_2S_4$. Since the crystal structures of the cadmium complexes **1**, **2** and **3** were reported earlier[18,19, 31], in this paper, we report the results of spectral and thermal characterization studies of the compounds(**1-3**) along with **4-6.** In addition the results of the bond valence sum (BVS) calculations are also reported.

EXPERIMENTAL

Preparation of [Cd(deadtc)$_2$]$_2$

Diethanoldithiocarbamic acid was prepared from 20 mmol of diethanolamine and 20 mmol of carbon-disulphide in ethanol (20 mL) under ice cold condition (5°C). To the yellow dithiocarbamic acid solution, aqueous solution of $Cd(NO_3)_2$ $4H_2O$ (308 g, 10 mmol) added with constant stirring. The complex was filtered and washed with alcohol and was then dried. Yield 80 %.

Preparation of [Cd(deadtc)$_2$(L)] (L = 1,10-phenanthroline or 2,2'-bipyridine or TMED)

Ethanolic solution of 1,10-phenanthroline (200 mg, 1 mmol) or 2,2'-bipyridine (156 mg, 1 mmol) or Tetramethylethylenediamine (0.148 ml, 1 mmol) was added to the suspension of $[Cd(deadtc)_2]_2$ (470 mg, 1 mmol) in ethanol (30 ml) . The resulting pale yellow solution was left undisturbed for evaporation at room temperature. After two days yellow crystals separated out. The yellow crystals analysed to the proposed formula. Yield 75 %.

$$[Cd(deadtc)_2]_2 + 2L \longrightarrow 2[Cd(deadtc)_2(L)]$$
$$\dots\dots\dots\dots\dots(1)$$
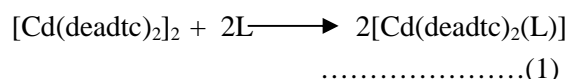
(L = 1,10-phen or 2,2'-bipy or TMED)

Preparation of [Cd$_2$(deadtc)$_4$(4,4'-bipy)]

$[Cd(deadtc)_2]_2$ (940 mg, 2 mmol) suspension in ethanol was added to ethanolic solution of 4,4'-bipyridine (156 mg, 1 mmol). The resulting pale yellow solution was left for evaporation at room temperature. After two days yellow precipitate separated out. The yellow solid analysed to the proposed formula. Yield 70 % .

$$2[Cd(deadtc)_2]_2 + 2L \longrightarrow 2[Cd_2(deadtc)_4(4,4'-bipy)]$$
$$\dots\dots\dots\dots\dots(2)$$
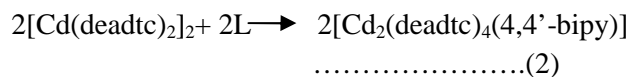
L = 4,4'-bipyridine .

Preparation of [Cd(deadtc)$_2$(py)]

The cadmium(II) complex, $[Cd(deadtc)_2]_2$ (470 mg, 1 mmol) was dissolved in a minute volume of toluene under mild heat. Excess (10%) pyridine was added to the prepared solution of parent cadmium compound. The resulting pale yellow solution was left undisturbed for evaporation at room temperature. After two days yellow crystals were isolated by means of slow evaporation of toluene at room temperature. The yellow crystals analysed to the proposed formula. Yield 75 %.

$$[Cd(deadtc)_2]_2 + L \longrightarrow 2[Cd(deadtc)_2(py)]$$
$$\dots\dots\dots\dots(3)$$
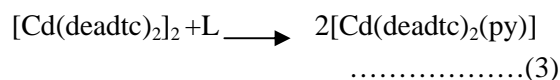
(L = Pyridine).

MATERIALS AND METHODS

All reagents and solvents employed were commercially available, high-purity materials (E-Merck) and were used as supplied without further purification. IR spectra were recorded on a JASCO IR – 700 spectrophotometer (range 4000 – 400 cm^{-1}) as KBR pellets. The UV-Visible spectra in ethanol were recorded on a JASCO UVDEC 340 double beam spectrophotometer. Elemental analyses (C,H,N) were carried out with an Heraeus Carlo Erba 1108 instrument at Indian Institute of Technology, Chennai, India. Thermogravimetric studies were useful in confirming the composition of the complexes. STA 1500 PL and Perkin – Elmer TGA7 Thermal Sciences instruments were used for the thermal analysis. The heating rate of the furnace was fixed at 10°C per minute. About 5 mg of the sample was taken in porcelain crucible for each thermogravimetric experiment.

RESULTS AND DISCUSSION

Infrared Spectra

The significant absorptions in the dithiocarbamate complexes are due to the νC–N and νC–S stretching modes. The νC–N has been used as a measure of the contribution of the thioureide group to the structure of the dithiocarbamate. The polar $\nu C \overset{+}{=} N$ appears at an intermediate value between the two extremes of (1250 – 1350 cm^{-1}) and (1650 – 1690 cm^{-1}) [32]. IR spectra of the complexes show that the shift of the thioureide (C –N) bands to lower frequencies compared to the parent bisdithiocarbamate is due to the increase in coordination number around cadmium ion [33]. The change in geometry has affected the extent of interaction between the dithiocarbamate and the cadmium ion which has resulted in the reduction of (C –N) value. In the case of 4,4'-bipyridine adduct the shift of (C –N) to lower value is due to the change in coordination geometry from tetrahedral to tetragonal pyramid. Also this observation is an indication of increased electron density on the cadmium in the adducts. The thioureide (C –N) band is well differentiated from the ring frequencies associated with N-donors, which are observed in the 1600-1000cm^{-1}. The (C –S) bands appear around 990 cm^{-1} in all the complexes, without any splitting, supporting the bidentate coordination of the dithiocarbamate moiety [33]. Other bands due to nitrogen donors are masked by those due to dithiocarbamate ligand. Important IR bands and analytical data for the adducts are given in Table 1. Fig.1 shows IR spectra of [Cd(deadtc)$_2$]$_2$ and [Cd(deadtc)$_2$(2,2'- bipy)] .

Table 1. Important IR bands and analytical data of the complexes

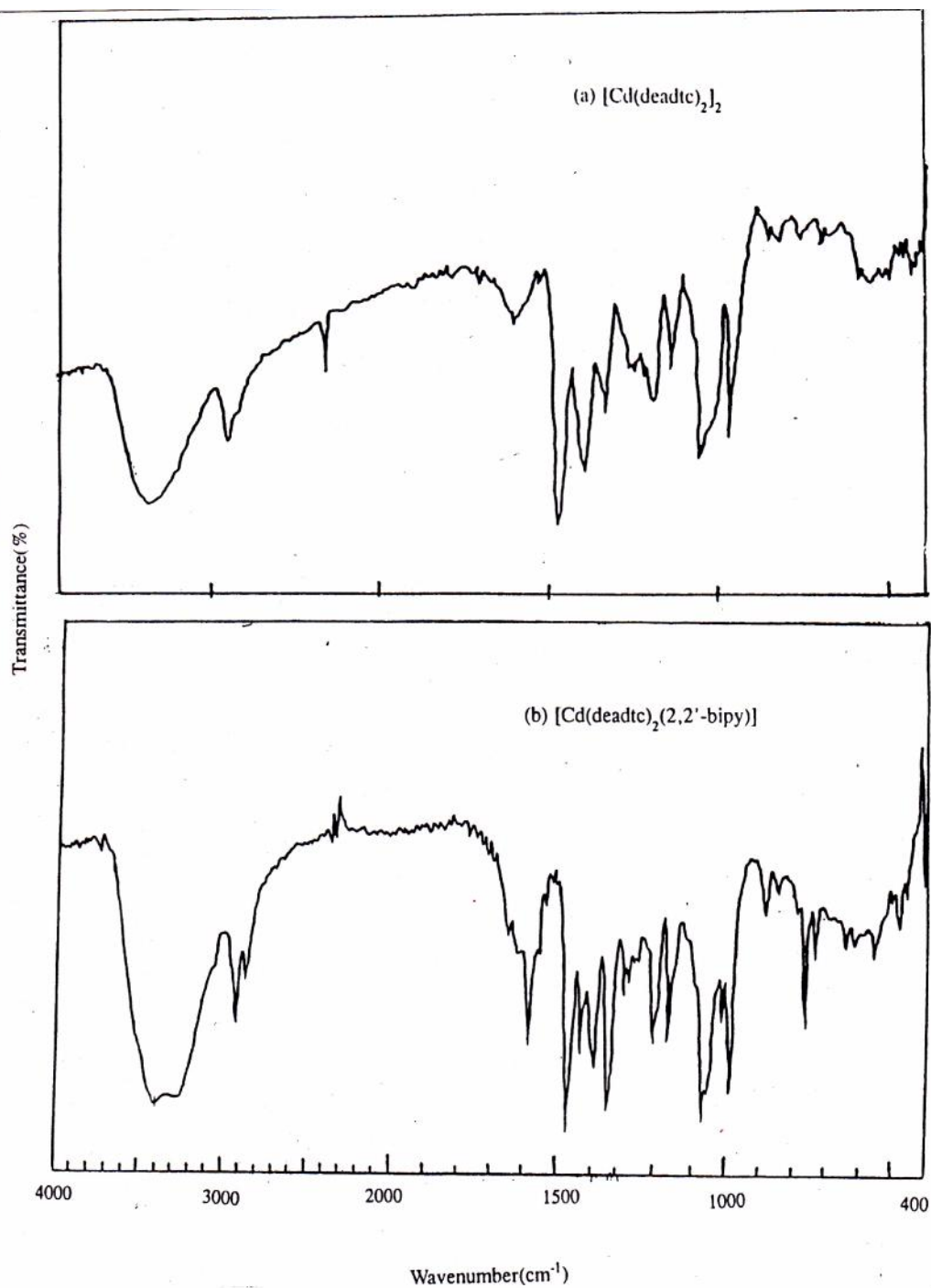| Compound	C - N	C - S	C%		H%		N%	
			Calcd	Found	Calcd	Found	Calcd	Found
[Cd(deadtc)$_2$]$_2$	1484	983	25.5	25.2	4.2	4.0	6.0	5.8
[Cd(deadtc)$_2$(2,2'-bipy)]	1473	986	38.2	38.0	4.5	4.4	8.9	8.6
[Cd(deadtc)$_2$(1,10-phen)]	1474	982	39.4	39.1	4.2	4.1	8.4	8.2
[Cd$_2$(deadtc)$_4$(4,4'-bipy)]	1478	983	32.7	32.4	4.4	4.2	7.6	7.3
[Cd(deadtc)$_2$(TMED)]	1472	980	32.7	32.5	6.1	6.0	8.2	8.0
[Cd(deadtc)$_2$(py)]	1479	981	32.6	32.3	4.5	4.3	7.6	7.4

Fig. 1. IR spectra of (a) [Cd(deadtc)$_2$]$_2$ and (b) [[Cd(deadtc)$_2$ (2,2'- bipy)]

UV-Visible Spectra

The parent dithiocarbamate complex prepared in the present study is colourless. The 1,10-phenanthroline, bipyridine, pyridine and TMED adducts are all faint to intense yellow coloured. The electronic spectra of both the parent dithiocarbamate and their adducts show transitions only due to charge transfer. The d–d transitions are absent as Cd(II) is d^{10} ion. The ligand transitions of the dithiocarbamate and the charge transfer transition in the adducts are observed in the region 310 - 340nm.

Thermogravimetric Analysis

$[Cd(deadtc)_2]_2$ complex is stable upto 255°C and above that temperature there is single step decomposition. The final residue is mere CdS around 600°C. In the case of $[Cd(deadtc)_2(2,2'-bipy)]$ the decomposition starts at 195°C and there is an initial loss of 2,2'-bipyridine, which is not clearly showed as an independent step in the TGA. The 2,2'-bipyridine ligand and dithiocarbamate moiety appear to decompose simultaneously. But in the case of $[Cd(deadtc)_2(1,10-phen)]$ there is a well defined step for the loss of 1,10-phenanthroline in the TGA. Thermal loss of the 1,10-phenanthroline at 215 °C is followed very closely by the decomposition of the

dithiocarbamate moiety. The decomposition of cadmium dithiocarbamate leads to the formation of $Cd(SCN)_2$. In both the adducts the final residue is a mixture of CdS and $CdSO_4$ around 600 °C. The above comparision shows that the 2,2'-bipyridne adduct is thermally less stable than its 1,10-phenanthroline analogue. The curve obtained for $[Cd_2(deadtc)_4(4,4'- bipy)]$ adduct shows a single stage weight loss,which ultimately leads to the formation of a mixture of CdS and $CdSO_4$ around 600°C. The loss of 4,4'-bipyridine moiety is not observed as an independent step. In general the 4,4'–bipyridine adduct is thermally more stable than the 2,2'-analogue probably because of the dimeric nature. The TMED and Pyridine adducts show the initial decomposition of the TMED and pyridine respectively followed by dithiocarbamate. Comparison of the thermal stabilities of the parent and its adducts clearly shows a higher thermal stability of the parent during decomposition due to the polymeric nature. Thermograms for $[Cd(deadtc)_2]_2$ and $[Cd(deadtc)_2(2,2'-bipy)]$ are depicted in Fig.2. The proposed structures of adducts are given in Fig.3. Thermogravimetric data for the complexes are given in Table 2.
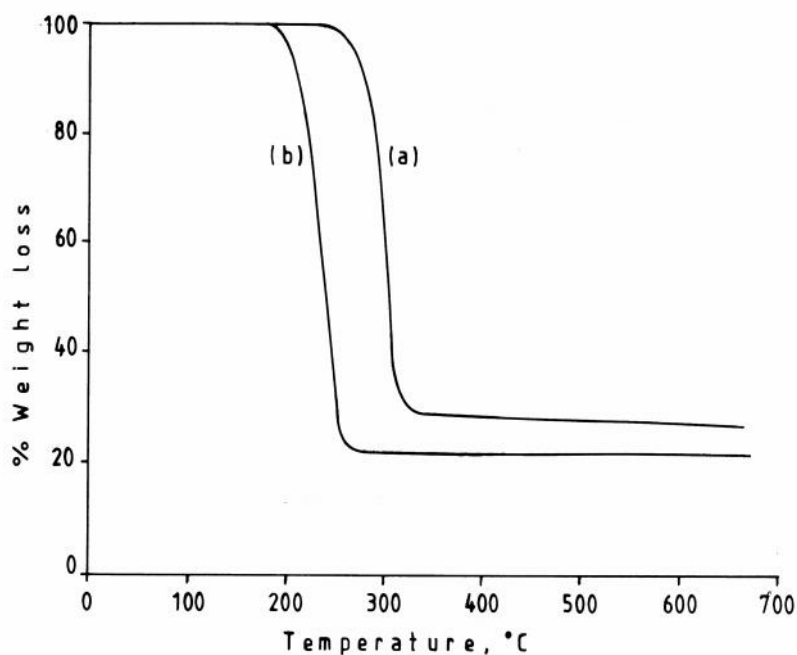

Fig. 2. Thermograms of (a) $[Cd(deadtc)_2]_2$ and (b) $[Cd(deadtc)_2 (2,2'- bipy)]$
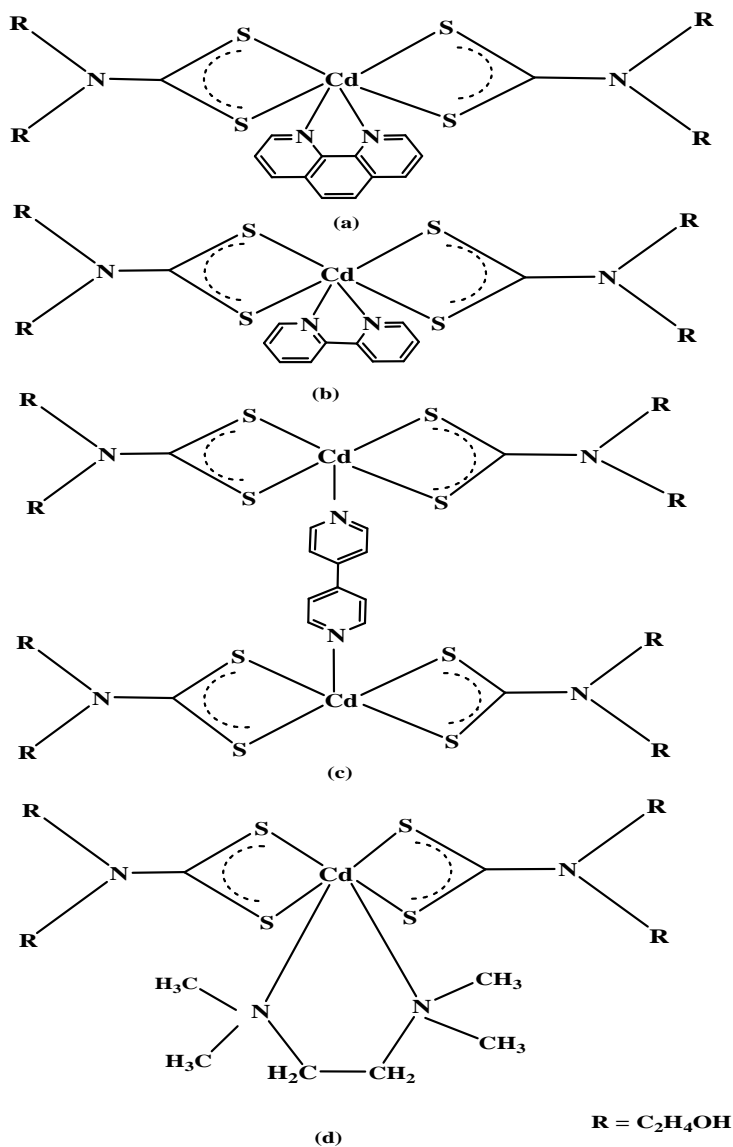
Fig. 3. Structure of the complexes (a) [Cd(deadtc)$_2$ (1,10-Phen)], (b) [Cd(deadtc)$_2$ (2,2'-bipy)], (c) [Cd$_2$(deadtc)$_4$ (4,4'-bipy)] and (d) [Cd(deadtc)$_2$ (TMED)]

Table 2. Thermogravimetric data for the complexes

Compound	Initial dec. temp °C	Decomp. range°C	Mass loss Exptl..	Mass loss Calcd.	End product/ Loss fragment
[Cd(deadtc)$_2$]$_2$	255	255 – 600	69.2	69.5	CdS
[Cd(deadtc)$_2$(2,2'-bipy)]	195	195 – 600	78.0	77.5	CdS
[Cd(deadtc)$_2$(1,10-phen)]	215	215 – 250	28.4	27.6	1,10-phen
		250 – 360	64.2	65.0	Cd(SCN)$_2$
		>600	72.8	73.0	CdS + CdSO$_4$
[Cd$_2$(deadtc)$_4$(4,4'-bipy)]	200I	200 – 600	86.0	86.7	CdS

Bond Valence Sum Analysis

The bond valence sum method (BVS) can be extremely useful to all chemists in resolving conflicts regarding oxidation states or in evaluating the results of a crystal structure analysis. The chemist wishing to estimate an unknown bond length in a molecule or crystal is confronted with intimidtating array of covalent radii, ionic radii and metallic radii etc., from which to choose [34]. The bond valence method [35,36] has recently had considerable success in predicting and interpreting bond lengths in 'ionic solids'. As it can be applied to estimate the bond lengths, vice-versa the sum of these bond lengths should give information about the valence of the central ion.

The formation of a complex of any metal ion with multidentate ligand represent a compromise between the steric interactions in the ligand and the steric and electronic requirements of the metal [37]. The bond valence sum of the complexes determined from the bond valence parameters accounts for the valence of the central ion irrespective of the number of bonds and the strength of the interactions [38-40]. The V_{ij} of a bond between two atoms i and j is defined so that the sum of all the bond valences from a given atom i with valence V_i obeys $\sum v_{ij} = V_i$ where:

$v_{ij} = \exp[(R_{ij} - d_{ij}/B]$,

$R_{ij} = r_i + r_j - [r_i r_j (\sqrt{c_i} - \sqrt{c_j})^2] / [c_i r_i + c_j r_j]$

and B is a universal constant equal to 0.37. In the present study the BVS values have been calculated for the cadmium complexes **1-3** from their crystallographic distances reported in the literature, with two different sets of R_{ij} values. Since the crystal structures of 4,4'-bipyridine, TMED and pyridine adducts of bis(di(2-hydroxyethyl)dithiocarbamato) cadmium(II) have not been reported so far, we have collected the crystallographic distances for the similar type of cadmium adducts and calculated BVS values. The values obtained with two different sets of R_{ij} values are presented in Table 3. The examination of the results clearly show the BVS values to be close to '2', which is equivalent to the formal oxidation state of cadmium in the complexes. Significant differences in BVS values are observed and reported [41] for the parent zinc dithiocarbamates and their adducts. But in the case of the cadmium dithiocarbamate complexes and their adducts no observable changes are seen in BVS values. Due to larger size of cadmium ion compared to zinc ion, the Cd-S distances are not much affected by the change in coordination geometry. Interestingly, the bond valence sum values of [Cd(S$_2$COEt)$_2$(TMED)] are lower than the values of other adducts may be due the prevailing of less or more ionic interaction in cadmium-xanthate involving d^{10} metal ion. Change in coordination number and change in coordination environment around the cadmium ion have adjusted themselves in such a way that the valency of the central ion is satisfied.

Table 3. BVS values for the complexes

Compound	Vi(OK/B)	Vi(B/OK)	Ref
[Cd(deadtc)$_2$]$_2$	1.97	2.02	31
[Cd(deadtc)$_2$(2,2'-bipy)]	2.05	2.09	18
[Cd(deadtc)$_2$(1,10-phen))]	2.04	2.07	19
[Cd(S$_2$COEt)$_2$(TMED)]	1.88	1.91	22
[Cd$_2$(dedtc)$_4$ (trans-NC$_5$H$_4$C(H) = C(H)C$_5$H$_4$N)]	2.00	2.04	30
[Cd(S$_2$CN(i-C$_4$H$_9$)$_2$)$_2$(Py)]	2.04	2.16	29

OK/B = calculated by the Method due to O'Keeffee and Brese [37], B/OK = calculated by the method due to Brese and O'Keeffee [38], NC$_5$H$_4$C(H)=C(H)C$_5$H$_4$N = bis(4-pyridyl)ethylene, TMED = Tetramethylethylenediamine, S$_2$COEt = ethylxanthate, Py = Pyridine, dedtc = diethyldithiocarbamate

CONCLUSION

The parent dithiocarbamate, $[Cd(deadtc)_2]_2$, and their nitrogenous adducts have been synthesized and characterized by IR and UV-Visible spectra, elemental analysis, thermogravimetry. IR spectra of the complexes show that the thioureide (C-N) band values are lower than the values observed for the parent dithiocarbamate. A reduction in the thioureide stretching frequency is due to the increase in coordination around the cadmium ion and the resultant increase in electron density.

Thermogravimetry studies indicate that 1,10-phenanthroline adduct is more stable than other nitrogenous adducts. The charge transfer transition in the adducts are observed in the region 310 - 340nm. The results of the bond valence sum (BVS) analysis are also reported for the parent cadmium dithiocarbamate and their N-donor adducts.The BVS values close to 2.0 support the correctness of the crystal structures.

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