



International Journal of ChemTech Research CODEN(USA): IJCRGG ISSN : 0974-4290 Vol.5, No.4, pp 1486-1494, April-June 2013

Characterization Studies On 4,4'-Bipyridine And Cadmium Dithiocarbamates Involved Dimeric Complexes And Valence Bond Parameter Calculations On Some Cadmium Dithiocarbamate Complexes

A. Manohar*, K. Karpagavel and P. Thillai Arasu

¹Department of Chemistry, Kalasalingam University, Krishnankoil-626 190, India.

*Corres.author: navmanohar@yahoo.co.in

Abstract: Cyclic voltammetric, thermal and spectral characterization studies were made on (4,4'-bipyridine) bis(bis(dithiocarbamato)cadmium(II)), [Cd₂(dtc)₄(4,4'-bipy)], (dtc=nmedtc, N-methyl,N-ethanoldithio carbamate; dndtc, di-n-propyldithiocarbamate; dipdtc, diisopropyldithiocarbamate; pipdtc, piperidine dithiocarbamate; dedtc, diethyldithiocarbamate; deadtc, diethanoldithiocarbamate). The cyclic voltammetric study on the complexes show an increase of electron density on cadmium in the adducts compared to [Cd(dtc)₂]₂. IR spectra of the complexes show the contribution of the thioureide form to the structures. Reduction in C–N(thioureide) for the adducts is attributed to the sift in coordination number from four to five. The charge transfer transitions are observed in the region 310 - 340. Thermal studies show a single stage weight loss. Valence Bond Sum (BVS) analysis are made on some cadmium dithiocarbamate complexes and results are reported in this paper.

Key words: dithiocarbamate; thioureide; cyclic voltammetry; 4,4'- bipyridine; VBS analysis.

Indroduction

Dithiocarbamates of zinc and cadmium have continued to attract attention in recent years on account of their industrial applications [1,2] and biological profiles [3,4]. Dialkyl dithiocarbamato complexes of $[M(S_2CNR_2)_2]$ (M = Zn(II), Cd(II),R = alkyl) have been used as single-source precursors to prepare nanoparticles and to deposit ZnS or CdS thin films by metal–organic chemical vapour deposition (MOCVD) [5]. The affinity of 1,1-dithiolate ligands for metals such as zinc and cadmium was indicated by the fact that the ligands can be employed as scavengers for these elements in biological media. Besides that, nitrogen donor adducts of dithiocarbamate complexes are also widely used in the preparation of thin semiconductor [6–8] and electroluminescent [9,10] films of transition metal sulfides, the basis of electronic and solar cell technology [11].

Divalent zinc and cadmium tetrahedral complexes are known to expand their coordination number by adding neutral nitrogenous ligands. Synthesis, spectral, thermal, cyclicvoltammetry and single crystal X-ray structural studies on monomeric mixed ligand complexes involving bis(dithiocarbamato)M(II) (M= Zn,Cd) and nitrogenous bases such as 2,2'-bipyridine, 1,10-phenanthroline, tetramethylethylenediamine (TMED),were reported extensively. [12-23]. All the adducts are containing discrete molecular units with MS₄N₂ (M= Zn,Cd) chromophore in a distorted octahedral geometry. X-ray photoelectron spectroscopy (XPS), Cyclic voltammetry, C^{13} and H^1NMR studies showed the increased electron density on metal centre on adduct formation. Similarly the characterization studies were reported more on dimeric zinc complexes involving zinc dithiocarbamates and

4,4'-bipyridine [24-26]. X-ray structural studies show that the zinc ion is five coordinated with a ZnS₄N coordination environment in the dimeric complexes. X-ray photoelectron spectroscopy studies showed increased electron density on zinc and decrease of electron density on sulfur in all the 4,4'-bipyridine adducts. However cyclic voltammetric studies showed an increase of electron density on zinc in all the adducts compared to the parent dithiocarbamates. Recently the dimeric cadmium structure, $[Cd_2{S_2CN(n-Pr)_2}_4(C_{12}H_{10}N_4)]$ (S₂CN(nPr)₂ = di-n-propyldithiocarbamate anion; C₁₂H₁₀N₄ = Pyridinealdazine), has been reported [27]. Here also the cadmium ion is five coordinated with a CdS₄N coordination environment in the dimeric structure. The reactivity studies of parent cadium dithiocarbamates with iodine were made by using spectral studies and single crystal X-ray crystallography[28,29]. The formation of disulphide in the case of cadmium dithiocarbamates on their reaction with molecular iodine was proved, which depends on the relative ease with which dithiocarbamate ligands undergoing oxidation to form the disulphides.

To the best of our knowledge, the characterization studies reported on dimeric cadmium complexes involving cadmium dithiocarbamates and 4,4'-bipyridine in literatures have been very rare compared to zinc. This factor motivated us to report the electrochemical studies and other characterization studies on 4,4'-bipyridine adducts of cadmium dithiocarbamates. Though a few studies on 4,4'-bipyridine adducts of pipdtc, dedtc and deadtc have been reported previously by our groups[30,31], again the studies are reported here in detail in order to support for the electrochemical characterization studies. In continuation of our interest in valence bond sum analysis on coordination complexes[31-33] also the VBS calculations were made on some cadmium dithiocarbamate complexes and results are reported in this paper.

Experimental

Preparation of $[Cd_2(dtc)_4(4,4'-bipy)]$ (dtc⁻ = dedtc⁻ pipdtc⁻, dnpdtc⁻, dipdtc⁻). The adducts were prepared by adding hot solutions of 4,4'-bipyridine (156mg, 1mmol) in chloroform to the hot solutions of $[Cd(dedtc)_2]_2$ or $[Cd(pipdtc)_2]_2$ or $[Cd(dnpdtc)_2]_2$ or $[Cd(dnpdtc)_2]_2$ or $[Cd(dnpdtc)_2]_2$ (2mmol) in chloroform. The resulting solution was left for evaporation at room temperature. Yellow precipitate of the adduct separated out and analysed to the proposed formula.(Yield: 75%)

Preparation of [Cd₂(deadtc)₄(4,4'-bipy)]

The preparation of $[Cd_2(deadtc)_4(4,4'-bipy)]$ is reported already [31]. Ethanolic solution of 4,4'-bipyridine (156 mg, 1 mmol) was added to suspension of $[Cd(deadtc)_2]_2$ (940 mg, 2 mmol) in ethanol. 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 %.

Preparation of [Cd₂(nmedtc)₄(4,4'-bipy)]

 $[Cd(nmedtc)_2]_2$ (2mmol, 0.824 g) was ground to a fine powder, mixed with 4,4'-bipyridine (2 mmol, 0.31 g) and then ground again to mix thoroughly. The mixture was taken in a stoppered glass tube and was heated in water bath for about 6 hours. The mixture changed its colour from dirty white to yellow on heating. Then the solid was washed with ethanol and dissolved in chloroform. The yellow solution was filtered and left for evaporation. After two days yellow solid separated out. The complex analyzed to $[Cd_2(nmedtc)_4(4,4'-bipy)]$.

The parent dithiocarbamate complexes were prepared by literature method [34-39].

Analytical and physical measurements

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. BAS electrochemical analyzer was used for recording the cyclic voltammograms of the complexes. Working electrodes were hanging mercury drop electrode (HMDE) or platinum electrode, counter electrode was platinum wire and reference electrode was Ag/AgCl. The solvent was purified by distillation methods. Supporting electrolyte was tetrabutylammonium perchlorate (0.1M). Experimental solution was thermostated at $25 \pm 1^{\circ}$ C and oxygen free atmosphere was provided by bubbling purified nitrogen through the solution.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 5mg of the sample was taken in porcelain crucible for each thermogravimetric experiment.



Fig. 1. Cyclic voltammograms of (a) $[Cd(pipdtc)_2]_2$, (b) $[Cd_2(pipdtc)_4(4,4'-bipy)]$ and (c) [Cd(pipdtc)(2,2'-bipy)]

Results And Discussion

IR Spectral studies

The vC–N has been used as a measure of the contribution of the thioureide group to the structure of the complexes [40]. IR spectra of the complexes show (C –N) bands are lower than the band for parent dithiocarbamates. The reduction in (C –N) (thioureide) for the adducts is attributed to the change in coordination number from 4 to 5 [41]. 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. 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 4,4'-bipyridine, which are observed around 1600 cm⁻¹. The (C –S) bands appear around 1000 cm⁻¹ in all the complexes, without any splitting, supporting the bidentate coordination of the dithiocarbamate to the metal centre [42] Other bands are masked by those due to dithiocarbamate ligand. Important ir bands and analytical data for the adducts are given in Table 1.

Compound			С	%	H%		N%	
	C - N	C - S	Calcd	Found	Calcd	Found	Calcd	Found
$[Cd(nmedtc)_2]_2$	1489	975	23.3	23.1	3.9	3.6	6.8	6.6
$[Cd_2(nmedtc)_4(4,4'-bipy)]$	1485	982	31.8	31.6	4.1	3.9	8.6	8.5
$[Cd(dedtc)_2]_2$	1497	982	29.4	29.1	4.9	4.8	6.9	6.7
$[Cd_2(dedtc)_4(4,4'-bipy)]$	1492	983	37.0	36.7	5.0	4.8	8.6	8.5
$[Cd(pipdtc)_2]_2$	1478	973	33.3	33.0	4.6	4.4	6.5	6.3
$[Cd_2(pipdtc)_4(4,4'-bipy)]$	1474	974	40.0	39.7	4.7	4.5	8.2	8.1
$[Cd(dnpdtc)_2]_2$	1487	980	36.2	36.0	6.0	5.8	6.0	5.9
$[Cd_2(dnpdtc)_4(4,4'-bipy)]$	1482	982	42.1	42.0	5.9	5.7	7.7	7.5
$[Cd(dipdtc)_2]_2$	1486	982	36.5	36.3	5.2	5.0	6.1	6.0
$[Cd_2(dipdtc)_4(4,4'-bipy)]$	1481	981	42.4	42.1	5.2	5.0	7.8	7.7
$[Cd(deadtc)_2]_2$	1484	983	25.5	25.2	4.2	4.0	6.0	5.8
$[Cd_2(deadtc)_4(4,4'-bipy)]$	1478	983	32.7	32.4	4.4	4.2	7.6	7.3

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

Electronic Spectra

 $[Cd(dtc)_2]_2$ complexes prepared in the present study are colourless. The 4,4'-bipyridine adducts are all faint to intense yellow coloured. The electronic spectra of both the parent dithiocarbamates and their adducts show transitions only due to charge transfer. The d–d transitions are absent as Cd(II) is d¹⁰ ion. The ligand transitions of the dithiocarbamate and the charge transfer transition in the adducts are observed in the region 310 - 340nm.

Cyclic voltammetric studies

In the cyclic voltammorgam of $[Cd(pipdtc)_2]$ at a HMDE electrode, a new redox couple (-0.550 V/-0.400 V) is observed [43]. When CV is recorded with a platinum working electrode, the above process is absent. This trend shows that the process **1** (-0.550 V/-0.400 V) might be due to the formation of bimetallic complex such as $[HgCd_2(dtc)_6]$ as follows:

$$Hg(dtc)_2 + 2Cd(dtc)_2 = HgCd_2(dtc)_6$$

It has been reported synthetically, about the formation of bimetallic complexes [44]. Formation of the bimetallic complexes in all the dithiocarbamate complexes during electrochemical studies is due to the inherent nature of the mercury electrode to undergo exchange reaction with the metal dithiocarbamate complexes to ultimately from $Hg(dtc)_2$ and related complexes[45,46]. This is because of soft-soft interaction between Hg and S containing ligands.

However process 2 (-0.800 V/-0.675 V) in the cyclic voltammogram is for the two electron reduction reaction observed before. The process 2 can be written as

$$Cd(dtc)_2 + 2e^- + Hg == 2(dtc)^- + Cd(Hg)$$

The cyclicvoltammogram of $[Cd_2(pipdtc)_4(4,4'-bipy)]$ adduct shows two reductive responses viz., -0.750 V/-0.575 V and -1.125V under indentical conditions. The two reduction processes are identified by process **3** and **4**. Process **3** is a redox couple with a medium voltage separation. The couple does not appear unless a HMDE electrode is used for the CV studies. The response is totally absent when a platinum electrode is used. Therefore the redox couple indentified by process **3** must be due to an electroactive species produced as a result of the interaction of Hg with other species. Similar trends were observed for other 4,4'- bipyridine adducts also.

The important observation is that in the adducts the electron addition process becomes difficult compared to the parent bisdithiocarbamate complexes. This trend is supported by the shift in negative reduction potentials of the adducts compared to the parent dithiocarbamates. This findings clearly indicates the presence of excess electron density on cadmium in the adducts compared to the parent dithiocarbamates. As the electron density increases the electron addition is more difficult and hence a shift in negative reduction potential is observed. The CV study is also carried out on 2,2'-bipyridine analogue for comparison. Of the two type of adducts, 4,4'-bipyridine adducts are showing lower reduction potentials than the 2,2'-bipyridine analogue indicating less effective electron donation compared to 2,2'-bipyridine [47,48]. The cyclicvoltammograms of

 $[Cd(pipdtc)_2]_{2,}$ $[Cd_2(pipdtc)_4(4,4'-bipy)]$ and $[Cd(pipdtc)_2(2,2'-bipy)]$ are given in Fig.1. The cyclic voltammetry data are given in Table 2.

Thermogravimetric analysis

The thermograms obtained for all the 4,4'-bipyridine adducts show a single stage weight loss, which ultimately leads to the formation of CdS around 600°C. The loss of 4,4'-bipyridine is not observed as an independent step. In a comparative analysis, a well defined step associated with the loss of 2,2'-bipyridine with similar end product (CdS) around 600°C has been observed for 2,2'-bipyridine analogue. Also the initial decomposition temperature is lower than 4,4'-bipyridine adducts. This trend supports that, the 4,4'-bipyridine adducts are thermally more stable than the 2,2'-analogues probably because of the dimeric nature. In addition, the TG analysis support the proposed molecular formulae of the complexes. The end products from all the cadmium complexes were confirmed by the bulk thermal decomposition and powder X-ray diffraction data. The proposed structure of the adduct is given in Fig.2.

Table 2. Voltammetric data for the reduction of $Cd(pipdtc)_2$ and its adducts at HMDE in DMF (0.1M Bu_4NClO_4) at $20^{\circ}C$

	Cyclic voltammetry ^a					
Compound	Ep V					
	Ep ^{red}	Ep^{ox}	Epred	Ep ^{ox}		
[Cd(pipdtc) ₂] ₂	-0.800	-0.675	-0.550	-0.400		
$[Cd_2(pipdtc)_4(4,4'-bipy)]$	-1.125		-0.750	-0.575		
[Cd(pipdtc) ₂ (2,2'-bipy)]	-1.250		-0.775	-0.550		

^aHanging mercury drop electrode scan rate = 500 mVs^{-1}



Fig. 2. Structure of the complex [Cd₂(dtc)₄(4,4'-bipy)]

Valence bond parameter calculations

The valence bond method (VBS) can give valuable additional information, if used with chemical common sense because of the interplay of bonding and structural exigencies that influences the interatomic distances in a crystal structure. Valence bond sum (VBS) analysis can be applied to estimate the bond lengths; vice-versa the sum of the bond lengths should give information about the valence of the central metal ion. Hence, VBS studies indirectly prove the correctness of the crystal structures determined. VBS values were calculated for some cadmium complexes from their crystallographic distances reported in the literature, by two procedures [49, 50]. The values obtained with two different sets of R_{ij} values are presented in Table 3.

The results clearly show that VBS values are close to '2', which is equivalent to the formal oxidation state of cadmium in the complexes. No observable changes are seen in BVS values between parent cadmium dithiocarbamates and their adducts, whereas in zinc complexes that differences could be observed significantly [14, 20, 32,]. 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. For the complex $Cd[S_2CN(C_7H_7)(C_2H_2OH)]_2(C_{12}H_8N_2)$, the VBS values are little higher than the expected formal oxidation state of +2. The observed higher value may be due to the increased covalent character. 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. The results proved the statement "Formation of a complex involving metal ion and multidentate ligands represents a compromise between the steric interactions in the ligand and the steric and electronic requirements of the metal ion".

Table 3.	VBS values	for the	cadmium	complexes
----------	------------	---------	---------	-----------

Compound	Vi(OK/B)	Vi(B/OK)	Ref
$[Cd(S_2CN(nPr)_2)_2]_2$	1.97	2.02	38
$[Cd{S_2CN(Me)Bu}_2(C_{10}H_8N_2)]$	1.98	2.02	51
$Cd[S_2CN(C_7H_7)(C_2H_2OH)]_2(C_{12}H_8N_2)$	2.08	2.11	52
$[Cd(S_2CN(C_7H_7)_2)_2(C_5H_5N)]$	1.97	2.01	53
$[Cd_{2}{S_{2}CN(n-Pr)_{2}}_{4}(C_{12}H_{10}N_{4})]$	1.97	2.02	27
[Cd(dedtc)I]	1.98	2.02	54

OK/B = calculated by the Method due to O'Keeffee and Brese [49], B/OK = calculated by the method due to Brese and O'Keeffee [50], $S_2CN(nPr)_2$ = di-n-propyldithiocarbamate anion, $S_2CN(Me)Bu = N$ -butyl-*N*-methyldithio carbamate anion, $S_2CN(C_7H_7)(C_2H_2OH)=N$ -benzyl,*N*-hydroxyethyl)dithiocarbamate anion, $S_2CN(C_7H_7)_2=N,N$ -dibenzyldithiocarbamate anion, $C_{10}H_8N_2 = 2,2$ '-Bipyridine, $C_{12}H_8N_2 = 1,10$ -phenanthroline, $C_{12}H_{10}N_4 =$ Pyridinealdazine, dedtc⁻ = diethyl dithiocarbamate anion, $C_5H_5N =$ Pyridne

Conclusions

Characterization studies were made on dimeric cadmium complexes involving bis (dithiocarbamato)cadmium(II) and 4,4'-bipyridine and results are presented in this paper. IR spectra of the complexes show the contribution of the thioureide form to the structures. UV-Visible spectra of the adducts show weak bands in the region 260 - 320nm only due to charge transfer. The electrochemical studies on the complexes show an increase of electron density on cadmium in the adducts compared to parent cadmium dithiocarbamate complexes. Thermogravimetry tudies show a single step mass loss in all the adducts. VBS values proved the correctness of the crystal structures reported by the crystallographers.

References

- Nieuwenhuizen J., Ellers A. W., Haashoot J.G., Janse S.R., Reedijk J. and Baernads J., The mechanism of zinc(II)-dithiocarbamate-Accelerated Vulcanization uncovered: Theoretical and experimental evidence, J. Am. Chem. Soc., 1999, 121, 163-168.
- [2] McCleverty J. A. and Gill S., Aspect of the inorganic chemistry of rubber vulcanization. Part 3. Anionic cadmium complexes derived from dialkyl dithiocarbamates, 2- Mercapto benzothiazole and its derivatives and dialkyl dithiophosphates and the crystal and molecular structures of [NBuⁿ₄][Cd(S₂CNEt₂)₃], [NEt 4][Cd(C₇H₄NS₂)₃] and [NMe₄] [Cd{S₂P(OPrⁱ)₂}], J. Chem. Soc., Dalton Trans., 1982, 493 503.
- [3] Casa E. E., Sanchez A., Vavo J. B., Garcia-Fontan S., Castellano E. E. and Jones M. M., Cadmium coordination chemistry related to chelate therapy, Inorg. Chim. Acta, 1989, 158, 119 -126.
- [4] Jones M. M. and Jones S.G., Structure and reactivity relationship with therapeutic chelating agents, Inorg. Chim. Acta, 1983, 79, 288 -289.
- [5] Pike R. D., Cui H., Kershaw R., Dwight K., Wold A., Blanton T. N., Wernberg A. A. and Gysling H. J., Preparation of zinc sulfide thin films by ultrasonic spray pyrolysis from bis(diethyldithiocarbamato)zinc, Thin Solid Films, 1993, 224, 221-226.

- [6] Brien P. O'., Bruce D. W. and Hare D. O'., (Eds.), Inorganic Materials, Wiley, New York, 1992.
- [7] Srinivasan N. and Thirumaran S., Effect of pyridine as a ligand in precursor on morphology of CdS nanoparticles, Superlattices and Microstructures, 2012, 51, 912–920.
- [8] Brien P. O'., Otway D. J. and Walsh J. R., Novel precursors for the growth of $-In_2S_3$ trisdialkyldithiocarbamate of indium, Thin Solid Films, 1998, 315, 57 61.
- [9] Bessergenev V. G., Belyi V. I., Rastorgner A. A., Ivanova E. N., Kovalerskaya Y. A., Larinov S.V.,Zemskova S. M., Kirichenko V. N., Nadolinnyi V. A. and Gromilov S. A., Electroluminescent ZnS:Mn films prepared at 220-450°C using complex compounds with sulphur containing ligands,Thin Solid Films, 1996, 279, 135 -139.
- [10] Bessergenev V. G., Ivanova E.N., Kovalevskaya Y.A., Vasilieva I.G., Varand V.L., Zemskova S.M., Larinov S.V., Kolesov B. A., Ayupov B.M. and Logvinenko V.A., Synthesis and properties of ZnS:Eu films grown from volatile compounds, Mater. Res. Bull. 1997, 32, 1403-1410.
- [11] Havel H.J., Semiconductors/Semimetals: Solar Cells, vol. 11, Academic Press, New York, 1975.
- [12] Manohar A., Venkatachalam V., Thirumaran S., Ramalingam K., Bocelli G. and Cantoni A., Synthesis, spectral and single crystal X-ray structural studies on (2,2'- bipyridyl)bis(dimethyldithiocarbamato) Zinc (II)and(1,10phenanthroline)bis(dimethyldithiocarbamato) zinc(II), J. Chem. Crystallogr., 1998, 28, 861-865.
- [13] Subha P. V., Valarmathi P., Srinivasan N., Thirumaran S. and Saminathan K., Effect of size of metal ion on MS_4N_2 chromophore: Synthesis, spectral and single crystal X-ray structural studies on (2,2'-bipyridine)bis(N-cyclohexyl-N-methyldithiocarbamato)M(II)(M = zinc, cadmium), Polyhedron, 2010, 29, 1078 1082.
- [14] Arul Prakasam B., Ramalingam K., Bocelli G., Cantoni A., Arul Prakasam B., Ramalingam K., Bocelli G. and Cantoni A., NMR and fluorescence spectral studies on bisdithiocarbamates of divalent Zn, Cd and their nitrogenousadducts: Single crystal X-ray structure of (1,10-phenanthroline)bis(4methylpiperazinecarbodithioato)zinc(II), Polyhedron, 2007, 26, 4489 – 4493.
- [15] Manohar A. and Ramalingam K., X-ray photoelectron spectral and cyclic voltammetric studies on ZnS₄, ZnS₄N and ZnS₄N₂ chromophores, Main Group Met. Chem., 2001, 24, 789 - 792.
- [16] Thirumaran S., Ramalingam K., Bocelli G. and Cantoni A., Synthesis, Infrared spectroscopic, and cyclic voltammetric studies on 1,10-phenanthroline and 2,2' bipyridine adducts of bis(4-morpholine carbodithioato-s,s')zinc(ii) and single-crystal structure determination of (2,2'-bipyridine)bis(4-morpholinecarbodithioato-s,s') zinc(II), Phosphrous Sulphur, Silicon and the related elements, 2009, 184, 418 426.
- [17] Srinivasan N., Rani P. J. and Thirumaran S., Synthesis and spectral studies on mixed ligand complexes of Cd(II) dithiocarbamates with nitrogen donors: single crystal X-ray structure of bis(4methylpiperidinecarbodithioato-S,S')(1,10-phenanthroline)cadmium(II), J. Coord. Chem., 2009, 62, 1271-1277.
- [18] alarmathi P, Thirumaran S., Rani P. and Ciattini S., Synthesis and spectral studies on nitrogen donor adducts of bis(4-ethylpiperazinecarbodithioato-S,S')M(II) (M = Zn, Cd) and use of adducts of cadmium dithiocarbamate for the preparation of cadmium sulfide, J. Coord. Chem., 20011, 64, 4157-4167.
- [19] Thirumaran S., Ramalingam K., Bocelli G. and Cantoni A., NMR, single crystal X-raydiffraction and cyclic voltammetric studies on 1,10-phenanthroline and 2,2'-bipyridine adducts of bis(morpholin ecarbodithioato-S,S')cadmium(II) with CdS₄N₂ environment, J. Mol. Struct., Communicated.
- [20] Ramalingam K., Uma S., Rizzoli and Marimuthu.G., Supramolecular interactions in high molecular weight bisdithiocarbamate adducts of divalent Zn(II), Cd(II), and Hg(II): spectral, VBS, and single crystal X-ray structural studies on MS₄N₂ chromophores J. Coord. Chem., 2010, 63, 4123 - 4135.
- [21] Srinivasan N., Thirumaran S. and Ciattini S., Effect of position of methyl substituent in piperidinedithiocarbamate on the ZnS₄N chromophore: Synthesis, spectral, valence- bond parameters and single crystal X-ray structural studies on bis(2- methylpiperidine carbodithioato-S,S')-(pyridine)zinc(II) and bis(4-methylpiperidinecarbodithioato-S,S')(pyridine)zinc(II), J Mol. Struct., 2009, 936, 234 – 238.
- [22] Srinivasan N., Thirumaran S. and Ciattini S, Synthesis and crystal structures of diimine adducts of Cd(II) tetrahydroquinolinedithiocarbamate and use of (1,10 phenanthroline) bis(1,2,3,4-tetrahydroquinoline carbodithioato-S,S')-cadmium(II) for the preparation of CdS nanorods, J. Mol. Struct., 2012,1026,102 107.

- [23] Ajibade P. A. and Onwudiwe D.C., Synthesis, characterization and thermal studies of 2, 2'- bipyridine adduct of bis- (*N*-alkyl-*N*-phenyldithiocarbamato-*S*, *S*)cadmium(II),J. Mol. Struct.,(in press).
- [24] Manohar A., Ramalingam K., Bocelli G. and Righi L., Synthesis, spectral and cyclic voltammetric studies on(4,4'-bipyridyl)bis(di(2-hydroxyethyl)dithiocarbamato)zinc(II) and (4,4'-bipyridyl)bis(bis(N-methyl, Nethanol ditiocarbamato)zinc(II) and their X- ray crystal structures, Inorg. Chim. Acta, 2001, 314, 177-183.
- [25] Manohar A., Ramalingam K. and Bocelli G., Characterization studies on 2:1 adducts involving zinc(ii)dithiocarbamates and 4,4'-bipyridine with ZnS₄N environment Materials science Poland, Communicated.
- [26] Marimuthu G., Ramalingam K. and C. Rizzoli., Synthesis, spectral, thermal and BVS investigations on ZnS₄N^N/N coordination environment: Single crystal X-ray structures of bis(dibenzyldithiocarbamato)(N^N)Zinc(II) complexes (N^N=1,10-phenanthroline,tetramethyl ethylene diamine and 4,4'-bipyridine), Polyhedron, 2010, 29, 1555 – 1560.
- [27] Popluakhin P. and Tiekink E. R.T., (#-2-Pyridinealdazine- $\pi^4 N, N': N'', N'''$)bis[bis(N, N-di-n-propyldithiocarbamato- $\pi^2 S, S'$)cadmium(II)], Acta Cryst. 2008, E64,m1176 m1177.
- [28] Thirumaran S, Ramalingam K, Bocelli G. and Cantoni A., Spectral and single crystal X- ray structural studies on disulfide complexes: reaction of bis(dialkyldithiocarbamato) M(II) with iodine and crystal structure determination of diiodo(bipiperidinethiuram disulfide)M(II) (M = Zinc, Cadmium), Polyhedron, 2000, 19, 1279 –1282.
- [29] Saravanan M., Arul Prakasam B., Ramalingam K., Bocelli G., and Cantoni A., $M(S)_2(I)_2$ (M = Zn, Cd) and Hg(S)₃I coordination environment of transition metal complexes- synthesis, spectral, and single crystal X-ray structural investigations, Z. Anorg. Allg. Chem., 2005, 631, 1688-1692.
- [30] Manohar A., Ramalingam K., Bocelli G. and Cantoni A., Synthesis, 2:1 adducts involving cadmium dithiocarbamates and 4,4'-bipyridine. Single crystal X-ray structural studies on bis(piperidine carbodithioato-S,S')cadmium(II)benzene solvate, Polish J. Chem., 2005,79, 671- 678.
- [31] Manohar A., Ramalingam K., Karpagavel K. and Kulandaisamy A., Bis(di(2-hydroxyl ethyl)dithiocarbamato)Cadmium(II) with N- donor ligands: Synthesis, Spectral Thermal studies and Bond Valence Sum(BVS) Analysis, Intl. J. ChemTech Res., 2012, 4, 1023-1032.
- [32] Manohar A., Ramalingam K., Bocelli G. and Cantoni A., Bond Valence Sum (BVS) of metal ligand bond lengths in some Zn(II), Cd(II) dithiocarbamate complexes and their adducts, Polish J. Chem., 2001, 75, 147-151.
- [33] Manohar A., Ramalingam K., Karpagavel K. and Bocelli G., Crystallographic distancesbased Bond Valence Sum (BVS) analysis on Nickel(II) complexes containing Ni-S and Ni-P bonds, Advanced Materials Research, 2012, 584, 84 – 87.
- [34] Thirumaran S., Venkatachalam V., Manohar A., Ramalingam K., Bocelli G. and Cantoni A., Synthesis and characterization of bis(N-methyl, N- ethanoldithiocarbamato) M(II) (M=Zn,Cd,Hg) and bis(N,N'-(Iminodiethylene)bis(phthalimide)dithiocarbamato) M(II) (M=Zn,Cd,Hg)complexes and single crystal Xray structure determination of bis(di(2-hydroxyethyl) dithiocarbamato) zinc(II) complex, J. Coord. Chem., 1998, 44, 281-288.
- [35] Thirumaran S., Ph.D. Thesis, Annamalai University, Annamalainagar, India.
- [36] Domenicano A., Torelli L., Vaciago A. and Zambonelli., Structural studies of metal dithiocarbamates. PartIV. The crystal and molecular structure of cadmium(II)NN- diethyldithio carbamate 1968, 1351-1361, J. Chem. Soc., 1968, 1351-1361.
- [37] Marcotrigiano G., Pellacani G. C. and Preti C. J., Piperidine, thiomorpholine-4 and methylpiperazine-4carbodithioate transition metal complexes. Inorg. Nucl. Chem., 1974, 36, 3709 - 3712.
- [38] Jian F., Wang Z., Bai Z., You X., Fun H. K. and Chinnakali K., Structure of bis(dipropyldithiocarbamate) cadmium(II), [Cd₂(n-Pr₂dtc)₄] (dtc = dithiocarbamate), J. Chem. Crystallogr, 1999, 29, 227-231.
- [39] Jain F. F., Wang Z.W., Fun H. K, Bai Z. P. and You X. Z., A binuclear cadmium(II) complex: bis[bis(N,N-diisopropyldithiocarmato)cadmium(II)], Acta Crystallogr. Sect. *C*, 1999, 55, 174-176.
- [40] Baggio R., Frigerio A., Halac E. B., Vega D. and Perec M., Anionic halide and isothiocyanate adducts of zinc and cadmium dithiocarbamtes, J. Chem. Soc., Dalton Trans., 1992, 549-554.

- [41] Hassaan A.M.A., Soliman E.M., El-Roudi A.M., Adduct formation by nickel(II) complexes of Smethylhydrazinecarbodithioate schiff basses with 2,2'- bipyridyl and1,10-phenanthroline, Polyhedron, 1989, 8, 925 - 927.
- [42] Bonati F. and Ugo R., Organotin(IV) disubstituted dithiocarbamates, J. Organometal. Chem., 1967, 10, 257-268
- [43] Bond A.M., Colton R., Dillon M.L., Hollen Kamp A.F., Moir J.E., Reversible electrode processes involving multistep mechanisms for cdmium dithiocarbamates and diseleocarbamates at mercury electrodes, Inorg. Chem., 1985, 24, 1591 1597.
- [44] Aggarwall R.C., Singh B. and Singh M.K., J. Indian Chem. Soc., 1982, 59, 269.
- [45] Bond A.M., Thackeray J.R. and Casey A.T., Polarographic behaviours of bis(pi- cyclopentadienyl)-N,Ndialkyldithiocarbamatovanadium(IV)tetraphenylborates inacetone. Example of an ECEC mechanisms, Inorg. Chem., 1973, 12, 887 - 893.
- [46] Randle T.H., Cardwell J. J. and Magee R. J., Behaviours of disubstituted dithiocarbamates at the mercury electrode, Aust. J. Chem. 1975, 28, 21-31.
- [47] Nadijo L. and Saveant J. M., Dimerization, disproportionation and ECE mechanisms in the reduction of imines in acetonitrile and dimethylformamide J. Electroanal. Chem. 1971, 33, 453 -461.
- [48] Andriense C. P., Nadjo L. and Saveant J.M.,Electrodimerization: VII. Electrode and solution electron transfers in the radical substrate coupling mechanism discriminative criteria from the other mechanisms in voltammetric studies(Linear, sweep, rotating disc, polarography) J. Electroanal. Chem., 1973, 42, 223 -242.
- [49] Keeffe M. O. and Brese N. E., Atom sizes and bond lengths in molecules and crystals, J. Am. Chem. Soc., 1991, 113, 3226 - 3229.
- [50] rese N. E. and Keeffe M.O'., Bond-valence parameters for solids, Acta Crystallogr. Sec. B., 1991, 47, 192-197.
- [51] Samaluddin N. A., Baba I., Mohamed Tahir M.I. and Tiekink E R.T., (2,2'- Bipyridyl-*²N,N') bis(N-butyl-N-methyldithiocarbamato-*²S,S')cadmium(II), ActaCryst. 2011, E67, m384-m385.
- [52] Saravanan M., Ramalingam R., Arulprakasam B., Bocelli G., Cantoni A., and Tiekink E. R.T, Crystal structure of bis[(*N*-benzyl,*N*-hydroxyethyl)-dithiocarbamato] (1,10-phenanthroline) cadmium(II), Cd[S₂CN(C₇H₇)(C₂H₂OH)]₂(C₁₂H₈N₂) Z. Kristallogr., 2005, NCS 220, 477-478.
- [53] Wei F W., Yin X., Zhang W.G., Fan J., Jiang X.H., and Wang S.L, Crystal structure of (pyridine-*N*)bis(*N*,*N* dibenzyldithiocarbamato)cadmium(II), Cd(C₅H₅N)[S₂CN- (C₆H₅CH₂)₂]₂, Z. Kristallogr. 2005, NCS 220, 417- 419.
- [54] Kropidlowska A., Chojnacki J. and Becker B., Tetraethylammoniumbis(N,N'-diethyl- dithiocarbamato) iodocadmate(II), Acta Cryst., 2006, C62, m95 - m96.
