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

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Abstract: Cyclic voltammetric, thermal and spectral characterization studies were made on (4,4’-bipyridine) bis(bis(dithiocarbamato)cadmium(II)), [Cd₂(dtc)₂(4,4’-bipy)], (dtc=nmedtc, N-methyl,N-ethanolidithiocarbamate; dndtc, di-n-propyldithiocarbamate; dipdtc, diisopropyldithiocarbamate; pipdtc, piperidine dithiocarbamate; dedtc, diethylidithiocarbamate; 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 νC–N(thiourea) for the adducts is attributed to the shift 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.

Introduction

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(S₂NRCR’R’’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, cyclic voltammetry 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, tetramethylenelediamine (TMED),were reported extensively. [12-23]. All the adducts are containing discrete molecular units with MS₅N₂ (M= Zn,Cd) chromophore in a distorted octahedral geometry. X-ray photoelectron spectroscopy (XPS), C¹³ and H¹NMR 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, [Cd₂S₂CN(n-Pr)₂]₄(C₁₂H₁₀N₄)₁₋₂ (S₂CN(nPr)₂ = di-n-propylidithiocarbamate 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 cadmium 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 [Cd₂(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(dipdtc)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 [Cd₂(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)]**

[Cd₂(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 [Cd₂(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 ± 1°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.
All reagents and solvents employed were commercially available, high-purity materials (E-Merck) and were used as supplied without further purification.

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 v(C –N) bands are lower than the band for parent dithiocarbamates. The reduction in v(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 v(C –N) value. Also this observation is an indication of increased electron density on the cadmium in the adducts. The thioureide v(C –N) band is well differentiated from the ring frequencies associated with 4,4'-bipyridine, which are observed around 1600 cm⁻¹. The v(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.
Electronic Spectra

[Cd(dtct)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 voltammogram 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 [HgCd2(dtct)4] as follows:

$$\text{Hg(dtct)}_2 + 2\text{Cd(dtct)}_2 \rightleftharpoons \text{HgCd}_{2}\text{(dtct)}_4$$

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(dtct)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

$$\text{Cd(dtct)}_2 + 2e^- + \text{Hg} \rightleftharpoons 2(\text{dtct})^- + \text{Cd(Hg)}$$

The cyclicvoltammogram of [Cd(pipdtc)2(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

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

<table>
<thead>
<tr>
<th>Compound</th>
<th>νC - N</th>
<th>νC - S</th>
<th>C% Calcd</th>
<th>C% Found</th>
<th>H% Calcd</th>
<th>H% Found</th>
<th>N% Calcd</th>
<th>N% Found</th>
</tr>
</thead>
<tbody>
<tr>
<td>[Cd(nmedtc)2]2</td>
<td>1489</td>
<td>975</td>
<td>23.3</td>
<td>23.1</td>
<td>3.9</td>
<td>3.6</td>
<td>6.8</td>
<td>6.6</td>
</tr>
<tr>
<td>[Cd4(nmedtc)4(4,4'-bipy)]</td>
<td>1485</td>
<td>982</td>
<td>31.8</td>
<td>31.6</td>
<td>4.1</td>
<td>3.9</td>
<td>8.6</td>
<td>8.5</td>
</tr>
<tr>
<td>[Cd(dedtc)2]2</td>
<td>1497</td>
<td>982</td>
<td>29.4</td>
<td>29.1</td>
<td>4.9</td>
<td>4.8</td>
<td>6.9</td>
<td>6.7</td>
</tr>
<tr>
<td>[Cd4(dedtc)4(4,4'-bipy)]</td>
<td>1492</td>
<td>983</td>
<td>37.0</td>
<td>36.7</td>
<td>5.0</td>
<td>4.8</td>
<td>8.6</td>
<td>8.5</td>
</tr>
<tr>
<td>[Cd4(pipdtc)4]2</td>
<td>1478</td>
<td>973</td>
<td>33.3</td>
<td>33.0</td>
<td>4.6</td>
<td>4.4</td>
<td>6.5</td>
<td>6.3</td>
</tr>
<tr>
<td>[Cd4(dipdtc)4(4,4'-bipy)]</td>
<td>1474</td>
<td>974</td>
<td>40.0</td>
<td>39.7</td>
<td>4.7</td>
<td>4.5</td>
<td>8.2</td>
<td>8.1</td>
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<td>[Cd4(dnpdtc)4(4,4'-bipy)]</td>
<td>1487</td>
<td>980</td>
<td>36.2</td>
<td>36.0</td>
<td>6.0</td>
<td>5.8</td>
<td>6.0</td>
<td>5.9</td>
</tr>
<tr>
<td>[Cd4(dnpdtp)4(4,4'-bipy)]</td>
<td>1482</td>
<td>982</td>
<td>42.1</td>
<td>42.0</td>
<td>5.9</td>
<td>5.7</td>
<td>7.7</td>
<td>7.5</td>
</tr>
<tr>
<td>[Cd4(dipdtc)4(4,4'-bipy)]</td>
<td>1486</td>
<td>982</td>
<td>36.5</td>
<td>36.3</td>
<td>5.2</td>
<td>5.0</td>
<td>6.1</td>
<td>6.0</td>
</tr>
<tr>
<td>[Cd4(dedtc)4]2</td>
<td>1481</td>
<td>981</td>
<td>42.4</td>
<td>42.1</td>
<td>5.2</td>
<td>5.0</td>
<td>7.8</td>
<td>7.7</td>
</tr>
<tr>
<td>[Cd4(deadtc)4(4,4'-bipy)]</td>
<td>1484</td>
<td>983</td>
<td>25.5</td>
<td>25.2</td>
<td>4.2</td>
<td>4.0</td>
<td>6.0</td>
<td>5.8</td>
</tr>
<tr>
<td>[Cd4(deadt)4(4,4'-bipy)]</td>
<td>1478</td>
<td>983</td>
<td>32.7</td>
<td>32.4</td>
<td>4.4</td>
<td>4.2</td>
<td>7.6</td>
<td>7.3</td>
</tr>
</tbody>
</table>
[Cd(pipdtc)$_2$], [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$_4$NClO$_4$) at 20°C**

<table>
<thead>
<tr>
<th>Compound</th>
<th>Cyclic voltammetry$^a$</th>
<th>Ep V</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Ep$_{red}$</td>
<td>Ep$_{ox}$</td>
</tr>
<tr>
<td>[Cd(pipdtc)$_2$]$_2$</td>
<td>-0.800</td>
<td>-0.675</td>
</tr>
<tr>
<td>[Cd$_2$(pipdtc)$_4$(4,4'-bipy)]</td>
<td>-1.125</td>
<td>-0.750</td>
</tr>
<tr>
<td>[Cd(pipdtc)$_2$(2,2'-bipy)]</td>
<td>-1.250</td>
<td>-0.775</td>
</tr>
</tbody>
</table>

$^a$Hanging mercury drop electrode scan rate = 500 mVs$^{-1}$

**Fig. 2. Structure of the complex [Cd$_2$(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 VBS 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\(_2\)CN(C\(_6\)H\(_5\))\(_2\)(C\(_2\)H\(_2\)OH)]\(_2\)(C\(_{12}\)H\(_8\)N\(_2\)), 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

<table>
<thead>
<tr>
<th>Compound</th>
<th>V(OK/B)</th>
<th>V(B/OK)</th>
<th>Ref</th>
</tr>
</thead>
<tbody>
<tr>
<td>[Cd(S(_2)CN(nPr)(_2))(_2)]</td>
<td>1.97</td>
<td>2.02</td>
<td>38</td>
</tr>
<tr>
<td>[Cd(S(_2)CN(Me)Bu)(<em>2)(C(</em>{10})H(_8)N(_2))]</td>
<td>1.98</td>
<td>2.02</td>
<td>51</td>
</tr>
<tr>
<td>Cd[S(_2)CN(C(_6)H(_5))(_2)(C(_2)H(_2)OH)](<em>2)(C(</em>{12})H(_8)N(_2))</td>
<td>2.08</td>
<td>2.11</td>
<td>52</td>
</tr>
<tr>
<td>[Cd(S(_2)CN(C(_6)H(_5))(_2)](_2)(C(_2)H(_4)N)]</td>
<td>1.97</td>
<td>2.01</td>
<td>53</td>
</tr>
<tr>
<td>[Cd(_2)[S(_2)CN(n-Pr)(_2)](<em>2)(C(</em>{12})H(_8)N(_4))]</td>
<td>1.97</td>
<td>2.02</td>
<td>27</td>
</tr>
<tr>
<td>[Cd(dedtc)I]</td>
<td>1.98</td>
<td>2.02</td>
<td>54</td>
</tr>
</tbody>
</table>

OK/B = calculated by the Method due to O’Keeffe and Brese [49]. B/OK = calculated by the method due to Brese and O’Keeffe [50]. S\(_2\)CN(nPr)\(_2\) = di-n-propyldithiocarbamate anion, S\(_2\)CN(Me)Bu = N-butyl-N-methyldithio carbamate anion, S\(_2\)CN(C\(_6\)H\(_5\))(C\(_2\)H\(_2\)OH) = N-benzyl,N-hydroxyethyl) dithiocarbamate anion, S\(_2\)CN(C\(_6\)H\(_5\))\(_2\) = N,N-dibenzyl dithiocarbamate anion, C\(_{10}\)H\(_8\)N\(_2\) = 2,2’-Bipyridine, C\(_{12}\)H\(_8\)N\(_2\) = 1,10-phenanthroline, C\(_{12}\)H\(_{16}\)N\(_4\) = Pyridinealdazine, dedtc = diethyl dithiocarbamate anion, C\(_3\)H\(_8\)N = Pyridine

### 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 studies show a single step mass loss in all the adducts. VBS values proved the correctness of the crystal structures reported by the crystallographers.

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