X-RAY PHOTOELECTRON SPECTRAL AND CYCLIC VOLTAMMETRIC STUDIES ON ZnS_4, ZnS_4N AND ZnS_4N_2 CHROMOPHORES

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ABSTRACT

X-ray photoelectron spectral and cyclic voltammetric studies were made on the complexes such as $Zn(dmdtc)_2$ (**1**), $[Zn(dmdtc)_2(2,2'\text{-bipy})]$ (**2**), $[Zn_2(dmdtc)_4(4,4'\text{-bipy})]$ (**3**), $[Zn(dmdtc)_2(1,10\text{-phen})]$ (**4**) $Zn(deadtc)_2$ (**5**), $[Zn_2(deadtc)_4(4,4'\text{-bipy})]$ (**6**) (dmdtc=dimethyldithiocarbamate, deadtc=di(2-hydroxyethyl)dithiocarbamate, 2,2'-bipy = 2,2'-bipyridine, 4,4'-bipy = 4,4'-bipyridine, 1,10-phen = 1,10-phenanthroline). The $Zn2p_{3/2}$ binding energy value for the 2,2'-bipyridine adduct was significantly different (1021.0 eV), from that of the parent bisdithiocarbamate, indicating increased electron density on the metal ion in the adducts. For the 4,4'-bipyridine adduct, the binding energy value of S2p electrons is 163.5 eV, clearly indicating a dearth of electron density on sulphur. The cyclic voltammetric studies indicated a significant increase in reduction potential for the adducts compared to the parent bisdithiocarbamate. The observation is a proof of increased electron density on zinc ion in the adducts.

INTRODUCTION

Tetrahedral complexes of divalent zinc are known to expand their coordination shells by adding neutral nitrogenous ligands[1-3]. The additional ligand shows its steric and electronic effects structurally on the complex formed[4-9]. X-ray photoelectron spectral and cyclic voltammetric studies were carried out on bis(piperidinedithiocarbamato)zinc(II) and its 2,2'-bipyridine, 1,10-phenanthroline adducts in our laboratory[10]. XPS studies showed a significant reduction in binding energy values of S2p electrons in 2,2'-bipyridine and 1,10-phenanthroline adducts compared to the parent dithiocarbamate. The increased electron density on zinc on adduct formation is shown by the reduction in $Zn2p_{3/2}$ binding energy. It was also confirmed by cyclic voltammetric studies. The electron addition process for the adducts occur at higher potential than the value observed for the parent dithiocarbamate, which clearly shows increased electron density on zinc in the adducts.

In continuation of our interest on ZnS_4 chromophores, the present study was undertaken to determine the electron density on the zinc ion of bis(dimethyldithiocarbamato)zinc(II) and its adducts. Recently, the crystal structures of $[Zn(dmdtc)_2(2,2'\text{-bipy})]$ and $[Zn(dmdtc)_2(1,10\text{-phen})]$ have been reported from our laboratory[11].

MATERIALS AND METHODS

All the reagents and solvents employed were commercially available analytical grade materials, used as supplied without further purification.

XPS studies

XP spectra were recorded on a VG mark II ESCA spectrometer equipped with twin anodes, aluminium and magnesium. Samples were studied using Mg-Kα radiation and the resolution of the instrument was 0.2 eV. The overall minimum peak width was 0.8 eV. Samples were well powdered and packed tightly on nickel stubs. All measurements were made at room temperature (25°C) and at 10^{-9} Torr pressure. The peaks were calibrated by the methods described earlier for the dithiocarbamato complexes[12].

Cyclic voltammetry

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, dichloromethane 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.

Preparation of $[Zn(dmdtc)_2(2,2'\text{-bipy})]$(2) and $[Zn(dmdtc)_2(1,10\text{-phen})]$(4)

The parent bis(dimethyldithiocarbamato)zinc(II) was prepared by established procedure[1]. The adducts were prepared by adding hot solutions of 2,2'-bipyridine(310mg, 2mmol), (or) 1,10-phenanthroline (400mg, 2mmol) in benzene to a hot solution of bis(dimethyldithiocarbamato)- zinc(II)(1mmol) in benzene. The resulting solution was allowed to cool. Yellow precipitate of the adduct separated out and analysed to the proposed formula. C,H,N: found (calcd.) for (**2**)%C:41.4(41.6), %H:4.3(4.4), %N:12.0(12.1) and for compound (**4**) %C44.2(44.5), %H:3.9(4.1), %N:11.3(11.5).

Preparation of [$Zn_2(dmdtc)_4$(4,4'-bipy)](3) and [$Zn_2(deadtc)_4$(4,4'-bipy)](6)

The adduct was prepared by adding a hot solution of 4,4'-bipyridine(155mg, 1mmol) in benzene to a hot solution of bis(dimethyldithiocarbamato)zinc(II) (2mmol) in benzene. The resulting yellow solution was left for evaporation at room temperature. After two days yellow crystals separated out. The crystals analyzed to [$Zn_2(dmdtc)_4$(4,4'-bipy)]. Similar method was employed to prepare [$Zn_2(deadtc)_4$(4,4'-bipy)] in ethanol. C,H,N: found (calcd.) for compound **(3)** %C: 34.2 (34.4), %H: 4.0(4.2), %N:10.6 (10.9) and for compound **(6)** % C:35.4 (35.7), %H:4.6 (4.8), %N: 8.1 (8.3).

RESULTS AND DISCUSSION

XPS studies

Important binding energy values for the complexes are given in Table 1. The binding energy of the N1s electrons in the parent dithiocarbamate is observed at 400.1 eV. In the case of adducts, presence of amine nitrogen along with the nitrogens of the dithiocarbamate ligand makes the comparison difficult. The N1s binding energy of $Zn(phen)_2(ClO_4)_2$ was observed in the same region[13].

TABLE 1. BE's (FWHM)* and binding energy shifts (eV)**

Compound	1	ΔE	2	ΔE	3	ΔE	4	ΔE
$Zn2p_{3/2}$	1022.1(1.0)	+2.4	1021.0(1.1)	+1.3	1022.0(1.2)	+2.3	1022.0(1.1)	+2.3
S2p	162.7(1.1)	-2.1	162.5(1.0)	-2.3	163.5(1.2)	-1.3	162.8(1.1)	-2.0
N1s	400.1(1.1)	-1.5	400.0(1.1)	-1.6	400.2(1.8)	-1.4	400.0(1.1)	-1.6

* Full width at half maximum

** Shift in binding energies with respect to 'bare' atom quoted in the operation manual for the VG ESCA mark II spectrometer, count rate 10^3 counts/sec

The S2p binding energy was observed at 162.7 eV for $[Zn(dmdtc)_2]_2$. For the adducts involving 2,2'-bipyridine and 1,10-phenanthroline, the binding energies are 162.5 and 162.8 eV respectively. But for the 4,4'-bipyridine adduct the binding energy is 163.5 eV clearly indicating a dearth of electron density on sulphur. This observed effect is due to a geometrical distortion forced on the tetrahedrally coordinated ZnS_4 chromophore to form a distorted penta coordinated ZnS_4N chromophore.

The BE values associated with $Zn2p_{3/2}$ electron in the parent compound is 1022.1 eV close to the value reported for $Na_2Zn(pen)_2.4H_2O$ (pen =penicillamine)[14]. On adduct formation, the BE decreased considerably for the 2,2'-bipyridine adduct to the tune of 1.0 eV. The observed shift in binding energy very clearly shows the increased electron density on the metal in the adducts. But the BE values for the other adducts do not show appreciable increase with respect to the parent dithiocarbamate.

The metal-dithiocarbamate complexes are known to be highly covalent with effective bonding[15-17]. Unlike the truly planar nickel-dithiocarbamate complexes, tetrahedral zinc dithiocarbamate complexes are dimeric because of less effective charge transfer from the ligands to the metal. On adduct formation, the zinc dithiocarbamato complexes are hexacoordinated and the electron density on zinc increases relatively due to the chelating nitrogenous bases. Weakening of Zn-S bond on adduct formation is shown by the reduction in S2p binding energy. The increase in electron density on zinc, on adduct formation is shown by the reduction in $Zn2p_{3/2}$ binding energy. Therefore, the present XPS study supports the weakening of Zn-S bond and increase of electron density on zinc as a result of adduct formation.

Cyclicvoltammetric studies

The cyclicvoltammograms on the parent zinc dithiocarbamates and their adducts were recorded in CH_2Cl_2 with TBAP as supporting electrolyte. The cyclicvoltammetric data are given in Table 2. The study is restricted mainly to the bis(dimethyldithiocarbamato)zinc(II) complex and its adducts. For comparison, cyclicvoltammograms of a few other dithiocarbamato complexes also were recorded.

TABLE 2. Voltammetric data for the reduction of $[Zn(dtc)_2]_2$ and its adducts at HMDE in dichloromethane (0.1M Bu_4NClO_4) [a]Hanging mercury drop electrode; scan rate = 500 mVs^{-1}

Compound	Cyclic voltammetry[a]Ep v			
	Ep^{red}	Ep^{red}	Ep^{ox}	Ep^{ox}
$[Zn(dmdtc)_2]_2$	-1.050	-0.750	-0.625	-0.375
$[Zn(dmdtc)_2$(1,10-phen)]	-1.400	-1.025	-0.675	-
$[Zn(dmdtc)_2$(2,2'-bipy)]	-1.575	-1.100	-0.725	-
$[Zn_2(dmdtc)_4$(4,4'-bipy)]	-1.475	-0.925	-0.675	-
$[Zn(deadtc)_2]_2$	-1.000	-0.750	-0.675	-0.400
$[Zn_2(deadtc)_4$(4,4'-bipy)]	-1.550	-0.950	-0.750	-

A two electron reduction process with the formation of zinc amalgam Zn(Hg) has been proposed[18]

$$Zn(dtc)_2 + 2e^- \xrightarrow{Hg} 2dtc^- + Zn(Hg) \quad (I)$$

The CV responses for $[Zn(dmdtc)_2]_2$ and $[Zn(deadtc)_2]_2$ at -1.050 V and -1.00 V respectively correspond to the process(I). Oxidation of Zn(Hg) in the reverse scan was observed at 0.375 V and 0.400V for the dimethyl and diethanol analogues. The process envisaged is:

$$Zn\,(Hg) \longrightarrow Zn^{2+} + 2e^- + Hg$$

The processes corresponding to -0.750/-0.625V and -0.750./0.675 are ascribed to the reaction:

$$dtc^- + \_Hg \longrightarrow \_Hg(dtc)_2 + e^-$$

The present set of data on the parent dithiocarbamates is completely in line with the earlier observations[18,19]. In the case of the adducts, two reductive responses are observed in general. $[Zn(dmdtc)_2(1,10\text{-phen})]$ shows a couple at -1.025/-0.675 and at -1.400V. Of the two processes, the couple at -1.025/-0.675 was absent when a platinum electrode was used. The observation indicates the involvement of an electroactive species produced as a result of the interaction of mercury electrode with the complex as envisaged earlier[20,21]. But the stoichiometry could not be established because attempts to synthesise the bimetallic complex were not successful.

Formation of the bimetallic complexes in all the dithiocarbamate complexes during electrochemical studies is due to the inherent nature of mercury electrode to undergo exchange reaction with metal dithiocarbamate complexes to form $Hg(dtc)_2$ and related complexes ultimately[22-24]. This is because of soft-soft interaction between Hg and S containing ligands.

The reduction process corresponding to -1.050 V for $[Zn(dmdtc)_2]_2$ can be easily ascribed to the $2e^-$ reduction on the basis of many earlier reports[18]. In the case of $[Zn(dmdtc)_2(1,10\text{-phen})]$, the process corresponding to -1.400V must be due to the electron addition process such as,

$$[Zn(dmdtc)_2(1,10\text{-phen})]+2e^-=[Zn(dmdtc)_2(1,10\text{-phen})]^{2-}$$

Controlled potential electrolysis could not be carried out because the response was observed very close to the solvent decomposition potential. The absence of the corresponding oxidative couple is noteworthy.

Similarly, for the 2,2'-bipyridyl and 4,4'-bipyridyl adducts, the reduction of electroactive species involving the bimetallic species were observed at -1.100/-0.725V, -0.925/-0.675V respectively. The $2e^-$ reduction processes were observed at -1.575 and -1.475V for the two complexes. The most important observation is the significant increase in the reduction potential for the adducts compared to the parent dithiocarbamate. Similarly, the 2,2'-bipyridyl adduct shows the largest reduction potential. XPS studies on the complexes showed increase of electron density on zinc and decrease of electron density on S in (**2**) and (**3**) respectively. However, the CV studies showed an increase of electron density on zinc in all the adducts significantly.

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