

## Studies on Some Organic Disulphide Complexes of Metals

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Complexes of some solid and stable di (1-substituted tetrazoline)-5,5'-disulphides have been prepared and investigated using various physico-chemical methods such as microanalysis, conductometric, magnetic, infrared, far infrared, UV and visible spectroscopy with Zr(IV), VO(IV), Fe(III), Ru(III), Cr(III), Bi(III), Co(II) and Hg(I) at pH 6. All complexes are generally insoluble in common organic solvent but fairly soluble in DMF. *Trans*-octahedral configuration for Zr(IV), Ru(III) and Cr(III); square planar for Co(II) and Pd(II), polymeric tetrahedral for Hg(I), square pyramidal for VO(IV) and distorted octahedral geometry for Bi(III) having inert pair electrons at one of the corners of the octahedral sites. The crystal field parameter ( $\beta$ ) for Cr(III) complex has been calculated and found to be 0.96 which puts these ligands into strong end of nephelauxetic series.

### INTRODUCTION

Organic disulphides are very important class of compounds having great biological significance<sup>1-3</sup> and several types of organic disulphides have been found in sulphur containing enzymes<sup>4</sup>, wool<sup>5</sup>, garlic<sup>6,7</sup> and a number of foodstuffs<sup>8,9</sup>. In view of such biological importance of disulphides and absence of adequate available data on metal-disulphide linkage to provide a fairly coherent picture of the donor acceptor relationship between sulphur and metal ions, the present work is undertaken. Thus, some solid and stable disulphides such as di(1-phenyl tetrazoline)-5,5'-disulphide (TDS) and di(1-metatolyl tetrazoline)-5,5'-disulphide (t-TDS) have been selected and their complexing behavior has been investigated using Zr(IV), VO(IV), Bi(III), Cr(III), Fe(III), Ru(III), Co(II), Pd(II) and Hg(I) ions. The preparation, characterisation, investigation of structures and nature of bonding in complexes have been reported in this paper.

### EXPERIMENTAL

All chemicals used were chemically pure grade. 1-Substituted tetrazoline-5-thione was prepared by the method of Leiber and coworker<sup>10</sup>. The ligands were prepared by adding ethanolic iodine solution into alcoholic solution of above formed compounds with stirring till decolourisation occurred. It was warmed on water bath for twenty minutes and cooled. The solid separated was filtered and dried.

The complexes were prepared generally by refluxing the 1 : 3 (molar ratio) mixture of alcoholic metal ions solution to ligand solution (in ethylacetate for Cr(III) and VO(IV) ions and in C<sub>6</sub>H<sub>6</sub> for other ions) with

few drops of mineral acids upto 2–3 hrs. But M:L ratio kept 1:2 for Pd(II) and Bi(III) complexes. The pH of mixture solution was adjusted to *ca.* 6 using corresponding mineral acids and NaOH solutions. Then the volume of solution was evaporated *ca.* 20 ml and cooled. The separated complexes were filtered, washed with absolute ethanol and dried over CaCl<sub>2</sub> in a vacuum desiccator.

## RESULTS AND DISCUSSION

Di(1-substituted tetrazoline)-5,5'-disulphide contains several donor sites and may act as monodentate, bidentate or tridentate ligands. Moreover, the ligands TDS and t-TDS form fairly stable complexes with Zr(IV), VO(IV), Bi(III), Cr(III), Fe(III), Ru(III), Co(II) and Hg(I) ions which are insoluble in common organic solvents such as methanol, ethanol, benzene, carbon-tetrachloride, nitrobenzene, chloroform but fairly soluble in DMF. Only Pd(II) complex was soluble in common organic solvents and Hg(I) complex was insoluble even in DMF. The magnetic moment measurement indicates the paramagnetic nature of VO(IV), Cr(III), Fe(III), Ru(III) and Co(II) complexes at room temperature (Table 1). Moreover, the low magnetic moment of VO(IV) complexes is most probably due to partial overlapping of metal-metal bonding arising from overlapping of d-orbitals of neighbouring d-orbital vanadium atom<sup>11</sup>. Besides this, the high melting point of Hg(I) complexes indicates polymeric nature and diamagnetic nature of Hg(I) complexes suggests existence of Hg<sub>2</sub><sup>++</sup> ion having metal-metal bonding. All other complexes are found to be diamagnetic as expected.

The analytical data of all complexes have been given in Table 1. The hydrated complexes do not lose in weight below 80–90°C indicating the water molecules are either coordinated or closely associated in crystal lattice. Only [Pd(t-TDS)<sub>2</sub>Cl<sub>2</sub>].3H<sub>2</sub>O, [Co(t-TDS)<sub>2</sub>(ac)<sub>2</sub>].2H<sub>2</sub>O and [Co(t-TDS)<sub>2</sub>(H<sub>2</sub>O)<sub>2</sub>](ClO<sub>4</sub>)<sub>2</sub>.3H<sub>2</sub>O lose in weight below 90° suggesting the presence of crystal water.

The electronic spectra of di(1-substituted tetrazoline)-5,5'-disulphide displays two distinct bands at 43478 and 32258 cm<sup>-1</sup>. These may be assigned due to n – π\* transition of ligand. A very strong band at 27027 cm<sup>-1</sup> in [VO(TDS)(H<sub>2</sub>O)(SO<sub>4</sub>)] may be assigned due to charge transfer band having mixed contribution from e<sub>g</sub> → b<sub>1g</sub> transition. There is also a very weak broad band at 16393 cm<sup>-1</sup> which may be assigned due to e<sub>g</sub> → a<sub>1g</sub> transition suggesting the distorted octahedral geometry of VO(IV) complex. The electronic spectrum of [Fe(TDS)<sub>3</sub>Cl<sub>3</sub>] consists strong absorption bands at 40816 and 34602 cm<sup>-1</sup> which are due to strong charge transfer absorption of M → L or L → M and eliminating the probability of d–d transition. There is very strong absorption band at 39216 cm<sup>-1</sup> in [Ru(TDS)<sub>4</sub>Cl<sub>2</sub>]Cl which is due to L → M transition<sup>12</sup>. The impossibility

TABLE I  
ANALYTICAL AND PHYSICAL DATA OF COMPLEXES

Compdn.	Colour	$\mu_{\text{eff}}$ (B.M.)	Molar conductance $\text{ohm}^{-1} \text{cm}^{-2} \text{mol}^{-1}$	Analysis % Found (Calcd.)				Probable Structure
				M	C	H	N	
$[\text{Hg}(\text{TDS})_2(\text{NO}_2)_2(\text{H}_2\text{O})_2]$	Gray	D.M.	—	32.01(31.61)	26.32(26.47)	1.8(1.89)	9.98(10.85)	$T_d$
$[\text{Pd}(\text{tTDS})_2\text{Cl}_2 \cdot 3\text{H}_2\text{O}]$	Yellow	D.M.	3.2	12.02(12.12)	37.62(37.95)	2.2(2.26)	25.1(25.3)	Sq.-Planer
$[\text{Co}(\text{tTDS})_2(\text{H}_2\text{O})_2]$ $(\text{ClO}_4)_2 \cdot 3\text{H}_2\text{O}$	Black	2.1	85.71	6.12(5.88)	33.42(33.54)	2.38(2.40)	22.30(22.35)	Sq.-Planer
$[\text{Co}(\text{tTDS})_2(\text{ac}_2)_2 \cdot 2\text{H}_2\text{O}]$	Blue	2.13	1.56	6.7(6.6)	43.28(43.40)	2.90(2.94)	25.5(25.32)	Sq.-Planer
$[\text{Co}(\text{tTDS})_2(\text{H}_2\text{O})_2(\text{NO}_2)_2]$	Blue	2.10	79.32	6.01(6.00)	39.16(39.06)	3.22(3.25)	25.71(25.63)	Sq.-Planer
$[\text{Bi}(\text{TDS})_2(\text{NO}_2)_2]$	Pale Cream	D.M.	1.3	19.02(18.95)	30.33(30.46)	1.8(1.82)	24.02(24.11)	Dist.-Oh.
$[\text{Cr}(\text{tTDS})_2(\text{H}_2\text{O})_4(\text{NO}_2)_2]$	Smoke Gray	3.72	101.86	6.12(5.32)	40.11(39.36)	2.80(2.86)	22.98(23.11)	Trans.-Oh.
$[\text{Fe}(\text{TDS})_2\text{Cl}_2]$	Pale Cream	5.76	1.05	4.23(4.61)	41.32(41.14)	2.32(2.45)	27.93(27.43)	Mer.-Oh.
$[\text{Ru}(\text{TDS})_2\text{Cl}_2\text{Cl}]$	Black	2.1	71.3	6.32(6.23)	41.3(41.39)	2.42(2.46)	27.23(27.59)	Trans.-Oh.
$[\text{VO}(\text{TDS})(\text{H}_2\text{O})_2 \cdot \text{SO}_4]$	Marine Gray	1.69	2.3	9.02(9.23)	30.32(30.49)	2.10(2.19)	20.21(20.34)	Sq.-Pyramidal
$[\text{ZrO}(\text{TDS})_2\text{Cl}_2\text{Cl}]$	Royal Ivory	D.M.	35.7	5.8(5.72)	42.01(42.15)	2.50(2.51)	28.01(28.1)	Oh.
$[\text{Zr}(\text{TDS})_2(\text{H}_2\text{O})_4(\text{NO}_2)_2]$	Golden Brown	D.M.	115.97	5.03(4.94)	36.62(36.79)	2.60(2.64)	26.01(27.59)	Trans.-Oh.
$[\text{Zr}(\text{TDS})_2(\text{SO}_4)_2]$	Brown	D.M.	3.2	5.23(5.31)	40.01(39.33)	2.44(2.41)	26.01(26.08)	Trans.-Oh.

D.M.—Diamagnetic in nature

of other bands are due to very dilute nature of solution, because on increasing the concentration the solution becomes opaque. The electronic spectrum of  $[\text{Cr}(\text{TDS})_2(\text{H}_2\text{O})_4](\text{NO}_3)_3$  displays a very strong band at 17,391, 20,000 and 29,850  $\text{cm}^{-1}$  and may be assigned due to  $4A_{2g}(\text{F}) \rightarrow 4T_{2g}(\text{F})$ ,  $4A_{2g}(\text{F}) \rightarrow 4T_{1g}(\text{F})$  and  $4A_{2g}(\text{F}) \rightarrow 4T_{1g}(\text{P})$  transition. The ligand field parameters that were calculated from above complex were found to be  $10 Dq = 12079$ ,  $B' = 998.3 \text{ cm}^{-1}$  and  $B = 0.96$ . These values show that the ligand used for complexation has fairly strong end of nephelauxetic series. A very strong absorption band, observed at 41,667  $\text{cm}^{-1}$  in UV spectrum of  $[\text{Bi}(\text{TDS})_2(\text{NO}_3)_3]$ , may be assigned due to charge transfer band as  $L \rightarrow M$  or  $M \rightarrow L$  as expected for  $d^{10}$  system. Moreover, it is not a five co-ordinated complex, because a five co-ordinated complex gives rise to two strong bands in 30,000–40,000  $\text{cm}^{-1}$ . Thus Bi(III) complex has most probably distorted octahedral structure<sup>13</sup> in which the inert pair is occupied at one of the corners of octahedral configuration. A very strong absorption band in 37,037–35,087  $\text{cm}^{-1}$  that has been observed in all Zr(IV) complexes may be assigned as charge transfer band. However, there is no single band in the range of 400–1500 nm (6,666–25,000  $\text{cm}^{-1}$ ) indicating that zirconium is in the form of Zr(IV) *i.e.*  $d^0$  system. All Co(II) complexes with (tTDS) absorb a very strong band at 37,037  $\text{cm}^{-1}$  may be assigned due to charge transfer band. A weak broad band at 17094 and 15432  $\text{cm}^{-1}$  in  $[\text{Co}(\text{t-TDS})_2(\text{ac})_2] \cdot 2\text{H}_2\text{O}$  at 16,722 and 13,157  $\text{cm}^{-1}$  in  $[\text{Co}(\text{t-TDS})_2(\text{H}_2\text{O})_2](\text{NO}_3)_2$  and at 16,892 and 15,432  $\text{cm}^{-1}$  in  $[\text{Co}(\text{t-TDS})_2(\text{H}_2\text{O})_2](\text{NO}_3)_2$  may be assigned due to  $2A_{1g} \rightarrow 2B_{1g}$  and  $2A_{1g} \rightarrow 2E_g$  transition respectively which clearly indicates square planar configuration of all Co(II) complexes. The absorbance band of  $[\text{Pd}(\text{t-TDS})_2\text{Cl}_2] \cdot 3\text{H}_2\text{O}$  displayed at 28,571 and 24,400  $\text{cm}^{-1}$  may be assigned as charge transfer and  $1A_{1g} \rightarrow 1B_{1g}$  transition respectively.

A comparison of the major infrared spectral bands of ligand and complexes indicate following :

All hydrated complexes display a broad medium band at 3403–3600  $\text{cm}^{-1}$  and a medium band at  $1615 \pm 10 \text{ cm}^{-1}$  which may be assigned as  $\nu\text{H}_2\text{O}$  and  $\delta \text{H}_2\text{O}$  respectively. The presence of water molecule is further supported by a weak band about 580  $\text{cm}^{-1}$  of  $\pi\text{H}_2\text{O}$  mode of vibrations. The IR spectrum of ligand displays  $\nu\text{CH}$  (aromatic) stretches in the range of 3060–2900  $\text{cm}^{-1}$  which are almost all identical in complexes indicating non-participation of CH group of phenyl ring. A medium band at 1390  $\text{cm}^{-1}$  in the spectrum of ligand may be assigned as  $\nu\text{CN}$  which is blue shifted in position after complexation. This shows the non-participation of nitrogen atom in coordination. The absence of bonding imino nitrogen atom is also supported by almost uncharged position of bands at 1275 and 1250  $\text{cm}^{-1}$  in the spectrum of the ligand assigned due to  $\nu\text{CN} + \nu\text{CH}$  mode of vibration. There are medium bands at 1085 and 1020  $\text{cm}^{-1}$  in the spectrum of ligand which has been assigned to mixed contribution of

$\nu\text{C-S}$  and  $\nu\text{C-N}$ . These are red shifted (*ca* 10–30  $\text{cm}^{-1}$ ) in all metal complexes suggesting the coordination of ligand through one of the disulphide sulphur. It is also supported by the red shifting of  $\nu\text{C-S-S-C}$  band of ligand at 570 and 555  $\text{cm}^{-1}$ . Above observation is further supported by the red shifting (*Ca* 30  $\text{cm}^{-1}$ ) of  $\nu\text{S-S}$  band<sup>14</sup> of ligand observed at 500  $\text{cm}^{-1}$  in the spectra of all complexes. A new strong broad band has been observed at 1300  $\text{cm}^{-1}$  in the spectrum of  $[\text{Co}(\text{tTDS})_2(\text{ac})_2]2\text{H}_2\text{O}$  indicating the presence of monodentate acetato<sup>15,16</sup> in the complex. The other new strong broad band has been observed at 1120–1070  $\text{cm}^{-1}$  and 690–550  $\text{cm}^{-1}$  in  $[\text{Co}(\text{tTDS})_2(\text{H}_2\text{O})_2](\text{ClO}_4)_2 \cdot 3\text{H}_2\text{O}$  which indicates the presence of ionic perchlorate<sup>17</sup>. There are medium bands at 965 and 900  $\text{cm}^{-1}$  of the spectra of oxozirconium and oxovanadium complexes respectively which may be assigned due to  $\nu\text{Zr=O}$  and  $\nu\text{V=O}$  mode of vibrations.

The appearance of  $\nu\text{V=O}$  band of the lower wave number may be due to hydrogen bonding of oxygen atom of  $\text{V=O}$  group. Metal oxygen bonding is further supported by the bands of far IR at 510 and 380  $\text{cm}^{-1}$  in  $\text{Zr(IV)}$  and 410  $\text{cm}^{-1}$  in  $\text{VO(IV)}$  complexes.

The fundamental modes of vibration are observed at  $990 \pm 5$ , 510, (1118, 1090) and 630  $\text{cm}^{-1}$  in  $[\text{VO}(\text{TDS})(\text{H}_2\text{O})(\text{SO}_4)]$ ,  $[\text{Zr}(\text{TDS})_4(\text{SO}_4)_2]$  indicating the presence of monodentate sulphato group<sup>18</sup> in these complexes. There are very strong bands about 1450, 1310 1030  $\text{cm}^{-1}$  in  $[\text{Bi}(\text{TDS})_2(\text{NO}_3)_3]$  and  $[\text{Hg}_2(\text{TDS})_2(\text{NO}_3)_2(\text{H}_2\text{O})_2]$  and at 1345–1360, 830 and  $615 \pm 10$   $\text{cm}^{-1}$  in  $[\text{Zr}(\text{TDS})_2(\text{H}_2\text{O})_4](\text{NO}_3)_4$ ,  $[\text{Cr}(\text{TDS})_2(\text{H}_2\text{O})_4](\text{NO}_3)_3$  and  $[\text{Co}(\text{tTDS})_2(\text{H}_2\text{O})_2](\text{NO}_3)_2$  which may be assigned as  $\nu_{\text{asym}} \text{NO}_2$ ,  $\nu_{\text{sym}} \text{NO}_2$  and  $\nu\text{N-O}$  mode of vibration<sup>19</sup>. The higher frequencies group of vibrations are due to monodentate nitrate group and that of lower frequencies group is due to free nitrate ion vibrations<sup>20</sup>. It is due to less degree of symmetry of coordinated nitro group in comparison to free nitrate ion. Some new bands are observed for metal-ligand vibrations in far IR spectra of complexes.  $\nu\text{M-Cl}$  modes of vibration are observed at 290  $\text{cm}^{-1}$   $[\text{ZrO}(\text{TDS})_4\text{Cl}] \text{Cl}$ , at 490, 482, 470  $\text{cm}^{-1}$  in  $[\text{Fe}(\text{TDS})_3\text{Cl}_3]$  at 460, 420  $\text{cm}^{-1}$  in  $[\text{Ru}(\text{TDS})_4\text{Cl}_2]\text{Cl}$  and at 490, 420  $\text{cm}^{-1}$  in  $[\text{Pd}(\text{tTDS})_2\text{Cl}_2] \cdot 3\text{H}_2\text{O}$ . The  $\nu(\text{M-S})$  vibrations are observed at (410, 330 and 320), 350, 310 (240, 320), (280, 300), (290, 310), (290, 410, 420), (310, 340, 600), and (280, 300, 340,  $345 \pm 5$ )  $\text{cm}^{-1}$  for  $\text{Zr(IV)}$ ,  $\text{VO(IV)}$ ,  $\text{Hg(IV)}$ ,  $\text{Bi(III)}$ ,  $\text{Ru(III)}$ ,  $\text{Cr(III)}$ ,  $\text{Fe(III)}$ ,  $\text{Pd(II)}$  and  $\text{Co(II)}$  complexes respectively.

Moreover, the study of far infrared spectra of  $\text{Zr(IV)}$ ,  $\text{Ru(III)}$  and  $\text{Cr(III)}$  complexes reasonably suggests the *trans*-octahedral configuration having high symmetry and  $\text{Fe(III)}$  complex possesses *mer*-octahedral configuration.

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