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IR, PMR and Ligand Field Spectral Studies on Ti(III), Mn(III), Cr(III), Sb(III) and Bi(III) Complexes of Sulphur and Selenium Ligands

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Dibenzyl sulphide (DBS) and dibenzyl selenide (DBSe) form stable complexes with Ti(III), Mn(III), Cr(III), Sb(III) and Bi(III) ions having general formula $[ML_3Cl_3]$ (M = Ti, Mn, Cr; L = DBS/DBSe), $[ML_2Cl_3]$ (M = Sb and Bi) and $[TiL_2(Py)_2Cl_2]Cl$. Ti(III), Cr(III) and Mn(III) forms mer-octahedral and Sb(III) and Bi(III) forms distorted octahedral structure in which one of the corners is occupied by inert pair. *Bis*-ligand $[TiL_2(Py)_2Cl_2]Cl$ complexes have *trans* position of ligand in octahedral structure. The IR, UV-vis and ^1H NMR spectral data are in good agreement with assigned structure.

Key Words: Metal (III) complexes, Dibenzyl sulphide, Dibenzyl selenide, IR, UV-vis, ^1H NMR.

INTRODUCTION

Dibenzyl sulphide $(\phi CH_2)_2S$ has been used as ligand[1-3] and trichlorotris(dibenzylsulphide)rhodium(III) is used as catalyst[4] for the hydrogenation of maleic acid and *trans*-cinnamic acid. Still less work has been done with corresponding selenium analogue dibenzyl selenide $(\phi CH_2)_2Se$. The results of spectral investigations on the complexes of Ti(III), Mn(III), Cr(III), Sb(III) and Bi(III) with dibenzyl sulphide and dibenzyl selenide are reported in the present communication.

EXPERIMENTAL

All chemicals used were of CP-grade or AR-grade. Dibenzyl sulphide[5], dibenzyl selenide[5], manganese(III), acetate dihydrate[6] and chromium(III) acetate hexahydrate[7] were prepared by the method described in literature. Complexes were prepared using a general method. Methanolic metal salt and ligand were mixed in molar ratios M:L = 1:3 and stirred on magnetic stirrer at 85 ºC for 2 h. The pH of the mixture was adjusted 4/6 using mineral acid of corresponding salt and NaOH/pyridine and volume of the mixture was reduced to *ca.* 40 mL on water bath. The crystals were collected and washed with ice-cold methanol/ether and dried *in vacuo* over anhydrous $CaCl_2$. Analytical and physical data of complexes are given in Table-1.

The magnetic moment of the complexes were measure at 300 K using a gouy balance. Mercury tetrathiocyanato cobalt(II) complex was used as the standard for magnetic moment

TABLE-1
ANALYTICAL AND PHYSICAL DATA OF COMPLEXES

S. No.	Complex/(colour)	$\mu_{eff.}$ (BM)	Elemental analysis (%): Found (calcd.)			
			C	H	Cl	M
1	$[Ti(DBS)_3Cl_3]$ (Yellow)	1.77	63.31 (63.11)	5.26 (5.25)	13.51 (13.33)	6.82 (6.26)
2	$[Ti(DBSe)_3Cl_3]$ (Golden yellow)	1.78	54.11 (53.64)	4.48 (4.47)	11.32 (11.33)	5.41 (5.32)
3	$[Ti(DBS)_2(Py)_2Cl_2]Cl$ (Golden yellow)	1.76	61.66 (61.41)	5.12 (5.11)	14.45 (14.34)	–
4	$[Ti(DBSe)_2(Py)_2Cl_2]Cl$ (Deep yellow)	1.77	55.01 (54.51)	4.55 (4.54)	12.80 (12.73)	–
5	$[Cr(DBS)_3(OAc)_3]$ (Greenish yellow)	3.66	66.51 (66.13)	5.86 (5.85)	–	6.00 (5.97)
6	$[Cr(DBSe)_3(OAc)_3]$ (Greenish Brown)	3.67	57.10 (56.91)	5.11 (5.03)	–	5.50 (5.10)
7	$[Mn(DBS)_3(OAc)_3]$ (Yellowish red)	4.82	66.10 (65.90)	5.50 (5.49)	–	6.50 (6.29)
8	$[Mn(DBSe)_3(OAc)_3]$ (Yellowish brown)	4.87	57.01 (56.74)	5.11 (5.02)	–	5.55 (5.41)
9	$[Bi(DBS)_2Cl_3]$ (Yellow)	Diamag.	45.22 (45.19)	3.77 (3.76)	14.41 (14.32)	28.15 (28.11)
10	$[Bi(DBSe)_2Cl_3]$ (Yellow)	Diamag.	40.15 (40.11)	3.35 (3.34)	12.98 (12.71)	25.01 (24.95)
11	$[Sb(DBS)_2Cl_3]$ (Light yellow)	Diamag.	51.10 (51.19)	4.28 (4.26)	16.33 (16.22)	–
12	$[Sb(DBSe)_2Cl_3]$ (Yellow)	Diamag.	45.11 (44.78)	3.75 (3.73)	14.25 (14.19)	–

calibration, IR spectra of ligands and complexes were recorded by means of Perkin-Elmer 521 spectrophotometer using KBr pellets. All the spectra were calibrated using polystyrene film. The electronic spectra were recorded with Zeiss (Jena) model of automatic recording system. ^{1}H NMR spectra of ligands and complexes were recorded with 90 MHZ NMR spectrophotometer in $CDCl_3$ solution using TMS as the internal indicator in the range of 0-10 ppm. Molar conductance of complexes were measured in DMF using Wiss-Werkstatter weithen obb type conductivity meter. Analysis of chlorine[8] were carried out using standard methods.

RESULTS AND DISCUSSION

The analytical data (Table-1) show that metal complexes correspond to the formulae: (i) $[ML_3X_3]$ (M = Ti, Cr and Mn; X = Cl, CH_3COO, L = DBS or DBSe), (ii) $[ML_2Cl_3]$ (M = Sb and Bi; L = DBS or DBSe), (iii) $[ML_2(Py)_2Cl_2]Cl$ (M = Ti, L = DBS or DBSe).

The value of molar conductance was found to be less than 10 Ω^{-1} cm^2 mol^{-1} indicating coordinated anions. However, molar conductance of $[ML_2(Py)_2Cl_2]Cl$; was found to be 62-83 Ω^{-1} cm^2 mol^{-1} for 1:1 electrolyte[9]. The sodium-extract solution of complexes (S. No. 3 and 4) confirmed positive test of chloride ion with $AgNO_3$ solution indicating one of chloride ions in the outer sphere of complexes.

Magnetic moment and electronic spectra: The magnetic moment of Ti(III) complexes was found to be 1.77 BM correspond to one unpaired electron. One band at 19610-21275 cm^{-1} with a shoulder at 18520-19050 cm^{-1} in electronic spectra obviously derived from the transition $^2T_{1g} \rightarrow {}^2E_g$ for an octahedral symmetry[10]. The broad nature of band is probably due to John-Teller effect as expected in d^1-complexes[10,11]. The magnetic moment of Cr(III) complexes (3.67 BM) are well within the range reported for high spin octahedral complexes[12]. The visible spectra exhibits three bands at

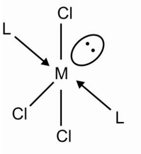
$$17300\ \text{cm}^{-1}\ (\nu_1) = {}^4A_{2g}(F) \rightarrow {}^4T_{2g}\ (F)$$
$$23100\ \text{cm}^{-1}\ (\nu_2) = {}^4A_{2g}(F) \rightarrow {}^4T_{1g}\ (F)$$
$$36100\ \text{cm}^{-1}\ (\nu_3) = {}^4A_{2g}(F) \rightarrow {}^4T_{1g}\ (P)$$

The ν_1 and ν_2 bands are intense, but ν_3 appears as shoulder. The crystal field parameters, $\nu_2/\nu_1 = 1.33$, Dq/B = 2.56, 10Dq = 17024 cm^{-1}, B = 665 cm^{-1} and $\beta = 0.64$ are in agreement with the reported values for octahedral Cr(III) complexes[13]. The lowering in value of B from the free ion value for Cr^{3+} (1030 cm^{-1}) suggest high degree of covalent bonding.

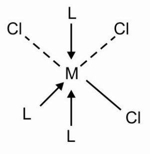
The magnetic moment value (4.87 BM) of Mn(III) complexes indicate $t_{2g^{3}e_{g}^{1}}$ configuration in octahedral surrounding is subject to Jahn-Teller distortion. All complexes (S. No. 7 and 8) display bands at 13400, 17500 and 20750 cm^{-1} which are consistent with hexa coordinate octahedral environment around the metal atom. The first band (13400 cm^{-1}) assignable to $^5B_{1g} \rightarrow {}^5E_g$ is most convincing evidence for D_{4h} symmetry. The other bands may be assignable to $^5B_{1g} \rightarrow {}^5B_{2g}$ and $^5B_{1g} \rightarrow {}^5E_g$, respectively. The high energy band (35140 cm^{-1}) in the complexes may be assigned to CT band. However, it is difficult to interpret in all their details the spectra of octahedral Mn(III) presumably because both steric and dynamic John-Teller effects perturbs the simple picture based on fixed and perfect octahedral symmetry[14]. All complexes of Sb(III) and Bi(III) display a single band of very high intensity at 41150 and 40,000 cm^{-1}, respectively as expected for d^{10}-system. They are probably distorted octahedral in which the inert pair is occupied at one of the corner of octahedral structure[15] (Str. I).

Infra-red spectra: A comparison of IR spectra of DBS, DBSe and complexes indicate metal-S and metal-Se bonding. The and bands of DBS and DBSe ligands, respectively shift from 720 to 685 ± 5 cm^{-1} and from 615 cm^{-1} to 565 ± 5 cm^{-1} on complexation and bonding through S and Se atom is indicated[16]. The ν(C-H) (aromatics) and ν(C-H) (aliphatic) of DBS and DBSe are observed almost unchanged in position as expected. The presence of pyridine in complexes (S. No. 3 and 4) is confirmed by its characteristic vibrations. The four ν(C=C) and ν(C=N) pyridine skeletal bands are observed at 1605-1590 (band I), 1580-1560 (band II), 1490-1450 (band III) and 1440-1430 cm^{-1} (band IV). These vibrations are not shifted appreciably on coordination to Ti(III) ion. However, in-plane deformation (604 cm^{-1}) and out-of-plane-ring deformation (405 cm^{-1}) shifted to higher frequencies indicating the formation of metal-Py bond[17]. The presence of a single Ti-Py stretching mode at 255 cm^{-1} indicates two pyridine molecules are at *trans*-position in octahedral structure. Addition bands for the complexes (S. No. 5, 6 and 8) were observed in the region 1584-1567 and 1367-1352 cm^{-1} attributable to ν_{as}(COO) and ν_s(COO) modes of vibration of the acetato group, respectively. The frequency difference between symmetric and antisymmetric stretches ($\Delta\nu$) *ca.* 210 cm^{-1} is typical monodetate coordination of acetato group[18] (Str. II).

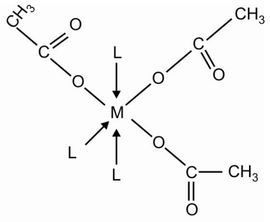
Far IR spectra of Ti(III) complexes (S. No. 1 and 2) display three Ti-Cl stretching modes of medium intensity at 320, 335 and 345 cm^{-1} and two bands of weak intensity at 300 and 310 cm^{-1} assignable to ν(Ti-S) mode, indicate Mer-O_h structure (Str. III) for $[TiL_3Cl_3]$[19-21] (L = DBS/DBSe). However, *bis*-ligand complexes (S. No. 3 and 4) display a single ν(Ti-Cl) (345 cm^{-1}) and ν(Ti-S) (315 cm^{-1}) band indicating *trans* position of two ligands in octahedral structure (structure IV).



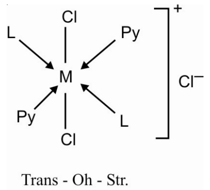
(Str. I)
M = Sb(III), Bi(III)
and
(L = DBS/DBSe)



(Str. III)
(Mer-Oh-Str.)
(L = DBS/DBSe)



(Str. II)
(M = Cr(III) & Mn(III))
(L = DBS/DBSe)



Trans - Oh - Str.
(Str. - IV)

^{1}H NMR spectra: ^{1}H NMR spectra of DBS, DBSe and Ti(III) complexes were recorded in $CDCl_3$/TMS to substantiate further metal-ligand bonding. The spectrum of $Ti(DBS)_3Cl_3$ shows a complex peak at δ 7.18 ppm corresponding to aromatic protons and two peaks centred at δ 4.50 ppm and δ .89 ppm due to CH_2 protons. The CH_2 groups are in two magnetic environments. The complexes have probably mer-octahedral configuration (Str. III) in which two of the two axially coordinated DBS ligands are in one magnetic environment which the equitorial DBS is in different magnetic environment. The axially coordinated $C_6H_5CH_2$ group is adjacent to three chlorine atoms while equatorial $C_6H_5CH_2$ group is adjacent to two chlorine atoms. ^{1}H NMR spectum of $Ti(DBSe)_3Cl_3$ also shows a complex peak centered at δ 7.31 ppm corresponding to aromatic protons. The CH_2 region does not contain a single peak as is expected for a facial-isomer (1,2,3) but it contains complex multiplets in this region. This change in the two CH_2 peak indicates larger interactions in $Ti(DBS)_3Cl_3$ to that in Ti(III) complex with DBSe. Thus, these complexes have mer-octahedral configuration reported by earlier workers[19-21].

The other titanium(III) complexes (S. No. 3 and 4) exhibits resonances in the region δ 7.2, 8.07 and 8.84 ppm assignable to the protons of the pyridine ligand along with the resonances due to aromatic protons. The protons of coordinated pyridine are observed at δ 7.65, 8.17 and 8.88 ppm (S. No. 3) and at δ 7.38, 8.26 and 8.84 ppm (S. No. 4) due to α, β and γ protons, respectively. In these complexes, pyridine resonances exhibited down field shift as compared to that in free ligand indicating the complexation of pyridine nitrogen atom with metal centre[22].

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