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Studies on Dibenzyl Sulphide & Dibenzyl Selenide Complexes of Iridium(III)

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Iridium(III) complexes of the type $Ir(L)_3Cl_3$ (where L = dibenzyl sulphide or dibenzyl selenide) have been prepared and characterized on the basis of analytical, molecular weight and spectral studies. IR data indicate that the ligands coordinate through sulphur or selenium atoms of the $C = S$ or $C = Se$ groups respectively. Octahedral structures with meridional configurations have been assigned to the complexes. νIr-Cl, νIr-S and νIr-Se modes of vibration have been assigned in the far infrared region of the spectra of the complexes.

DIALKYL sulphide and selenide complexes of a number of metal ions have been studied by several workers[1-7]. However, comparatively less work has been done with aromatic sulphide or selenide ligands[8-10]. Some complexes of dibenzyl sulphide (DBS) have been reported by Paul Haake *et al.*[11-13] $\{RhCl_3[(PhCH_2)_2S]_3\}$ has been used[14] as a catalyst for the hydrogenation of maleic acid and *trans*-cinnamic acid, but thorough investigations on the complexing behaviour of this ligand have not been made. Still less work has been done with the corresponding selenium ligand, dibenzyl selenide (DBSe). In view of this, we undertook studies on the synthesis and characterization of complexes of dibenzyl sulphide and dibenzyl selenide, and the results on iridium(III) complexes are reported here.

Materials and Methods

All the chemicals used were of C.P. grade.

Dibenzyl sulphide and dibenzyl selenide were prepared by the methods described in the literature[15] and the products were analysed and their purities checked spectroscopically.

Preparation of complexes — Iridium trichloride hydrated (0·2 g) was dissolved in methanol (20 ml), the solution was filtered and the filtrate was treated with a similarly prepared solution of the ligand (0·6 g in 50 ml of methanol). The mixture was refluxed on a water-bath for 1 hr when yellow (for DBS complex) or orange (for DBSe complex) coloured precipitate was obtained. This was filtered, washed with water, ice-cold ethanol and finally with ether. The complex was recrystallized from hot methanol. It was dried *in vacuo* over anhydrous $CaCl_2$.

Microanalyses of the compounds were carried out at IIT, Kanpur. Analyses of metal ions[16] and chlorine[17] were carried out using standard methods.

$Ir(DBS)_3Cl_3$: m.p. 184° (Found: C, 53.5; H, 4·7; Cl, 10·9; Ir, 20·9. Calc.: C, 53·6; H, 4·4; Cl, 11·3; Ir, 20·4%).

$IR(DBSe)_3Cl_3$: m.p. 93° (Found: C, 46·9; H, 3·6; Cl, 9·3; Ir, 17·1. Calc.: C, 46·5; H, 3·8; Cl, 9·8; Ir, 17·7%).

Results and Discussion

Analytical data indicate that the complexes have the stoichiometry ML_3Cl_3 where M = Ir(III) and L = DBS/DBSe. Both these complexes are soluble in benzene, chloroform, hot ethanol and DMF. Their high solubility in most of the organic solvents and molecular weight determination (determined cryoscopically in benzene) suggest their monomeric nature. Their solutions in benzene are nonconducting indicating coordinated nature of the chlorides. The compounds are diamagnetic and hence they may be assigned octahedral structures.

On the basis of IR band assignments[18] of the analogous compound, $C_6H_5CH_2CH_2C_6H_5$, the bands between 3000 and 3100 cm^{-1} in the spectrum (IR spectra of the complexes were recorded in KBr while those of the ligands were recorded using their thin films on a Perkin-Elmer 521 instrument) of $C_6H_5CH_2SCH_2C_6H_5$ may also be assigned to aromatic νC—H. Similarly bands in the range 2800-3000 cm^{-1} may be assigned to νC—H (aliphatic) in DBSe.

A comparison of the spectrum of $C_6H_5CH_2SCH_2C_6H_5$ and $C_6H_5CH_2CH_2C_6H_5$ indicates that a medium band at 1240 cm^{-1} is present in the spectrum of the former but is absent in the spectra of $C_6H_5CH_2CH_2C_6H_5$ as well as $C_6H_5CH_2SeCH_2C_6H_5$. It is therefore, suggested that this band has major contribution from νCS. Sharp and strong bands are present at 756 and 702 cm^{-1} in the spectrum of $C_6H_5CH_2CH_2C_6H_5$ which are due to five adjacent hydrogen atoms[19,20] of the monosubstituted phenyl group. A doublet at 768, 758 cm^{-1} and a very broad band in the range 720-690 cm^{-1} (multiplet) are present in the spectrum of $C_6H_5CH_2SCH_2C_6H_5$. There are significant changes in the positions and intensities of the bands in the spectrum of $Ir(DBS)_3Cl_3$ due to coordination of the ligand through thioketo sulphur atom. Thus, the band at 1240 cm^{-1} in dibenzyl sulphide is considerably reduced in intensity, the doublet (768, 758 cm^{-1}) is reduced in intensity while the broad multiplet in the region 720-690 cm^{-1} becomes a very strong singlet centred at 700 cm^{-1}. These changes, especially the red-shifting of the 720 cm^{-1} band, indicate coordination of dibenzyl sulphide to Ir(III) through sulphur. Similar red-shifting, on coordination through sulphur, of organosulphur ligands have been reported[21-26]. A comparison of the far infrared spectra of DBS and Ir(DBS)$_3$Cl$_3$ in the range 400-300 cm^{-1} indicates that there are strong bands in the spectrum of the latter at 300, 315 and 325 cm^{-1} which are absent in the spectrum of DBS. Most probably these bands are due to νIr—Cl modes and the presence of three bands indicates[10,27,28] that it is a *mer*-isomer of the octahedral form. Several sharp and weak bands are also noticed in the range 370-380 cm^{-1} in the spectrum of Ir(DBS)$_3$Cl$_3$ which are not present in the spectrum of DBS. These may have contribution from νIr—S. A strong band observed at 825 cm^{-1} in the spectrum of DBSe is absent in the spectrum of DBS. Hence it may be assigned to νC=Se. Similarly two bands at 615 and 580 cm^{-1}, present in the spectrum of DBSe but absent in the spectrum of DBS, may be assigned to ν_{as} C—Se—C and ν_{sym} C—Se—C modes respectively. The νCSe band of the free DBSe ligand almost disappears in the IR spectrum of Ir(DBSe)$_3$Cl$_3$ indicating coordination of DBSe through selenium. Similar disappearance of 615 and 580 cm^{-1} bands of DBSe is also found on coordination of the ligand.

In the region 300-250 cm^{-1}, the IR spectrum of Ir(DBSe)$_3$Cl$_3$ shows a number of strong multiplets which are not present in the spectrum of DBSe. They may be due to νIr—Cl modes of vibration and indicate that the six coordinated complex, Ir(DBSe)$_3$Cl$_3$ may have octahedral meridional configuration.

The meridional configurations of Ir(DBS)$_3$Cl$_3$ and Ir(DBSe)$_3$Cl$_3$ are also supported by their PMR spectra (taken in CDCl$_3$ using TMS as standard). The PMR spectrum of DBS shows a strong peak at 2·8 τ corresponding to ten aromatic protons and another peak at 6·5 τ corresponding roughly to four methylene protons. In addition to this, there is a very small peak at 5·5 τ which persists in the spectrum and which may be due to some impurity. Multiple peaks at 5·6 and 7·1 τ are observed in the PMR spectrum of dibenzyl selenide.

The PMR spectrum of Ir(DBS)$_3$Cl$_3$ which shows a complex peak at 2·82 τ corresponding to aromatic protons, and two peaks centred at 5·48 and 6·1 τ respectively, with peak area ratio of 2:1. The two different peaks may be due to two CH$_2$ groups in different magnetic environments. This can happen if Ir(DBS)$_3$Cl$_3$ has meridional octahedral structure in which the two axially coordinated DBS ligands are in one magnetic environment while the equatorial DBS is in a different magnetic environment (Fig. 1).

It is clear from Fig. 1 that the axially coordinated ϕCH$_2$S group is adjacent to three chlorine atoms while equatorial ϕCH$_2$S group is adjacent to two chlorine atoms.

PMR spectrum of Ir(DBSe)$_3$Cl$_3$ also shows a complex peak centred at 2·7 τ corresponding to aromatic protons. The CH$_2$ region does not contain a single peak as is expected for a facial isomer, but it contains complex multiplets in this region. This change in the two CH$_2$ peaks indicates larger interaction in Ir(DBSe)$_3$Cl$_3$ as compared to that in iridium complex with DBS. Thus, Ir(DBSe)$_3$Cl$_3$ may probably have meridional configuration. This is in agreement with the fact that various IrL$_3$Cl$_3$ complexes have been found to be meridional isomers[27,28].

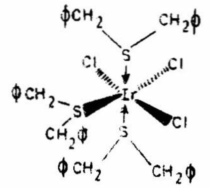

Fig. 1

The electronic spectra (recorded in DMF or absolute ethanol) of Ir(DBS)$_3$Cl$_3$ and Ir(DBSe)$_3$Cl$_3$ are almost identical with a band at 30300 cm^{-1} and shoulders at 28500 and 21800 cm^{-1}. However, the molar extinction coefficients of the bands for Ir(DBSe)$_3$Cl$_3$ are almost twice those for the bands of Ir(DBS)$_3$Cl$_3$. The meridional isomers of general formula Ir(R$_2$S)$_3$Cl$_3$ generally show three bands[28] around 31000-32000 ($\epsilon = 10^2$-10^3), 29000 ($\epsilon = 10^2$-10^3) and 21000 cm^{-1} ($\epsilon = 10$-10^2). The positions and intensities of the electronic spectral bands of Ir(DBS)$_3$Cl$_3$ and Ir(DBSe)$_3$Cl$_3$ are in agreement with this and hence these may also have meridional configurations.

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