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SPECTROSCOPIC EVIDENCE FOR STERIC ENHANCEMENT OF RESONANCE IN RHODIUM (III) CHLORIDE COMPLEXES

Penke Vijaya Babu[1], Sunder Kumar Kolli[2] and Manam Sreenivasarao[3]*

[1]Department of Organic Chemistry, The Weizmann Institute of Science, Rehovot, Israel, 76100.
[2]Department of Chemistry, Annamacharya Institute of Technology Sciences, Hyderabad, T.S. India.501512.
[3]Department of Chemistry, Chundi Ranganayakulu college, Chilakaluripet, Guntur, A.P. 522616, India.

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***Corresponding Author**
Manam Sreenivasarao
Department of Chemistry,
Chundi Ranganayakulu
college, Chilakaluripet,
Guntur, A.P. 522616,
India.

ABSTRACT

The assignments reveal that the carboxyl substituted complexes are isolated as fac- isomers and all the remaining seven complexes are having mer-octahedral configuration. Using these sulphides as ligands Rhodium (III) chloride complexes have been synthesized and analyzed. The infrared spectra of these complexes have been recorded in the region 600– 200 cm^{-1}. Generally the electron releasing group in Benzene ring decreases the ν(Rh-S) stretching frequency value from the present one where as the electron withdrawing group increases the ν(Rh-S) stretching frequency value form its parent one. Otherwise the electron donor exerts a weakening effect on the Rh-S band and the σ-electron acceptor removes from the metal. The appearance of –OH bond in the complexes of carboxylic substituted ligands shows the absence of intra molecular hydrogen bonding between –OH of carboxylic group and chlorine. The carboxyl frequency of meta and para carboxylic groups gets increased when compared with the ligands. But in the case of higher stability of the meta and para isomers. In recording the electronic spectra the same solvent was used both for the complex and ligand. Generally the bathochromic shift is observed when there is an electron releasing group present in the benzene ring and the presence of electron withdrawing group or steric inhibition results in a hypsochromic shift. The complexes involving p-NO_2 and p-COOH substituted phenyl methyl sulphides have the absorption bands almost identical with those of ligands. When an electron donor is present in the benzene ring the electronic transition is from S(of S_{me}) to Rh and when there is a π-electron acceptor in benzene ring the electronic transition is from Rh to S is quite possible. The phenomenon of steric enhancement of resonance is observed in these complexes from infrared, electronic and ‘H NMR spectral studies are presented.

KEYWORDS: Stretching frequency, Molecular hydrogen bonding and absorption bands.

INTRODUCTION

Spectroscopy has become a major tool for chemists in getting information about the structure of organo-metal complexes. Low frequency infrared spectra of Rhodium (III) complex with methyl phenyl sulphide as has been recorded[1] and three strong sharp bands at 336 cm^{-1}, 318 cm^{-1} and 292 cm^{-1} are in consistent with the assumption that the complex is meridional octahedral. Complexes of facial configuration would be expected to have two M-X infrared active stretching frequencies.[2] Relatively weaker bands and are at lower range are predicted to v (Rh-S)Modes.[3] For Cis- MX_3 L_3 two v(M-X) modes (a_1+e) are predicted, three such modes ($2a_1+b_1$) should arise the fact that the metal-chlorine stretching frequencies to be lower in cis than in trans complexes is to be expected on the basis of chatt’s theory of partial d_π –bonding between metal and the ligand. This has been noticed in the case of Rh(III) complex with ethyl phenyl sulphide as ligand in which two strong bands at 313 cm^{-1} and 299 cm^{-1} for Rh-Cl are observed. Generally metal-donor bands are much less intense than metal – halogen (stretching) bands.[4]

Although metal-donor bonds are more polar than metal-halogen bonds, the infrared intensity depends on the rate of change of bond moment with the bond length the extension of a metal-halogen bond would result in the formation of highly polar ion pair (M-X ----M^+ +X^-). Where as that of a metal-donor bond would presumably give two neutral species.

$$(M – L --- M+: L)$$

The far infrared spectra of $RhCl_3$ –$(Et_2\ S)_3$ complex had sharp bands at 317 and 340 cm^{-1} and the same complex had sharp bands at 316 and 344 cm^{-1}, it is thought to be 1,2,6 isomer.[5] The dibenzyl sulphide complex of $RhCl_3$ is also assumed to have the same trans configuration. Complexes of trans-configuration of the type $(Rh(co)L_2cl)$ are prepared[6] $L=S(C_2H_5)_2$, $Se(C_2H_5)_2$ and $Te(C_2H_5)_2$, these complexes add easily with benzene sulphonyl chloride to give Rh(III) derivatives. The IR spectra exhibit two strong bands at about 1235 and 1065cm^{-1} ascribed to the asymmetric and symmetric stretching modes of the $-SO_2-$ group bound to the metal through sulphur.[7] A strong band for v(Rh-Cl) is observed at 304cm^{-1} in the complex trans-Rh(CO)(S(C_2 H_5)$_2$Cl) where as a strong band for v(Rh-Cl)is observed at 335cm^{-1} in the complex Rh(CO)(S(C_2H_5))$_2$, (C_6 H_5SO_2)Cl_2. The results conclude that the ligands affect differently the promotion energy for the Rh(III) oxidation state. Complexes trans- [Rh(CO)L_2Cl] have strong tendency to undergo oxidation addition and can be attributed to a balance of and π factors in the Rhodium-ligand bond, with the factor dominant. Complexes of Rhodium chloride with dimethyl sulphoxide, tetra methylene sulphoxide.[8]

These complexes are of mer-$RhCl_3$ L_3. The nature of Rh-S bonding is discussed in terms of a contribution of metal-sulphur π-back bonding. Crystallographic and infrared analysis[9-10] show that in the solid state the isomer present in mer-$RhCl_3$ (DMSO)$_2$ (DMSO). The crystals of $RhCl_3$ (DMSO)$_3$ are prepared from 2-propanol & water. The infrared spectra of free sulphoxide and co-ordinated sulphoxide is selective replacement of the o-bonded DMSO ligand by other oxygen donors in solution occurs with the relation of mer- stereo chemistry in all cases. The infrared data of $RhCl_3L_3$complexes (L= methyl phenyl sulphoxide, methyl phenyl tolyl sulphoxide and tetra methylene sulphoxide) are consistent with two S-bonded and one o-bonded ligands. Three metal-chloride bands are detected for the dimethyl sulphoxide. Only two Rh-Cl bands are detected in the case of tetra methylene sulphoxide, methyl phenyl sulphoxide and methyl p-tolyl sulphoxide and they are more consistent with a fac-configuration, but in view of the nmr data the mer formulation is favoured. Rhodium (III) complex of salicylaldehyde thio semicarbazone is isolated[11] in acidic medium and formulated as Rh (III) [(SAT-H)$_2$Cl. The salicylaldehyde thiosemicarbazone functions as a tridentate uninegative ligand and co-ordinates through the deprotonated thiolic sulphur. Hydrazine nitrogen and deprotonated phenolic oxygen. The Rh-S, Rh-N and Rh-O stretching frequencies are assigned at 395cm^{-1}, 490cm^{-1} and 455cm^{-1} respectively. Such frequencies are slightly changed when the complexes are isolated at higher P^H solutions.

There are in general two bands toward the blue end of the visible, which together with any additional absorption in the blue due to charge transfer transitions are responsible for the characteristic orange, red, yellow or brown colors of Rhodium (III) compounds.[12] These bands are assigned as transitions from the $1A_{1g}$ ground state to the $^1T_{1g}$ and $^1T_{2g}$ upper states. The ground state for d[6] configuration is 5D. This is only quintet state, the higher state being triplets and singlets. Hence in weak octahedral ligand fields, the ground state is $^5T_{2g}$ and the only exited state of the same spin multiplicity is the ^5E_g state, also originating from 5D. In sufficiently strong fields, however it is possible for a singlet state arising from one of the excited free ion states to drop far enough to become the ground state. Charge transfer bands have been observed in the region 39,000cm^{-1} – 45,000cm^{-1} for the complexes of $RhX_3[Et_2S]_3$.[13]

Charge transfer band moves to lower energy as the atomic weight of the halogen increases. The observation is correlated to the charge transfer from halogen to metal or charge transfer from sulphide ligand to metal, the M-S bonding being dependent on the halogen. Similar change in bond position occurs for he ligand field band (20,000-23,600 cm^{-1}) which one either $^1A_1 \rightarrow {}^1T_1$ (or) $^1A_1 \rightarrow {}^1T_2$ spin allowed transitions. The complexes $RhCl_3\,[Et_2\,S]_3$ and $Rh\,Br_3\,[Et_2\,S]_3$ have the same charge transfer band at 34,000 cm^{-1} which could be due to the co-ordinated diethyl sulphide. The observed results indicated that the halogen ligands can have a considerable effect on the bonding of the other ligands, especially when the donor atoms can participate in π-bonding. $RhCl_3\,[Et_2S]_3$ was prepared.[14] Electronic spectra in ethanol gave peaks at 421($\in$=330) and 292nm ($\in$ =20,100) which was somewhat different from those reported. The electronic spectra of $RhX_3[C_4H_8OS]_3$ have been studied.[15]

The lowest energy bands shift to lower wave numbers as X changes as expected. These bands are assigned to the first pin–allowed d–d transitions of octahedral Rhodium (III).[16] The broad nature of these two bands in the solution spectrum almost certainly the results from the lowering in the molecular symmetry MX_6-Cis MX_3L_3 the spin forbidden transitions $^1A_1 \rightarrow {}^3T_1$ was not observed. These spectra differ from those of the analogous complexes Cis–$Rh\,X_3(Et_2S)_3$ for which only the first spin allowed d-d transitions was observed. The Rh(III) – Cl system $[Rh\,(H_2O)_6]^{3+}$ is heated with dil.HCl and have been studied by ion exchange method and the yellow cations, $[RhCl(H_2O)_5]^{2+}$ and $[RhCl_2\,(H_2O)_4]^+$, their formation constants spectra characterized. Additional acid gives Cis and Trans isomers of red $[RhCl_3(H_2O)_3]$. Rh(III) chloride complexes of Dibenzyl sulphide and Dibenzyl selenide have been prepared and their electronic spectra have been studied in DMF. The strong band at 26,000 cm^{-1} ($\in$= 1000) assigned to the transitions $^1A_1 \rightarrow {}^1T_2$. The other two should at 22,000($\in$= 700) and at 18,400($\in$= 172) are assigned to the transitions $^1A_1 \rightarrow {}^1T_1$ and $^1A_1 \rightarrow {}^3T_1$ respectively. N-methyl cyclohexyl di thiocarbamate complex of Rhodium (III) Chloride has been studied and the bands in the electronic spectra at 22,800 cm^{-1} (log$\in$=7.07) and at 28,000 cm^{-1} (log $\in$ = 2.74) are attributed to $^1A_{1g} \rightarrow {}^1T_{1g}$ and $^1A_{1g} \rightarrow {}^1T_{2g}$ transitions respectively which suggested octahedral stereochemistry. Rh(III) chelate of 3-methyl-4-benzyl di imino -5-mercapto-1,2,4-thiozole showed three bands at 17,450 cm^{-1}, 20,000 cm^{-1} and 23,850 cm^{-1} which are assigned to $^1A_{1g}\rightarrow{}^3T_{1g}$, $^1A_{1g}\rightarrow{}^1T_{1g}$ and $^1A_{1g}\rightarrow{}^1T_{2g}$ transitions respectively ($\in$=80–95$mol^{-1}cm^{-1}$) indicating an octahedral geometry.[17] Electronic spectra of tri nuclear complexes of Rhodium(III) with N-alkylphenthiazine have been studied and the bands in the region 240 nm -270 nm are assigned to $\pi \rightarrow \pi^*$ and 270 nm -300 nm region are assigned to n- π transitions. Bands in the region 405-420 nm region in the spectra of the complexes are assigned to

$^1A_{1g}\rightarrow{}^1T_{2g}$ transitions.[18]

Steric Enhancement of Resonance

The phenomenon of stericenhancement of resonance was discovered by Balaiah and Uma[19] while studying the electric dipole moments of some substituted anisoles and acetophenones. The data obtained by them are given in table 1.

Table 1: Dipolemoments of substituted anisoles and acetophenones.

Compound	Dipole moment [D]		
	Observed D in C_6H_6 at 30^0	Calculated D for free rotation of OCH_3	D mesomeric moment
P-Nitroanisole	4.74	4.51	0.23
2.Methyl-4-Nitroanisole	5.29	4.71	0.58
2,6-Dimethyl-4-Nitroanisole	4.77	4.89	-0.12
P-Methoxy acetophenone	3.51	3.37	0.14
4-Methoxy -3-methyl acetophenone	3.91	----	----
3,5-Dimethyl -4 Methoxyacetophenone	3.49	3.62	-0.13

The difference between the observed and calculated moments of p-nitroanisole is 0.23 D which is attributed to the mesomeric interaction of the $–OCH_3$ and $–NO_2$ groups, but in the case of 2-Methyl-4-Nitroanisole, the mesomeric moment is 0.58 D. This significantly larger moment indicates a greater mesomeric interaction of the $–OCH_3$ and $–NO_2$ groups in 2-Methyl-4-Nitroanisole than in P-Nitroanisole. The larger moment of 2-Methyl-4-Nitroanisole was attributed to the o-methyl occupying a position away from the methyl group (I and II) such a preferred orientation restricts the rotation of $–OCH_3$ and the probability of its attaining planarity with the benzene ring increases. This phenomenon, caused by the steric effect, was termed steric enhancement of resonance.[20] Stericenhamcement of resonance was also observed in 4-methoxy-3-methyl-acetophenone. The existence of stericenhancement of resonance in the above compounds became even more apparent from the fact that the dipole moments of 2,6-dimethyl-4-nitroanisole and 3,5-dimentyl-4-methoxy acetophenone are almost the same or even lower than those of P-Nitroanisole and P-methoxy acetophenone respectively, indicating that the two methyl groups ortho to the $–OCH_3$ group cause steric inhibition of resonance. The preferred orientation of $–OCH_3$ group and consequent stericenhancement of resonance are possible only when there is a single substituent ortho to the $–OCH_3$ group. After the discovery of steric enhancement of resonance used this term to describe a different phenomenon which, according to them may properly termed as stericdimination of electronic suppression of resonance interaction. They are not aware of Balaiah and Uma's publication as they themselves acknowledged.[21] The studies of diamagnetic susceptibility measurements and kinetic studies of several trisubstituted benzenes provided additional evidence in support of this view.[22]

The kinetic data obtained on the oxidation of substituted phenyl methyl sulphoxides by Chloramine-T also furnish the evidence for stericenhancement of resonance (Table 1.2).

Table 1.2: Oxidation of phenyl methyl sulphoxides by chloramines–T in buffered ethanol (1:1V/V p^H=7.3).

Substrate	**K_2 X 10^2 mol^{-1} sec^{-1}**
Phenyl methyl sulphoxide	4.34
3-Tolyl methyl sulphoxide	5.99
4-methoxyphenyl methyl sulphoxide	13.45
4-methoxy -3-methyl phenyl methyl sulphoxide	20.54
3,5-Dimethyl -4-methoxyphenyl methyl sulphoxide	8.80

Infrared, Electronic and ^1H NMR spectra palladium (II) Chloride complexes of aryl methyl sulphides provided[23] further evidence for the existence of stericenhancement of resonance (Table 1.3).

Table 1.3: IR, Electronic and ^1H NMR spectra of the complexes.

Complex	**IR** $\nu(Pd-S)cm^{-1}$	**Elec-Spec**		**^1H NMR**			
		$\lambda\ max$	$\in$	**$-SCH_3$** (δ)	**$-CH_3$** (δ)	**OCH_3** (δ)	**Ph Protons** (δ)
Trans-$PdCl_2$ $(C_6H_5SCH_3)_2$	298	332 277	11,600 7,100	2.66	—	—	7.2-7.86
Trans-$PdCl_2$ (m-CH_3 $C_6H_4SCH_3)_2$	297	335 277	11,900 6,600	2.49	2.26	—	7.09-7.49
Trans-$PdCl_2$ (p-OCH_3 $C_6H_4SCH_3)_2$	277	365 277	10,000 6,800	2.52	—	3.69	6.69-7.67
Trans-$PdCl_2$ (4-OCH_3-3-CH_3 $C_6H_3SCH_3)_2$	270	372 277	10,800 8,700	2.52	2.18	3.80	6.66-7.66
Trans-$PdCl_2$ (3,5-Di-CH_3 -4-$OCH_3C_6H_2SCH_3)_2$	312	356 277	10,400 5,700	2.46	2.18	3.60	7.12-7.32

It is observed that the electron-releasing substituent present in the ligand decreases the $\nu(Pd-S)$ stretching frequency, where as electron with drawing group increases.[24] The $\nu(Pd-S)$ stretching frequency in the complex trans- $PdCl_2(p\text{-}OCH_3\ C_6H_4SCH_3)_2$ is at 277 cm^{-1}. (Table-III) which is much less than the corresponding frequency in Trans-$PdCl_2$ $(C_6H_5SCH_3)_2$.[25] The decrease is caused by p-OCH_3, an electron releasing group. The $\nu(Pd-S)$ stretching frequency in Trans-$PdCl_2$ (m-CH_3 $C_6H_4SCH_3)_2$ is 297 cm^{-1} Which is almost the same as that of the parent compound. The $\nu(Pd-S)$ stretching frequency in Trans-$PdCl_2$ (4-OCH_3-3-CH_3 $C_6H_3SCH_3)_2$ is at 270 cm^{-1}, which is less than that of Trans-$PdCl_2$ (p-OCH_3 $C_6H_4SCH_3)_2$ because of the 3-methyl group in 4-Methoxy-3-Methyl phenyl methyl sulphide exerts an accelerating influence of the conjugation of methoxy group with the phenyl ring. In the electronic spectral data (Table III). The band at 274 is due to $L(\pi)$-$L(\pi^*)$ transition. The other intense one is of ligand to metal charge transfer band. The large bathochromic shift of the charge transfer band (332 nm to 365 nm) in the complex Trans-$PdCl_2$ (p-OCH_3 $C_6H_4SCH_3)_2$ is due to the presence of electron repelling –OCH_3 in p-position.

The λ_{max} value still increases to 372 nm in the complex Trans-$PdCl_2$ (4-OCH_3-3-CH_3 $C_6H_3SCH_3)_2$ which due to steric enhancement of resonance. The phenyl protons in the complex Trans-$PdCl_2$ $(C_6H_5SCH_3)_2$ are in the range δ 7.2 to7.86. In the complexes Trans-$PdCl_2$ (m-CH_3 $C_6H_4SCH_3)_2$ and Trans-$PdCl_2$ (p-OCH_3 $C_6H_4SCH_3)_2$ the phenyl protons are in the range δ 7.09 to 7.49 and δ 6.69 to 7.67 respectively. The shift to upfield in these complexes is due to the electron-releasing nature of 3-CH_3 and 4-OCH_3 groups present in the phenyl ring. In the complex Trans-$PdCl_2$ (4-OCH_3-3-CH_3 $C_6H_3SCH_3)_2$ phenyl protons range still decreases (δ6.66 to 7.66) which are due to steric enhancement. It was thought worth while to study the infrared, electronic and NMR spectra of certain Rhodium complexes containing appropriate ligands with a view to explore the possible existence of this phenomenon in such compounds.

Hence in the present study appropriate mono, di and tri substituted phenyl methyl sulphides and their $RhCl_3$ complexes have been prepared in order to study the following.

1) Low frequency infrared spectral data to explain the substituent effects over

$$\nu\ (Rh-S) and\ \ \nu(Rh-Cl).$$

2) Electronic spectra of these complexes to study the substituent effects over charge transfer bands.

3) The existence of steric enhancement of resonance in these complexes.
4) Fragmentation pattern of some ligands of these complexes in mass spectra is also been presented.

Experimental Methods

Preparation of Thiophenol

A mixture of 240 g of concentrated sulphuric acid and 720 g of crusted ice was taken in a 2-litre flask. Sixty grams (0.33 mol) of Benzene sulphonyl chloride was added to the flask. Zinc dust added in a few lots, while the contents of the flask were shaken gently. After stream-distillation, the distillate was ether extracted, dried with anhydrous sodium sulphate, ether evaporated and distilled. The fraction coming over at b.p 167-169^{0}c was collected.[26]

Preparation of Methyl phenyl sulphide

To a solution of thiophenol (14g) in 10% sodium hydroxide solution (65 ml), dimethyl sulphate (16 g) was added with shaking under cooling. The mixture was refluxed for half an hour. Some more sodium hydroxide solution (15 ml) was added to the refluxing mixture so as to make it distinctly alkaline. The refluxing was continued for another half an hour. After cooling oil and the aqueous layer were extracted with ether. The ether extract was washed with water and dried over anhydrous sodium sulphate. The ether was removed and the sulphide was distilled, b.p 190-192^{0}c.[27]

Preparation of Methyl p-nitrophenyl sulphide

Para-Nitro thiophenol was prepared by the procedure of Price and Stacy and methylated at once without isolating the thiophenol.[28] To a solution of p-chloronitrobenzene (78.8 g) in boiling ethanol (125 ml), an ehanolic solution of sodium disulphide, prepared from sodium sulphide monohydrate (87.5 g) and sulphur (11.7 g) was added gradually in about 10 minutes. Then an ethanolic solution of sodium hydroxide (20 g) was added dropwise over a period of 20 min, the mixture boiling under reflux. The heating was stopped and dimethyl sulphate (63 ml) was added carefully so that the mixture refluxed gently. The reaction mixture was allowed to settle and filtered. The filtrate on dilution with water furnished the sulphide (50 g). It was filtered, dried and crystallized from ethanol: m.p. 72-73^{0}C.

Preparation of p- Methoxy thiophenol[29]

To a solution of potassium ethylxanthate (75 g) in water (175 ml) kept at 70-80^{0}c was added slowly with vigorous stirring a cold solution of diazotized p-anisidine (31 g) to which had been added enough sodium acetate to neutalise the free acid. Stirring and heating were continued for 1.5 hr to complete the decomposition of diazonium ethylxanthate. The mixture was cooled and extracted with ether. The ether solution was washed with sodium hydroxide solution (5%), then with water and dried over anhydrous sodium sulphate. After the removal of ether the xanthogenic ester was heated under reflux for 3 hours with a solution of potassium hydroxide (29 g) in ethanol (95% in 500 ml) to which had been added glucose (5 g). The solution was concentrated to about 75 ml, acidified with dilute sulphuric acid, zinc dust (about 1 g) added and the thiophenol was removed by distillation with stream. The compound was extracted with ether, the ether solution dried over calcium chloride, the solvent removed and the compound distilled, b.p 88-89^{0}c/5mm; b.p 89-90^{0}c/ 5mm.

Preparation of p- Methoxy phenyl methyl sulphide

This was obtained by the methylation of the above thiophenol as usual. The compound boiled at 243-244^{0}c; Suter and Hanses[29] report b.p 99-100^{0}c /4 mm.

Preparation of o-Carboxythiophenol(Thiosalicylic acid)

In a 4-litre beaker 290 ml of water was heated to boiling and 260g (1.08 mol) of crystallized sodium sulphide ($Na_2S.9H_2O$) and 34 g of powdered sulphur were dissolved by heating and stirring. A solution of 40 g of sodium hydroxide in 100 ml of water was then added and the mixture cooled, first in cold water and finally by a freezing of ice and salt. In a 2-litre beaker, set in freezing mixture and provided with a stirrer and a thermometer for reading temperature at 0^{0}c were placed 500 ml of water. 137 g (1 mol) of anthranilic acid and 200 ml of concentrated hydrochloric acid, the stirrer was started and the mixture cooled to about 6^{0}c. Meanwhile 69 g (1 mol) sodium nitrate was dissolved in 280 ml of hot water and the solution cooled in ice; portions were then placed in a separate funnel of convenient size, supported in such a way that the lower end of the steam extends beneath the surface of the antranilic acid solution. When temperature has fallen to 5^{0}c, the nitrite solution was run about 500 g of cracked ice was added at such a rate as keep the temperature below 5^{0}c. A drop of solution should give an immediate blue colour with starch-iodide paper. The stirrer and thermometer were transferred to the alkaline sulphide solution, the temperature of which must be below 5^{0}c. The diazonium solution was added over a period of 20-30 minutes along with 950 g of ice to prevent a rise above 5^{0}c. When addition was complete, the water bath was removed and the mixture allowed to warm up to room temperature, after two hours the evolution of Nitrogen ceases. About 180 ml of concentrated hydrochloric acid was added until the solution was acid to con red paper, and the precipitate of dithio salicylic acid was filtered and washed with water. To remove the excess of sulphur, the precipitate was dissolved by boiling with a solution of 60 g of anhydrous sodium carbonate, in 2 litre of water, and the mixture was filtered while hot. It was divided into five equal parts and the dithio salicylic acid reprecipitated as before with concentrated hydrochloric acid. The solid was filtered, the cake sucked as dry as possible. The moist cake was mixed with 27 g of zinc dust and 300 ml of glacial acetic acid in a 1- litre round bottomed flask, and the mixture was refluxed vigorously for about four hours. When the reduction was complete, the mixture was cooled and filtered with suction. The filter cake was washed once with water and then transferred to a one litre beaker. The cake was suspended in 200 ml of water and the suspension was heated to boiling. The hot solution was made strongly alkaline by the addition of about 40 ml of 33% aqueous sodium hydroxide solution. The alkaline solution was boiled for about twenty minutes to ensure complete extraction of the product from the filter cake, filtered from the insoluble material and the thiosalicylicacid was then precipitated by the addition of sufficient concentrated hydrochloric acid to make the solution acid to congored paper. The product was filtered with solution, washed once with water and dried in an oven 100-110^{0}c. The yield of a product which melts at 162-163^{0}c is 110-130g. This product was sufficiently pure for most purposes. For crystallization 5 g of this material was dissolved in 20 ml of hot 95% alcohol and 40 ml of water was added. The solution boiled with a little decolorizing carbon, filtered hot and then allowed to cool. The product crystallized in yellow flakes. The yield of crystallized material was 4.7 g; m.p 163-164^{0}c.[30]

Preparation of o-Carboxyphenyl methyl sulphide

o-carboxythiphenol was refluxed with sodium hydroxide aqueous solution and dimethyl sulphate. On cooling and acidifying with hydrochloric acid, the crude o-carboxyphenyl methyl sulphide sepearated. On crystallization in ehanol it gives sharp needles; m.p 169-170^{0}c.

Preparation of m-Carboxyphenyl methyl sulphide

m-Aminobenzoic acid (17 g) was diazotized with sodium nitrite (15 g) and hydrochloric acid (50 ml) under the usual conditions. The resulting diazonium salt solution was poured into a hot (70^{0}c) freshly prepared solution of potassium ethyl xanthate (20 g in 100 ml of water) containing sodium carbonate (50 g) to neutralize the acid in diazonium salt solution. After the brisk evolution of gases had subsided, the mixture was treated with sodium hydroxide solution (5 g in 50 ml of water) and dimethyl sulphate (15.8 g) and refluxed for 5 hours. On cooling and acidifying with hydrochloric acid, the crude m-carboxyphenyl methyl sulphide separated, yield 80%. This on crystallization from dilute alcohol melting at 126-127^{0}c.

Preparation of p-Carboxyphenyl methyl sulphide

It was prepared from p-aminobenzoic acid. The procedure adopted was an in the case of the m-isomer. The compound, crystallized from ethanol; melted at 189-190^{0}c. Gattermann (Ber 32, 1151) who prepared it by oxidizing p-methylmercaptobenzaldehyde reports the same melting point.

Preparation of m-Thiocresol

This was prepared from m-toludine by the same procedure that was adopted for o-chlorothiophenol. It boiled at 90-93^0/25 mm and reports b.p. 107.5^0 / 50 mm.[31]

Preparation of Methyl m-tolyl sulphide

This was obtained by the methylation of m-thiocresol with dimethyl sulphate and alakali. It boiled at 110-112^0/30mm. Tarbell and fukushima report b.p 110-112.5^0/ 31mm.[32]

Preparation of 2,6-Dimethylthiophenol

This was prepared from 2,6-dimethylaniline by diazotization and coupling with potassium ethyl xanthate, the product boils at 66-67^0/10mm; b.p. 91^0/ 50 mm.[33]

Preparation of Methyl 2,6-dimethylphenyl sulphide

Methylation of the above thiophenol with dimethyl sulphate and alkali gave the sulphide. It boiled at 216-218^0; 80^0/13 mm. Baliah and Uma report b.p. 217-218^{0}c.[34]

Preparation of 4-Methoxy-3-methylbenzene sulphonyl chloride

This was prepared following the procedure of Huntress and Carbon.[35] Dry methyl o-tolyl ether (61 g) was dissolved in dry chloroform (100 ml). The solution was cooled to 0^{0}c and freshly distilled chloro sulphonic acid (150 ml) was added slowly with constant stirring by means of a mechanical stirrer. The temperature was not allowed to rise above 5^{0}c. After the addition was complete, the mixture was stirred for a further period of half an hour. It was then poured into crushed ice (1Kg) with stirring. The chloroform layer was separated and the solvent evaporated off. The yield was 85%. The compound was used as such for the next step.

Preparation of 4-Methoxy-3-methyl thiophenol

Concentrated sulphonic acid (130 ml) was added to crushed ice (720 g) in a 2-litre flask and to the mixture were added 4-methoxy-3-methyl benzene sulphonyl chloride (60 g) and zinc dust (100 g). The contents of the flask were then subjected to steam-distillation. The thiophenol which separated from the distillate as a solid was taken up in ether, dried over anhydrous sodium sulphate and the ether removed. The thiophenol was purified by distillation. It solidified melting at 44-45^{0}c, Kolthatkan and Bokil report m.p. 42-43^{0}c.[36]

Preparation of 4-Methoxy-3-methyl phenyl methyl sulphide

The foregoing thiophenol (17 g) was methylated with dimethyl sulphate (15 g) in 10% sodium hydroxide solution (65 ml). The yield of the sulphide was 85%. It boiled at 258-259^{0}c. Ekambaram reports the same boiling point. Baliah and Uma report b.p. 160^{0}c /7 mm[37]

Preparation of 3,5-Dimethyl-4-methoxybenzenesulphonyl chloride

Chlorosulphonation of 2,6-dimethylanisole gave this compound in 50% yield. 2,6-dimethylanisole was obtained by methylation of 2,6-dimethylphenol.

Preparation of 3,5-Dimethyl-4-methoxythiophenol

Reduction of 3,5-dimethyl-4-methoxybenzenesulphonyl chloride with zinc dust and sulphuric acid gives this compound, b.p. 246-248^{0}c. Baliah and Uma report the same boiling point.[38]

Preparation of 3,5-Dimethyl-4-methoxyphenyl methyl sulphide

The foregoing thiophenol was methylated with dimethyl sulphate in 10% sodium hydroxide solution; b.p.128^{0}c/ 9 mm and report b.p. 106^0/7mm.[38]

General method for the preparation of $RhCl_3$ complexes with substituted Phenyl methyl sulphides

Rhodium (III) chloride was treated with a few drops of concentrated hydrochloric acid and dissolved in 10 ml of methanol. This solution was mixed with the required amount of ligand in 50 ml of methanol. In all the cases 0.05 mol of $RhCl_3$ was mixed with 0.15 mol of ligand. The solutions were heated under reflux for about an hour. The colour changed from deep red to deep orange. The solutions deposited orange red crystals, orange mass and orange yellow mass during 18 hours to 48 hours. The products were washed with methanol and ether and dried in vacuo. The yield ranged from 40 to 60%.

Trichlorotris (methyl phenyl sulphide) Rhodium (III)

This compound was crystallized from methanol and ether as orange-red crystals, m.p.165-173^{0}C (d),

Report m.p 165-173^{0}c (d)

Found C, 43.18; H,4.10. $C_{21}H_{24}S_3RhCl_3$

Required C, 43.40; H, 4.20%.

Trichlorotris (m-methyl tolyl sulphide) Rhodium (III)

This compound was crystallized from methanol and ether as orange-red crystals, m.p. 118-120^{0}C (d).

Found C, 46.08; H, 4.80. $C_{24}H_{30}S_3RhCl_3$

Required C, 46.19; H, 4.85%.

Trichlorotris (2,6-dimethylphenyl methyl sulphide) Rhodium (III)

This compound was crystallized from methanol and ether as orange-red crystals, m.p. 218-225^{0}C.

Found C, 48.56; H, 5.42. $C_{27}H_{36}S_3RhCl_3$

Required C, 48.689; H, 5.448%.

Trichlorotris (4-methoxy phenyl methyl sulphide) Rhodium (III)

This compound was crystallized from methanol and ether as orange-yellow crystals, m.p. 164-165^{0}C.

Found C, 42.80; H, 4.4. $C_{24}H_{30}S_3RhCl_3$

Required C, 42.89; H, 4.5%.

Trichlorotris (4-methoxy phenyl methyl sulphide) Rhodium (III)

This compound was crystallized from methanol and ether as yellow crystals, m.p.165-168^{0} C.

Found C, 35.09; H, 2.86. $C_{21}H_{21}N_3O_6S_3RhCl_3$

Required C, 35.16; H, 2.95%.

Trichlorotris (3-methyl-4-methoxy phenyl methyl sulphide) Rhodium (III)

This compound was crystallized from methanol and ether as orange yellow crystals, m.p. 122-124^{0}C.

Found C, 45.30; H, 5.01. $C_{27}H_{36}O_3S_3RhCl_3$

Required C, 45.41; H, 5.08%.

Trichlorotris (3,5-dimethyl-4-methoxy phenyl methyl sulphide) Rhodium (III)

This compound was crystallized from methanol and ether as orange crystals, m.p.162-164^0 C.

Found C, 47.54; H, 5.48. $C_{30}H_{42}O_3S_3RhCl_3$

Required C, 47.65; H, 5.60%.

Trichlorotris (ortho carboxy phenyl methyl sulphide) Rhodium (III)

This compound was crystallized from methanol and ether as orange-yellow crystals, m.p. 200-210^{0}C.

Found C, 40.21; H, 3.26. $C_{24}H_{24}O_6S_3RhCl_3$

Required C, 40.37; H, 3.38%.

Trichlorotris (m- carboxy phenyl methyl sulphide) Rhodium (III)

This compound was crystallized from methanol and ether as orange-yellow crystals, m.p.225-230^{0}C.

Found C, 40.22; H, 3.25. $C_{24}H_{24}O_6S_3RhCl_3$

Required C, 40.37; H, 3.38%.

Trichlorotris (p- carboxy phenyl methyl sulphide) Rhodium (III)

This compound was crystallized from methanol and ether as reddish brown crystals ,m.p.220-225^{0}C.

Found C, 40.20; H, 3.28. $C_{24}H_{24}O_6S_3RhCl_3$

Required C, 40.37; H, 3.38%.

RESULTS AND DISCUSSION

In the present Rhodium (III) chloride complexes with some substituted phenyl methyl sulphides as ligands are prepared and these infrared spectra in the region 500-200 cm^{-1} are recorded. The vibrational frequencies in the region are given in table (4.1). The main interest in the present investigation is to assign the (Rh-Cl) and (Rh-S) stretching frequencies and to study the substituent effect on v(Rh-Cl) and v(Rh-S) stretching frequencies. The assignments of v(Rh-Cl) and (Rh-S) is tabulated (table 4.1) and the spectral charts are presented. For the assignment of v(Rh-Cl) and v(Rh-S) frequencies the spectra of both complexes and ligands are compared. The meridional generally having three bands assignable to v(Rh-Cl) and the facial only two (table 4.2) and the data are in close agreement with those reported earlier.

Table 4.1

Name of the complex	**vibrational frequencies in the region 500cm^{-1}-200cm^{-1}**
Trichloro tris-(methyl phenyl sulphide) Rhodium(III)	484(vs), 425(m), 401w), 382(vw), 354(s), 337(vs), 320(vs), 293(vs), 216(m).
Trichloro tris(P-methoxy phenyl methyl Sulphide)Rhodium(III)	524(vs), 499(m), 466(vw), 452(w), 422(vw), 398(m), 398(m), 367(m), 342(vs), 308(vs), 266(m), 229(vw), 206(m), 182(m), 173(m).
Trichloro tris-(methyl p-nitro-phenyl Sulphide)Rhodium(III)	521(m), 482(s), 471(s), 407(w), 369(w), 355(vs), 331(s), 313(vs), 266(m), 238(s)
Trichloro tris –(4-methoxy-3-methyl Phenyl methyl sulphide)Rhodium(III)	525(M), 5047(M), 444(M), 422(w), 382(vw), 344(s), 317(s), 293(s), 269(w), 178(vs)
Trichloro tris- (3,5-dimethyl-4-methoxy Phenyl methyl sulphide)Rhodium(III)	529(m), 503(m), 452(s), 421(w), 390(m), 372(m), 355(vs), 333(m), 289(vs), 246(w), 225(m), 191(s)
Trichloro tris-(2,6-dimethyl phenyl – Methyl sulphide)Rhodium(III)	512(m), 419(m), 335(vs), 313(vs), 287(vs), 247(m), 231(w), 215(m), 199(m), 183(m), 167(w)
Trichloro tris–(o-carboxy phenyl– Methyl sulphide)Rhodium(III)	498(s),464(w),405(vw),351(vs),319(vs),291(vs), 252(w),212(m),181(vw),154(m)
Trihloro tris-(m-carboxy phenyl-Methyl sulphide)Rhodium(III)	490(m), 478(w), 467(w), 420(vs), 385(w), 351(vs), 333(vs), (br), 290(w), 270(w), 254(w) 218(m), 200(w), 183(w), 164(m)
Trichloro tris-(p-carboxyphenyl- Methyl sulphide)Rhodium(III)	526(m), 487(s),416(m),333(vs)(br),307(vs), 214(vw),181(vw).

*Vs=very strong, s=strong, ms=medium strong, m=medium, mw=medium weak, w=weak, vw=very weak.

Table 4.2: Assignment of v(Rh-Cl) in RhCl$_3$ and v(Rh-Cl) and v(Rh-S) stretching frequencies in complexes.

Compound	**v(Rh-Cl)cm^{-1}**	**v(Rh-S)cm^{-1}**
Rhodium (III)chloride	334(vs)	
Mer-trichloro tris-(methyl phenyl Sulphide)Rhodium(III)	337, 320, 293	216
Mer-trichlorotris-(p-methoxy-phenyl Methylsulphide)Rhodium(III)	342, 307, 266	206
Mer-Trichlorotris-(methyl p-nitro phenyl sulphide) Rhodium(III)	(355)331, 313, (265)	238
Mer-trichlorotris-(4-methoxy-3- methyl phenyl methyl sulphide) Rhodium(III)	344, 317, 294	178
Mer-trichlorotris-(3,5-dimethyl 4-methonypheyl methyl sulphide)Rhodium(III)	355, 333, 289	246, 225, 191
Mer –trichlorotris-(2,6-dimethyl Phenyl methyl sulphide) Rhodium(III)	335, 313, 287	247
Fac-trichlorotris-(o-carboxy phenyl Methyl sulphide) Rhodium(III)	319, 291	251(212)
Fac-trichlorotris-(m-carboxy phenyl Methyl sulhide) Rhodium(III)	333, 290	287
Fac-trichlorotris-(p-carboxy Phenyl methyl sulphide) Rhodium(III)	333, 307	214

The carbonyl frequency of meta and para carboxylic groups in their complexes gets increased (Table 4.4) when compared with the ligands. But in the case of o- isomer it is almost same. This may be attributed to higher stability of the complexes having meta and para carboxylic substituted phenyl methyl sulphides.

OH stretches in carboxylic substituted phenyl methyl sulphides and in their complexes.

	Ortho(cm^{-1})	**meta(cm^{-1})**	**Para (cm^{-1})**
Ligand	3450	3400	3390
Complex	3410	3410	3410

The appearance of –OH band in the complexes of carboxylic substituted phenyl methyl sulphides shows the absence of intramolecular hydrogen bonding between –OH of carboxylic group and chlorine.

Electronic Spectra of Complexes

The results of the electronic spectra are in the good agreement with the infrared spectra. The electronic spectra of all the complexes are presented in the table 4.6. For comparison the spectra of ligands were also taken. Acetic acid was used as solvent for both the complex and the ligand. Each complex exhibits two bands which are due to intra-ligand transitions and ligand to metal or metal to ligand charge transfer transitions. The band at ~ 256 is assigned as $L(\pi) \rightarrow L(\pi^*)$ transition. The other intense band is assigned as ligand-metal charge transfer band or metal-ligand charge transfer band. The appearance of these two bands spaced $\sim 10{,}000$ inb AcOH shows that the complexes are in trans–(mer)- configuration except those of carboxy substituted complexes. The observed data are in good agreement with the premium spectral studies.[39-41]

For the complex $RhCl_3$ $(C_6H_5SCH_3)_3$. Three strong bands at 337cm^{-1}, 320cm^{-1} and at 293cm^{-1} for Rh-Cl are obtained and it suggests the complex has mer-configuration. Weaker band at lower range at 216cm^{-1} is predicted to v(Rh-S) mode. In the complex mer-$RhCl_3(P\text{-}OCH_3\ C_6H_4\ SCH_3)_3$, three strong bands at 342cm^{-1} 307cm^{-1} and at 266 $cm^{-1.}$ For Rh-Cl are obtained the v(Rh-S)stretching frequency is at 206cm^{-1} while in the unsubstituted one it is at 216cm^{-1}. This decrease is due to the fact that the OCH_3 group at para position behaves as a strong electron releasing one here the resonance effect outweighs the electron –with drawing inductive effect and the –OCH_3 group has a net electron-releasing tendency to the benzene ring, and so the v(Rh-S) stretching frequency is decreased to a lower region than that of the parent compound. The electron withdrawing $–NO_2$ group at para-position attracts electrons through conjugative interaction. So the mer-$RhCl_3(P\text{-}NO_2C_6H_4SCH_3)_3$ complex has its v(Rh-S) stretching frequency at higher region(238 cm^{-1}) than its parent compound. Three strong bands at 355 cm^{-1}, 331cm^{-1} and at 313 $cm^{-1}$for Rh-Cl are obtained.

A similar observation is made in NMR studies of some substituted phenyl methyl sulphides. The data are given in table 4.3.

Table 4.3: Chemical shift of aromatic multiplet of para-disubstituted benzenes (Half molecules).

Compound	chemical shift in cps centre of AB quarter
$C_6H_5SCH_3$	435.5
p-$OCH_3C_6H_4SCH_3$	423.5
p-$NO_2C_6H_4SCH_3$	461.8

Substituent in ortho-position cause other effects in addition to their well known inductive and resonance effects. Three additional effects are very often referred to as proximity effects and have been reported in various studies.[42] In an attempt to explain these proximity effects many hypotheses were proposed such as primary and secondary effects. Intramolecular hydrogen bonding. Field effects and solvation influencing effects and several less-understood effects. The proximity effect for a given ortho-substituent may vary with the nature of the reaction centre and reaction conditions. Brown emphasized the importance of the primary steric effects, Champan stressed the importance of solvent participation (including steric inhibition of salvation).[43] The resonance involving 2p-3dπ bond formation, because of the geometry and number of 3d orbitals available on sulphur, would suffer very little steric inhibition by ortho-substituents. This type of resonance involving sulphur has been invoked by many[44] authors.

In the complex mer-trichlorotris(2,6-dimethylphenyl methyl sulphide) Rhodium(III). The Rh-S stretching frequency appears at 247 cm^{-1}. The frequency increase is due to steric inhibition of resonance due to the two methyl groups present adjacent to $–SCH_3$. Three strong bands at 335 cm^{-1}, 313 cm^{-1} and at 287 cm^{-1} for Rh-Cl are obtained. The Rhodium (III) Chloride complexes of carboxylic substituted phenyl methyl sulphides only two strong bands for Rh-Cl are obtained.

A careful comparison is made with the spectra of ligands and complexes and facial-octahedral configuration are suggested for o-COOH, m-COOH and p-COOH substituted complexes.

Complex	**V (Rh-Cl)**
fac-$RhCl_3$(o -COOH C_6H_4 $SCH_3)_3$	319, 291
fac-$RhCl_3$(m -COOH C_6H_4 $SCH_3)_3$	333,289
fac-$RhCl_3$(p -COOH C_6H_4 $SCH_3)_3$	333,307

Table 4.4: $>C = O$ stretches in carboxylic substituted phenyl methyl sulphides and in their complexes.

	Ortho(cm^{-1})	**meta(cm^{-1})**	**Para (cm^{-1})**
Ligand	1695	1700	1697
Complex	1698	1708	1720

Table 4.5: Electronic spectral data of Rhodium(III) Chloride of phenyl methyl sulpjhides.

Compound	λ_{max}	$\in$
Trichlorotris-(methyl phenyl sulphide) Rhodium (III)	328, 256	11,500,10,900
Trichlorotris-(p-methoxy phenyl methyl sulphide) Rhodium (III)	349, 255	21,90015,500
Trichlorotris-(methyl p-nitro phenyl sulphide) Rhodium (III)	321, 260 256	11,700,13,600 13,100
Trichlorotris- (m-tolyl methyl sulphide) Rhodium (III)	322, 259	22,200,20,100
Trichlorotris-(4-methoxy-3-methylphenyl methyl sulphide) Rhodium (III)	354, 259	22,700,20,700
Trichlorotris- (3,5- dimethyl-4-methoxy- phenyl methyl sulphide) Rhodium (III)	341, 255	27,00016,200
Trichlorotris- (2,6-dimethyl phenyl methyl sulphide) Rhodium (III)	280, 260, 256	9,100,11,800 11,700
Trichlorotris- (o-carboxy phenyl methyl sulphide) Rhodium (III)	277,255	13,500,17,400
Trichlorotris-(m-carboxy phenyl methyl sulphide)Rhodium (III)	315, 259	14,300,21,700
Trichlorotris- (p-carboxy phenyl methyl sulphide) Rhodium (III)	291, 260 255	12,300,17,400 17,400
o-carboxy phenyl methyl sulphide	327, 257	2,700,6,200
m-carboxy phenyl methyl sulphide	315, 258 254	1,400,7,800 8,250
p-carboxy phenyl methyl sulphide	295, 256	22,950,23,900
p- nitro phenyl methyl sulphide	328, 256	---------

The spectral data given in the table 4.6 would reveal that the absorption bands of the complexes, mer-Rh-Cl_3 (p-COOH $C_6H_4SCH_3)_3$ and $RhCl_3$ (p-$NO_2C_6H_4SCH_3)_3$ and those of their ligands are almost identical. The absorption bands for the complex and the ligand must be different if the charge transfer is from S to Rh or from Rh-S. Since no downward or upward shift is observed this directional charge transfer of Rhodium to sulphur might have been opposed by the electron withdrawing nature if these substituents(p-COOH, p-NO_2) present in phenyl methyl sulphide. The large bathochomic shift of the charge transfer band (328 nm to 349nm) in the complex mer-trichlorotris–(p-methoxy phenyl methyl sulphide) Rhodium (III) is due to the presence of eelectron repelling –OCH_3 group in p-position of the ligand.in the complex where there is electron releasing group present in the p-position of the phenyl methyl sulphide the transition is from Sulphur to Rhodium. Two methyl groups cause steric inhibition in mer-$RhCl_3(2,6\text{-di}CH_3\ C_6H_3SCH_3)_3$ complex which results in a hypsochromic shift. The symmetry properties of sulphur p-orbitals require that in the polar excited form of methyl phenyl sulphide, the sulphur methyl- single band should lie in the same plane as the benzene ring. O-substituents would therefore be expected to inhibit sulphur benzene conjugation. So when there is an electron donor is present in the benzene ring the electronic transition is from sulphur (of –S Me) to Rhodium and when there is a π-electron acceptor present in the benzene ring or (if there is steric inhibition of resonance). The electronic transition is from Rhodium to Sulphur.

Evidence for steric enhancement of resonance

The λ_{max} of the charge transfer band in the complex mer-$RhCl_3(p\text{-}\ OCH_3\ C_6H_4\ SCH_3)_3$ is at 349 nm (Table 4.6) which is much higher than the charge transfer band of mer-$RhCl_3$ $(C_6H_5SCH_3)$. This increase is caused by the p-methoxyl, which is an electron releasing group. The λ_{max} of the transfer band in mer-$RhCl_3(4\text{-}OCH_3\text{-}3\text{-}CH_3\text{-}C_6H_3SCH_3)_3$ is at 354nm, which is higher than that of mer-$RhCl_3(p\text{-}\ OCH_3\ C_6H_4\ SCH_3)_3$, because the 3-methyl group in 4-methoxy-3-methyl phenyl methyl sulphide exerts an accelerating influence of the conjugation of methoxy group with the phenyl ring. The methyl group makes the methoxyl assume a trans-orientation and hence the probability of the methoxy group attaining planarity with the aromatic ring increases. There can, therefore, be enhanced interaction of the methoxy group with the aromatic ring, resulting in a greater mesomeric electron release to the sulphur of –SCH_3.

Table 4.6.

Compound	λ_{max}	$\in$	**Solvent**
$RhCl_3\ (C_6H_5\ SCH_3)_3$	328, 256	11,500, 10,900	Acetic acid
$RhCl_3(p\text{-}\ OCH_3\ C_6H_4\ SCH_3)_3$	349, 255	21,900, 15,500	Acetic acid
$RhCl_3(m\text{-}\ CH_3\ C_6H_4\ SCH_3)_3$	322, 259	22,150, 20,100	Acetic acid
$RhCl_3(4\text{-}OCH_3\text{-}3\text{-}CH_3\text{-}C_6H_3SCH_3)_3$	354, 259	22,700, 20,700	Acetic acid
$RhCl_3(3,5\ \text{–Di-}CH_3\text{-}\ 4\text{-}OCH_3\text{-}C_6H_2SCH_3)_3$	341, 255	27,000, 16,200	Acetic acid

Table 4.7.

Complex	**v(Rh-S) cm^{-1}**
$RhCl_3$ (C_6H_5 SCH_3)$_3$	216
$RhCl_3$(p- OCH_3 C_6H_4 SCH_3)$_3$	206
$RhCl_3$(4-OCH_3-3-CH_3-$C_6H_3SCH_3$)$_3$	178
$RhCl_3$(3,5 –Di-CH_3- 4-OCH_3-$C_6H_2SCH_3$)$_3$	246(225)

If a single substituent ortho to the –OCH_3 group enhances its resonance interaction with the para substituent, two ortho substituent should cause steric inhibition of resonance, because the two ortho substituents will prevent the –OCH_3 from attaining planarity with the benzene ring and hinder conjugation with the ring. Such steric inhibition of resonance is indeed observed in mer-trichlorotris-(3,5- dimethyl phenyl methyl sulphide) Rhodium (III).

Evidence is also available for steric enhancement of resonance in mer-trichlorotris-(4-methoxy-3-methyl phenyl methyl sulphide) Rhodium (III) from infrared spectral data as shown in table 4.8

Table 4.8.

Compound	- SCH_3 (δ)	-CH_3 (δ)	- OCH_3 (δ)	**Ph Protons** (δ)
$RhCl_3$ (C_6H_5 SCH_3)$_3$	2.82	2.12-2.24	----	7.22-7.67(c)
$RhCl_3$(p- OCH_3 C_6H_4 SCH_3)$_3$	2.83	2.1-2.38	----	7.16-7.66
$RhCl_3$(m- CH_3 C_6H_4 SCH_3)$_3$	2.80	2.1-2.8	3.82	6.72-7.66
$RhCl_3$(4-OCH_3-3-CH_3-$C_6H_3SCH_3$)$_3$	2.81	2.18-2.81	3.82	6.66-7.60
$RhCl_3$(3,5 –Di-CH_3- 4-OCH_3-$C_6H_2SCH_3$)$_3$	2.78	2.1-2.80	3.70	6.82-7.30

This phenomenon also gains support from proton magnetic resonance studies (table 4.9). The phenyl protons in the complex mer-trichlorotris-(methyl phenyl sulphide) Rhodium (III) are in the range 7.22-7.67. In the complex trischlorotris-(p-methoxy phenyl methyl sulphide) Rhodium (III) the phenyl protons are in the range 6.72-7.66. The shift to up field is due to electron releasing nature of –OCH_3 in p-position. In the complex mer-trichlorotris-(4-methoxy-3-methyl phenyl methyl sulphide) Rhodium (III) phenyl protons range still decreases which is due to stericenhancement. Hence 3-CH_3 group ortho to-OCH_3 in 4-methoxy -3-methyl phenyl methyl sulphide does not sterically inhibit the resonance interaction between –OCH_3 and –SCH_3 but actually enhance it. Indeed, when these are two –CH_3 groups ortho to –OCH_3 group steric inhibition is observed.

Mass Spectra

The occurrence of some skeletal rearrangement reactions in some sulphides have been demonstrated. The rearrangement fragment is formed in a one step process from the molecular ion as indicated by an appropriate metastable peak and the sulphide may eliminate a sulphur atom (and in same cases additional hydrogen atom) with the combination of the terminal groups. The spectra of the sulphides showed that one or two methyl groups at the ortho-position of the aryl rings markedly increase the intensity of M-R/ or M-SR ions. The mass spectra of $RhCl_3$ complex of m-tolyl methyl sulphide has been recorded. In recording the mass spectra of the complex only the organic material could be vaporized and for each the signal as its mass value is observed. Prominent peaks are accounted. The probable peaks have been proposed.

CONCLUSION

In the present Rhodium (III) chloride complexes with some substituted phenyl methyl sulphides as ligands are prepared and these infrared spectra in the region 500-200 cm^{-1} are recorded. For the complex $RhCl_3$ $(C_6H_5SCH_3)_3$ and three strong bands at $337cm^{-1}$, $320cm^{-1}$ and at $293cm^{-1}$ for Rh-Cl are obtained and it suggests the complex has mer-configuration. Weaker band at lower range at $216cm^{-1}$ is predicted to v(Rh-S) mode. In the complex mer-$RhCl_3(P\text{-}OCH_3\ C_6\ H_4\ SCH_3)_3$, three strong bands at $342cm^{-1}$ $307cm^{-1}$ and at 266 $cm^{-1.}$ For Rh-Cl are obtained the v(Rh-S)stretching frequency is at $206cm^{-1}$ while in the unsubstituted one it is at $216cm^{-1}$. This decrease is due to the fact that the OCH_3 group at para position behaves as a strong electron releasing one here the resonance effect outweighs the electron –with drawing inductive effect and the $–OCH_3$ group has a net electron-releasing tendency to the benzene ring, and so the v(Rh-S) stretching frequency is decreased to a lower region than that of the parent compound. In the complex mer-trichlorotris(2,6-dimethylphenyl methyl sulphide) Rhodium(III). The Rh-S stretching frequency appears at 247 cm^{-1}. The frequency increase is due to steric inhibition of resonance due to the two methyl groups present adjacent to $–SCH_3$.

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