Complexes with Ligands containing Group VB and VIB Atoms. Part IV.[1] Dialkyl Sulphide Complexes of Rhodium(III) and Iridium(III) Halides †

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A structural investigation of compounds of the type MX_3L_3 (M = Rh or Ir; X = Cl, Br, or I; L = dialkyl sulphide) has been carried out. The use of simple sulphides, L = Me_2S, Et_2S, C_4H_8S, or $C_5H_{10}S$ resulted in the formation of stable, crystalline solids facilitating the assignment of stereochemistry. I.r., u.v., ^1H n.m.r., and dipole moment measurements have been used to clearly show that the compounds obtained by the reaction of the appropriate metal halide with the dialkyl sulphide all have a common octahedral meridional configuration.

CHATT *et al.*[2,3] have recently reported their investigations on sulphide complexes of rhodium, iridium, and ruthenium halides with a view to the use of these compounds as potential catalysts in an analogous manner to the corresponding phosphine complexes. Fergusson and his co-workers [4] have also prepared a series of alkyl sulphide complexes of the platinum group metals and have compared the bonding in the compounds with the corresponding selenide complexes.

Following our preliminary communication [5] on the structure of $MCl_3(SEt_2)_3$ (M = Ir, Rh, and Ru), we now report fully on a series of dialkyl sulphide complexes of rhodium(III) and iridium(III) halides. Simple, symmetrical sulphides have been used in order to facilitate the assignment of the stereochemistry. Using such ligands stable, crystalline compounds of the type MX_3L_3 [M = Rh or Ir, X = Cl, Br, or I, and L = SMe_2, SEt_2, pentamethylene sulphide (pms), or tetramethylene sulphide (tms)] have been obtained (Table), in contrast to the formation of oily products obtained when the higher alkyl sulphide analogues are used.[2,4] Although the diethyl sulphide complexes have previously been prepared [6-10] the majority of the structural discussion [4,9,10] has been based on a *fac*-configuration [11] for $IrCl_3(SEt_2)_3$, whereas the compound has been shown to have a *mer*-configuration,[5] and therefore, a reassessment of these compounds is necessary. Complexes with dimethyl sulphide have received less attention. Both $IrCl_3(SMe_2)_3$ and $RhCl_3(SMe_2)_3$ have been prepared [7] and the latter treated with methylmagnesium iodide [12] to give $[Rh_2I_2Me_4(SMe_2)_3]$, which contains one bridging sulphide and two bridging iodine atoms. Russian workers [13] have

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recently reported the existence of both *fac*- and *mer*-isomers of $RhCl_3(SMe_2)_3$, which, however, we have been unable to substantiate. The remaining compounds in this paper are new.

EXPERIMENTAL

Rhodium Complexes.—The chlorides were prepared by refluxing rhodium trichloride hydrate and a slight excess of the dialkyl sulphide in ethanol for 15 min. After removal of most of the solvent, orange-red crystals were deposited. These were recrystallised from ethanol.

The bromides and iodides were prepared from the chlorides by metathetical replacement using LiBr or NaI.

Iridium Complexes.—The chlorides were prepared by reducing chloroiridic acid with boiling 2-methoxyethanol followed by addition of an excess of the dialkyl sulphide to the cooled solution. After heating under reflux for several hours the solution was evaporated to a small volume, and water was added dropwise to give a yellow solid. The yellow solid was recrystallised from ethanol.

The corresponding bromides were prepared from the chlorides by metathetical replacement using LiBr. We were unable to prepare any iodo-complexes by treatment of the chlorides with NaI.

	Analysis [a]			Far-i.r. spectra [b]				Electronic spectra [c]					^1H n.m.r. spectra [d]		
	% C	% H	% X	ν(M–X)	ν(M–S)	Bending modes	Others	$S \rightarrow M$, $X \rightarrow M$ charge transfer		$^1A_1 \rightarrow {}^1T_2$	$^1A_1 \rightarrow {}^1T_1$	$^1T_1 \rightarrow {}^3T_1$	α	α′	β
$RhCl_3(Me_2S)_3$	18·0 (18·2)	4·5 (4·6)	26·9 (26·9)	352s 330s 283m	315m	150m 140m	263m 170w 120m	43·6 (18,000)	35·5 (22,900)		24·2 (464)		7·57 (1·5)	7·76 (1·8)	
$RhBr_3(Me_2S)_3$	14·0 (13·6)	3·5 (3·4)	45·5 (45·3)	212s	312m	136s,br	95w	39·2 (25,800)	34·5 (21,240)		20·8 (306)		7·40 (2·0)	7·64 (2·0)	
$RhI_3(Me_2S)_3$	10·8 (10·8)	2·5 (2.7)	56·4 (56·8)		312w			37·0 (19,000)	34·2 (26,200)		20·3 (300)		7·04 (2·2)	7·47 (2·0)	
$IrCl_3(Me_2S)_3$	15·3 (14·9)	3·6 (3·7)	21·6 (21·9)	334s 321s	290w	150w 140m	250m 170w 120m	43·0 (19,400)		31·9 (505)	29·4 (332)	21·7 (53)	7·60	7·7	
$IrBr_3(Me_2S)_3$	12·0 (11·7)	3·0 (3·0)	38·7 (38·8)	210s	325w	139s,br	98w	42·0 (20,200)			25·2 (210)	20·4 (38)	7·40	7·59	
$RhCl_3(Et_2S)_3$	30·2 (30·4)	6·6 (6·3)		347s 319s	295w	190m		45·3 (23,200)	34·3 (25,800)		23·6 (370)		6·75	7·0	8·6
$RhBr_3(Et_2S)_3$	23·9 (23·5)	5·2 (4·9)		250m	325m	170m,br		40·2 (22,800)	34·05 (21,800)		21·25 (570)		6·56	6·86	3·87
$RhI_3(Et_2S)_3$	19·3 (19·1)	4·3 (4·0)			305w	140w,br		39·0 (20,200)	34·2 (22,600)	25·6 (2000)	20·0 (600)		6·48	6·75	8·52
$IrCl_3(Et_2S)_3$	25·5 (25·3)	5·5 (5·3)		324s 306s	270w	190m,br		42·2 (17,200)		31·8 (355)	29·0 (<100)	22·0 (32)	6·66	6·88	8·53
$IrBr_3(Et_2S)_3$	20·8 (20·5)	4·5 (4·3)		250m 218m	315m	180m,br		41·2 (17,700)			25·0 (200)	20·0 (30)	6·58	6·82	8·51
$RhCl_3(tms)_3$	30·7 (30·4)	5·3 (5·1)		350s 326s 309m	283m	147w	216s	43·5 (16,500)	34·2 (21,100)		24·4 (447)		7·0	6·0	7·75
$RhBr_3(tms)_3$	24·2 (23·7)	4·0 (4·1)		275w 238w		130m,br	190m	39·0 (17,500)	34·0 (18,400)		21·1 (334)		6·8	5·9	7·8
$RhI_3(tms)_3$	19·6 (19·3)	3·4 (3·2)			305w	140w	211s	36·7 (24,000)	34·0 (30,500)		20·4 (242)		7·0	6·1	7·9
$IrCl_3(tms)_3$	25·6 (25·6)	4·2 (4·3)		326s 305s	280sh	170m	218s 130w	41·6 (17,400)		31·2 (670)	29·2 (450)	21·7 (42)	7·0	6·2	7·7
$IrBr_3(tms)_3$	21·2 (20·7)	3·6 (3·5)		270m 250m	318w 300w	118m	196s	40·4 (19,100)			25·0 (230)	20·4 (41)	6·9	6·1	7·7
$RhCl_3(pms)_3$	34·9 (35·1)	6·0 (5·9)		345s 320m 305m	370sh	120w	215sh 300m	43·5 (20,400)	34·4 (29,100)		24·2 (434)		6·6	6·83	8·23
$RbBr_3(pms)_3$	27·9 (27·8)	4·7 (4·7)		270sh 240m	280m	130w	173m	38·4 (28,000)	34·0 (24,800)		20·8 (302)		6·5	6·66	8·2
$RhI_3(pms)_3$	23·3 (22·8)	3·9 (3·8)		163m	310w	125w		37·8 (18,200)sh	34·5 (25,000)	26·3 (2800)	20·4 (240)		6·43	6·84	8·28
$IrCl_3(pms)_3$	30·0 (29·8)	5·2 (5·0)		321s 305m 295m	272w	145m,br	198s	41·8 (21,600)		32·0 (650)	29·4 (380)	21·7 (38)	6·58	6·63	8·2
$IrBr_3(pms)_3$	24·9 (24·4)	4·1 (4·3)		245m 220s	310m	134w,br	184s	41·7 (25,300)			25·0 (220)	20·5 (35)	6·5	6·57	8·1

[a] Calculated values in parentheses. [b] In cm^{-1}; the spectra 400—250 cm^{-1} in benzene solution showed very similar features to the above. [c] In kK, data for diethyl sulphide complexes taken from refs. 4 and 10, extinction coefficients in parentheses. [d] $\alpha = \tau$ value of α groups, $\beta = \tau$ value of β alkyl groups, coupling constants in parentheses: Me_2S, τ 7·9; Et_2S, α, τ 7·47; β, τ 8·75; tms, α, τ 7·2, β, τ 8·1; pms, α, τ 7·45, β, τ 8·3.

Physical Measurements.—The i.r. spectra were recorded as Nujol mulls (CsI plates) on a Perkin-Elmer 457 spectrometer (4000—250 cm^{-1}) and as Nujol mulls (between Polythene discs) on a Beckman IR 11 spectrometer (350—70 cm^{-1}). ^1H N.m.r. spectra were recorded at 60 MHz on a Varian T60 spectrometer and at 100 MHz on a Varian HA 100 spectrometer using tetramethylsilane as internal standard, at 306 K. Solutions in nitrobenzene, $CDCl_3$, CH_2Cl_2, and benzene were studied. Measurements of electronic spectra were made on a Unicam SP800 instrument using ethanol (450—200 nm) and dichloromethane (850—400 nm) solutions. Dielectric constants of benzene solutions of $RhCl_3(SEt_2)_3$ and $RhCl_3(SMe_2)_3$ were measured at 298 K at a frequency of 2 MHz using a Wissenschaftlich-Technische Werkstatten Dipolemeter Type DMO1. *X*-Ray powder photographs of specimens in Lindemann tubes were taken using a Philips *X*-ray set with a normal cylindrical camera using Cu-K_α radiation.

RESULTS AND DISCUSSION

^1H *N.m.r. Spectra*.—For complexes of the type $MX_3(SR_2)_3$ (M = Rh or Ir; X = halogen), ^1H n.m.r. provides an unambiguous method of assignment of structure. The *fac*-isomer contains three equivalent dialkyl sulphide molecules whereas the *mer*-isomer contains dialkyl sulphide molecules in two different environments, two equivalent dialkyl sulphides which are *trans* to each other and one which is *trans* to a halogen atom. Therefore, the assignment of the geometrical isomeric forms is possible.

Whereas the ^1H n.m.r. spectrum of dimethyl sulphide shows a single resonance at τ 7·9 due to the methyl protons, the spectra of all the dimethyl sulphide complexes show two distinct peaks (Table) with intensity ratio 2 : 1, consistent with the formulation of the complexes as *mer*-isomers. In the case of the rhodium compounds each peak is split into a doublet as a result of coupling with the ^{103}Rh ($I = \frac{1}{2}$) nucleus. The coupling constants are small, 1—2 Hz, and therefore are difficult to measure accurately, however, similar splittings have been observed previously[12] for

$(\pi\text{-}C_5H_5\text{-Ti})RhMe_2(SMe_2)$ and $Rh_2I_2Me_4(SMe_2)_4$ in which there is coupling of the methyl groups bonded to the metal and also of the methyl groups of the dimethyl sulphide.

For the rhodium and iridium complexes the τ values of both methyl resonances decrease in the order Cl > Br > I. If this variation were due to a *trans*-effect one would expect the resonances due to the *trans* sulphide groups to be constant. Analogous behaviour has also been observed for the corresponding *mer*-dimethylphenylphosphine complexes.[14]

The ^1H n.m.r. spectrum of $IrCl_3(SEt_2)_3$ in $CDCl_3$ has been reported as a single methyl triplet and a single methylene quartet, and the complex formulated as the *fac*-isomer,[11] which has been shown to be incorrect.[5] At 60 MHz in CH_2Cl_2 and $CDCl_3$ the spectra of $IrCl_3(SEt_2)_3$ and all the other iridium and rhodium diethyl sulphide complexes show similar features. The spectra consist of a complex multiplet in the methylene region and a triplet in the methyl region. However, in nitrobenzene at 60 MHz, the rhodium compounds show two overlapping triplets in the methyl region whilst the methylene multiplet is resolved into two slightly overlapping quartets. In the case of the iridium complexes the splittings of the resonances in nitrobenzene are not as large as those for the rhodium complexes and only partial resolution of the methylene quartets is obtained. However, at 100 MHz the two methyl triplets can be resolved for both the rhodium and iridium complexes. The results for the rhodium and iridium compounds are consistent therefore with the formulation of the compounds as *mer*-isomers.

Confirmation of this formulation was obtained using double resonance on solutions of the diethyl sulphide compounds in CH_2Cl_2 at 60 MHz. Irradiation at the centre of the methyl triplet caused the complex methylene multiplet to collapse into two single peaks with intensity ratio 2 : 1 (Table).

The ^1H n.m.r. spectra of pentamethylene sulphide consists of a multiplet at τ 7·45 of the α-methylene groups and a broad multiplet due to the β- and γ-methylene groups centred at τ 8·3. The rhodium compounds all show two resonances with intensity ratio 2 : 1 arising from the α-methylene groups, indicating a *mer*-configuration. The iridium compounds show similar features but the difference in τ values between the two types of α-methylene protons is smaller than in the corresponding rhodium compounds.

The tetramethylene sulphide spectrum shows a triplet at τ 7·2 from the α-methylene protons and a complex multiplet centred at τ 8·1 from the β-methylene groups. The spectra of all the tetramethylene complexes show two sets of resonances (α-methylene groups) and a broad multiplet (β-methylene groups) in agreement with the formulation of the compounds as *mer*-isomers. In contrast to the other sulphide complexes the peak due to the two *trans* sulphide groups is at higher τ value than the peak due to the sulphide group *trans* to the halogen atom. We are unable to account for this difference in terms of electronic effects, however, tetramethylene sulphide has an almost planar ring system and would presumably have different steric requirements from the other sulphides giving rise to different shielding effects.

Low Frequency I.r. Spectra (400—90 cm^{-1}).—Low frequency i.r. spectroscopy affords a method of distinguishing between *mer*- and *fac*-isomers for compounds of the type MX_3L_3. Application of group theory indicates that three normal modes ($2a_1$ and b_1) involving metal–halogen stretching would be expected to be i.r.-active for the *mer*-isomer (C_{2v} symmetry), whereas only two such modes (a_1 and e) are expected for the *fac*-isomer (C_{3v} symmetry). However, it has been observed [15] that although the rhodium *mer*-isomers generally conform to the predicted number of Rh–Cl stretching vibrations the iridium-*mer*-isomers have two rather than the expected three bands. This has been attributed to accidental degeneracy of two of the normal modes. Thus, although in the case of the iridium compounds it is often not possible to distinguish between *mer*- and *fac*-isomers on the basis of the number of i.r. peaks corresponding to metal–halogen stretching vibrations, the peaks that are found for such vibrations of the *mer*-isomer occur at *ca.* 20—30 cm^{-1} higher frequency than those of the corresponding *fac*-isomer.[15]

The spectra 400—90 cm^{-1} of the compounds studied are given in the Table. Fergusson [4] has reported the i.r. spectra of the diethyl sulphide compounds and the results agree fairly well with our work.

The metal–chlorine stretching modes are readily identified by the strength of the bands and by comparison of the spectra with those of the corresponding bromide and iodide complexes in the appropriate region. Apart from the diethyl sulphide complex, the spectra of the rhodium chloro-complexes show three peaks indicative of a *mer*-configuration. The position of the peaks *ca.* 350, 325, and 300 cm^{-1} is relatively insensitive to the nature of the dialkyl sulphide. The bands *ca.* 250 and 325 cm^{-1} can be assigned to the two vibrations [b_1 and a_1 (2)] involving the mutually *trans*-chlorine atoms and the band *ca.* 300 cm^{-1} to the rhodium–chlorine stretching mode [a_1 (1)] of the chlorine *trans* to the sulphide. These bands occur at a slightly higher frequency than the corresponding peaks for the *mer*-$RhCl_3(PR_3)_3$ complexes.[15] The rhodium diethyl sulphide complex shows only two bands 347 and 319 cm^{-1} which can be assigned as metal–chlorine stretching modes. The appearance of only two peaks is presumably due to the accidental degeneracy of the third metal–chlorine mode with the one occurring *ca.* 320 cm^{-1}.

An attempt was made to obtain the Raman spectra of the compounds, but the samples decomposed in the laser beam (He–Ne or Ar–Kr) to give black solids.

The iridium compounds all show two peaks which can be assigned as metal–chlorine stretching vibrations.

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These occur at lower wavenumber than the rhodium complexes but are some 20—30 cm^{-1} higher than the corresponding *mer*-$IrCl_3(PR_3)_3$ complexes.[15]

In general, metal–bromine stretching modes are of much less value in the determination of stereochemistry as the number of peaks observed in the ν(M–Br) region is often less than that predicted by symmetry considerations. In several cases only a single broad peak was observed for the complexes under consideration in the region 210—270 cm^{-1}. For the corresponding rhodium and iridium complexes the peaks assigned as metal–bromine stretching vibrations fall in virtually the same range.

The literature pertaining to i.r. studies of rhodium iodo-complexes is very sparse and in view of the proximity of the bending modes in this region any assignments involving metal–iodine stretching vibrations (Table) must be regarded as being rather tentative

We have previously assigned [16] metal–sulphur stretching modes for square planar four-co-ordinate platinum and palladium complexes containing dialkyl sulphide ligands. The peaks assigned as metal–sulphur stretching modes in the octahedral rhodium and iridium complexes (Table) fall in the same region of the i.r. spectrum. It would be expected that increasing the co-ordination number from four to six would result in a fall in the metal–sulphur stretching frequency. This effect must therefore be compensated by the increase in oxidation state of the metal on passing from palladium and platinum to rhodium and iridium. Similar considerations of course also apply to the metal–halogen stretching frequencies.

In most cases the spectra of the complexes show a broad unresolved band in the 100—200 cm^{-1} region which must correspond to bending modes of some description. The bands observed varied with the nature of the dialkyl sulphide and with the halogen involved. For square planar complexes of the type *cis*- and *trans*-MX_2L_2 (M = Pd or Pt; X = Cl, Br, or I; L = Me_2S, Et_2S, tms, or pms) the bending modes due to the sulphide ligands occur *ca.* 130 cm^{-1}.[16] It appears likely that in the rhodium and iridium complexes there must be a considerable contribution from the motions of halogen atoms since the peaks for the chloro-complexes are at much higher wavenumber.

Dipole Moments.—Dipole moment measurements have previously been used [17,18] in the assignment of structures for complexes of the type *fac*- and *mer*-MX_3L_3 (M = Rh or Ir). Values of 7·0 and 6·85 D for the *mer*-chlorotriethylphosphine complexes are consistent with those expected from simple geometric arguments based on the dipole moment of *cis*-$PtCl_2(PEt_3)_2$.[19] In the case of the corresponding dialkyl sulphide complexes, if we neglect any effect of asymmetry of the dialkyl sulphide ligand and assume that the Cl–M–SEt_2 (M = Rh or Ir), and the Cl–Pt–SEt_2 moments are of the same order of magnitude, simple geometrical arguments [20] and a value of 9·5 D for *cis*-$PtCl_2(SEt_2)_2$ [21] can be used to predict a dipole moment of 6·7 and 11·6 D respectively for the *mer*- and *fac*-isomers of $MCl_3(SEt_2)_3$ (M = Rh or Ir). Thus the dipole moments of 5·1 D for the rhodium and 5·2 D for the iridium complex, calculated by the method of Halverstadt and Kumler,[22] are consistent with the complexes having a *mer*-configuration.

Similarly a dipole moment of 4·72 D for $RhCl_3(SMe_2)_3$ is further evidence of the proposed structure.

Electronic Spectra.—Assignments of the peaks of the electronic spectra (Table) follow readily from the earlier work of Jørgensen [11] and Fergusson.[10] The spectra vary only slightly with change of dialkyl sulphide ligand, indicating a common configuration for all the complexes.

The very intense peaks in the region 30—45 kK are assigned as charge transfer transitions. For the rhodium complexes the higher energy band moves to lower wavenumbers with increasing atomic weight of halogen and may be associated with charge transfer from halogen to metal. The peak at 34·0 kK in the spectra of all the rhodium complexes is almost invariant to change of halogen, and can be assigned as charge transfer from the dialkyl sulphide to the metal.

The peak around 41 kK for the iridium compounds changes only slightly with halogen and can be assigned as a charge transfer band involving both the dialkyl sulphide and the halogen.

In the visible region no splitting of the two spin allowed *d–d* transitions was observed.

The rhodium complexes show the $^1A_1 \longrightarrow {}^1T_1$, $^1T_2$ transition around 23 kK, the peak moving to lower energy with the heavier halogens. In the spectra of the iridium complexes the $^1A_1 \longrightarrow {}^1T_1$ and $^1A_1 \longrightarrow {}^1T_2$ transitions are observed as separate peaks. The spin-forbidden $^1A_1 \longrightarrow {}^3T_1$ transition is observed for the iridium compounds, but not for the rhodium complexes. This may be attributed to the large spin–orbit coupling constant in the iridium compounds.

X-*Ray Powder Measurements.*—It has previously been shown [10] that $RhCl_3(SEt_2)_3$ and $IrCl_3(SEt_2)_3$ are isomorphous and that there is a close structural similarity between these compounds and $RuCl_3(SEt_2)_3$. The latter compounds have been recently assigned a *mer*-configuration on the basis of e.s.r. measurements,[3] this together with the physical data reported in the paper is conclusive evidence that the compounds $MCl_3(SEt_2)_3$ (M = Rh, Ir, and Ru) all have a common *mer*-configuration.

Similarly, we also find that $RhCl_3(SMe_2)_3$ and $IrCl_3(SMe_2)_3$ are isomorphous.

During the course of our investigations Russian

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workers have reported[13] the preparation of *fac*-$RhCl_3(SMe_2)_3$ from sodium hexachlororhodate, and *mer*-$RhCl_3(SMe_2)_3$ from $RhCl_3$(dimethyl sulphoxide)$_3$. We found, however, the product obtained from the reaction of sodium hexachlororhodate and dimethyl sulphide was in fact the *mer*-isomer. We have also repeated the reaction of $RhCl_3$(dimethyl sulphoxide)$_3$ with dimethyl sulphide but in no instance were we able to isolate a product which did not contain co-ordinated dimethyl sulphoxide.

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