

473. Diethyl Sulphide Complexes of Ruthenium, Rhodium, and Iridium

By J. E. FERGUSSON, J. D. KARRAN, and S. SEEVARATNAM

The complexes $\text{RuCl}_3(\text{Et}_2\text{S})_3$ and $[\text{RuCl}_3(\text{Et}_2\text{S})_2]_2$ have been isolated. They have been characterised and compared with similar complexes of rhodium and iridium, leading to an estimate of the relative stability of the metal-sulphur bond.

A study of the dissociation pressures, X-ray powder photographs, and spectral properties of the complexes $\text{RuCl}_3(\text{Et}_2\text{S})_3$, $[\text{RuCl}_3(\text{Et}_2\text{S})_2]_2$, $\text{RhX}_3(\text{Et}_2\text{S})_3$ ¹ (X = Cl, Br, and I), and $\text{IrCl}_3(\text{Et}_2\text{S})_3$ ²⁻⁴ has been carried out in order to determine the ability of sulphur, as a

¹ F. P. Dwyer and R. S. Nyholm, *J. Proc. Roy. Soc. New South Wales*, 1944, **78**, 67.

² P. C. Ray and N. Adhikari, *J. Indian Chem. Soc.*, 1932, **9**, 251.

³ J. Kleinberg, *Inorg. Synth.*, 1963, **7**, 224.

⁴ G. B. Kauffman, J. H.-S. Tsai, R. C. Fay, and C. K. Jørgensen, *Inorg. Chem.*, 1963, **2**, 1233.

donor atom, to bond to heavy transition metals, and the effect of the metal and halogen ligands on the M-S bonding.

Trichlorotris(diethyl sulphide)ruthenium is a monomer with a magnetism of 2.1 B.M. at 20°, in accord with a spin-paired d^5 configuration in an octahedral environment. The value, higher than the spin-only moment (1.73 B.M.), is in agreement with the predictions of the Kotani theory.⁵ The bis(diethyl sulphide) complex is dimeric, undergoing slight dissociation in solution. It has a magnetic moment of 0.95 B.M./Ru. which indicates considerable spin-coupling between the ruthenium ions. Table 1 lists the properties of the complexes together with those of similar compounds of rhodium and iridium.

TABLE 1

Compound	Colour	Magnetic moment (B.M.)	Mol. wt. (cryoscopic in benzene)		Moles of Et ₂ S liberated per mole of complex at 40° (× 10 ⁴)	Equation to fit dissociation-pressure data
			obs.	calc.		
RuCl ₃ (Et ₂ S) ₃ ...	Orange	2.1	448	478	3.8	$\log_{10} P$ (mm.) = 9.54 - 3125/T
[RuCl ₃ (Et ₂ S) ₂] ₂	Black	0.95/Ru	610	776	2.0/Ru	$\log_{10} P$ (mm.) = 13.83 - 4490/T
IrCl ₃ (Et ₂ S) ₃ ...	Yellow	Diamag.	590	570	2.3	$\log_{10} P$ (mm.) = 11.17 - 2685/T
RhCl ₃ (Et ₂ S) ₃ ...	Red-orange	Diamag.	Monomeric (ref. 1)		1.3	$\log_{10} P$ (mm.) = 7.37 - 2525/T
RhBr ₃ (Et ₂ S) ₃	Brown	Diamag.	579	612	3.1	$\log_{10} P$ (mm.) = 11.42 - 3722/T
RhI ₃ (Et ₂ S) ₃ ...	Purple-red	Diamag.	Dissociates in solution (ref. 1)		14-31	$\log_{10} P$ (mm.) = 19.35 - 6060/T
					Free dissociation	

All the compounds smell strongly of diethyl sulphide. When heated in an evacuated soteniscope they dissociate irreversibly to give free diethyl sulphide. A plot of $\log_{10} P$ against $1/T$ is a straight line, the equations for which are given in Table 1. Continued heating at high temperatures, for the least stable compounds, leads to rapid and complete decomposition.

It is assumed that the dissociation of the tris-complexes is of the type,



On this basis, the number of moles of diethyl sulphide dissociated per mole of complex at 40° (Table 1) can be calculated from the equilibrium pressures. These figures can then be used as an estimate of the relative stabilities of the compounds. The validity of this assumption requires that the lattice energies be constant or vary in a regular manner for the complexes. The X-ray powder photographs of MCl₃(Et₂S)₃ (M = Ir or Rh) indicate isomorphism, and the photograph for RuCl₃(Et₂S)₃ shows close structural similarity. The photographs for RhX₃(Et₂S)₃ (X = Cl or Br) show isomorphism for the compounds, and RhI₃(Et₂S)₃ is structurally similar. This evidence suggests that the lattice energies of the compounds could be similar. In addition, the structural evidence shows that all the monomeric compounds are *cis*-(1,2,3)isomers, as has been found for IrCl₃(Et₂S)₃.⁴

It is clear from Table 1, therefore, that the stabilities of the metal sulphides vary with the halogen, in the order RhCl₃ > RhBr₃ > RhI₃. The greater ability of iodine to π -bond to Group VIII metals, and increased steric factors, would tend to reduce the metal-sulphur bond strength. Both iodine and diethyl sulphide can π -bond to the metal, and since a *trans*-effect must occur it is apparent that the Rh-S bond is weakened. The effect is reduced as the halogen is less able to participate in π -bonding. A similar comparison for the compounds MCl₃(Et₂S)₃ (M = Rh, Ru, or Ir) indicates that the stability of the M-S bond is in the order Rh > Ir > Ru. This trend is in agreement with the change in acceptor properties of the metals as classified by Ahrlund, Chatt, and Davies.⁶

The ultraviolet and visible spectra of the compounds are listed in Table 2. A comparison of the spectra of RhX₃(Et₂S)₃ complexes show a charge-transfer band (39,000—

⁵ B. N. Figgis and J. Lewis, "Modern Coordination Chemistry," Interscience, New York, 1960, p. 400.

⁶ S. Ahrlund, J. Chatt, and N. R. Davies, *Quart. Rev.*, 1958, **12**, 265.

45,000 cm^{-1}) which moves to lower energy with increasing atomic weight of halogen. It can be correlated with one, or both, of the following effects: (a) a charge transfer from halogen to metal, or (b) charge-transfer from sulphide ligand to metal, the M-S bonding being dependent on the halogens as discussed above.† A similar change in band position occurs for the ligand-field bands (20,000—23,600 cm^{-1}) which are either $^1A_1 \rightarrow ^1T_1$ or $^1A_1 \rightarrow ^1T_2$ spin-allowed transitions. The weaker ligand-field occurs for the heavier

TABLE 2

Compound	Wave number (cm^{-1})	Molar extinction coefficient	Band assignment
RuCl ₃ (Et ₂ S) ₃	42,550	13,300	S, Cl → Ru
	37,200	8600	Sulphide (Co-ord.) *
	26,000	1500	Charge-transfer or
	22,750	1100	$^2T_2 \rightarrow ^2A_2, ^2T_1$
IrCl ₃ (Et ₂ S) ₃	42,200	17,200	S, Cl → Ir
	31,800	355	$^1A_1 \rightarrow ^1T_2 \uparrow$
	29,000	(shoulder <100)	$^1A_1 \rightarrow ^1T_1 \uparrow$
	22,000	32	$^1A_1 \rightarrow ^3T_1 \uparrow$
RhCl ₃ (Et ₂ S) ₃	45,300	23,200	S, Cl → Rh
	34,300	25,800	Sulphide (Co-ord.) *
	23,600	370	$^1A_1 \rightarrow ^1T_1$ or 1T_2
RhBr ₃ (Et ₂ S) ₃	40,200	22,800	S, Br → Rh
	34,050	21,800	Sulphide (Co-ord.) *
	21,250	570	$^1A_1 \rightarrow ^1T_1$ or 1T_2
RhI ₃ (Et ₂ S) ₃	39,000	(Shoulder 20,200)	S, I → Rh
	34,200	22,600	Sulphide (Co-ord.) *
	25,600	2000	?
	20,000	600	$^1A_1 \rightarrow ^1T_1$ or 1T_2
[RuCl ₃ (Et ₂ S) ₂] ₂	39,200	9920/Ru	S, Cl → Ru?
	32,800	(Shoulder 5450/Ru)	?
	23,250	8680/Ru	?

* Band could be due to co-ordinated diethyl sulphide which does not appear for the free ligand.

† Assignments correspond to those in ref. 4.

halogen and where there is a corresponding weakening of M-S bond. A charge-transfer band at 34,000 cm^{-1} does not change with halogen and may be associated solely with the co-ordinated diethyl sulphide. For the compounds MCl₃(Et₂S)₃ (M = Ru, Rh, or Ir) the absorption bands (45,300—42,200 cm^{-1}) may be assigned to a charge-transfer Cl, S → metal.‡ There does not appear to be the same clear correlation with metal-sulphur bond strength as suggested for the rhodium diethyl sulphide complexes. The ligand-field bands for IrCl₃(Et₂S)₃ are assigned by Kaufman *et al.*⁴ as $^1A_1 \rightarrow ^1T_1$, $^1A_1 \rightarrow ^1T_2$, and the spin-forbidden band $^1A_1 \rightarrow ^3T_1$. The two bands at 26,000 and 22,750 cm^{-1} for RuCl₃(Et₂S)₃ may be spin-allowed ligand-field bands $^2T_2 \rightarrow ^2A_2$, 2T_1 , but in view of the rather high extinction coefficients could also be charge-transfer bands.

The results of this investigation indicate (a) that the halogen ligand can have a considerable effect on the bonding of other ligands, especially when the donor atoms can participate in π -bonding, (b) that the stability of chloro(diethyl sulphide) metal complexes increases from Ru(III) to Ir(III) and Rh(III), as more π -electrons on the metal become available for bonding.

EXPERIMENTAL

For measurements of dissociation pressure, the compound (*ca.* 0.06 g.) was placed in the bulb of an isoteniscope tube connected to a high-vacuum line. The isoteniscope was completely immersed in a thermostat bath and pressure differences measured by means of a cathetometer. Table 1 lists the results expressed in the equation form $\log_{10} P(\text{mm.}) = \text{const.} - \text{slope}/T$. The liberated diethyl sulphide was collected under a high vacuum and shown to have a retention time identical with that of a pure sample of the ligand on a gas chromatograph.

Ultraviolet and visible spectra were measured in ethanol solution using a Beckmann DK2A self recording spectrophotometer. Magnetic moments were measured at 20° by the Gouy

‡ Kauffman *et al.*⁴ assign a similar band in IrCl₃(Et₂S)₃ to S → Ir γ_3 .

method. X-Ray powder photographs were taken with a Phillips Debye-Scherrer camera using Cu K_{α} radiation. The d -values of the twelve strongest lines for $\text{RhCl}_3(\text{Et}_2\text{S})_3$ are: 7.65s, 6.89s, 6.08m, 4.37m, 4.16m, 3.95m—w, 3.27m, 2.95m—w, 2.66m—w, 2.54 diffuse, 2.34w, 2.28w.

Halides were determined gravimetrically as silver halide. Carbon and hydrogen were determined at the microanalytical laboratory, University of Otago, New Zealand.

Tetrachlorotetra(diethyl sulphide)bis- μ -chlorobisruthenium(III).—Ruthenium trichloride trihydrate (0.25 g.) and diethyl sulphide (0.9 ml.) were dissolved in ethanol (30 ml.) and heated under reflux for 1 hr. The solution was evaporated under a high vacuum until black needle-like crystals appeared which were collected, washed with cold ethanol and dried (0.1 g.) [Found: C, 24.75; H, 5.1; Cl, 27.7%; M (cryoscopic in benzene), 610. $\text{C}_{16}\text{H}_{10}\text{S}_4\text{Cl}_6\text{Ru}_2$ requires C, 24.8; H, 5.15; Cl, 27.5%; M , 776.4].

Trichlorotris(diethyl sulphide)ruthenium(III).—The solution above was further evaporated under a high vacuum, and the third crop of red flakey crystals were collected, washed, and dried (0.14 g.) [Found: C, 29.9; H, 6.3; Cl, 22.1%; M (cryoscopic in benzene), 448. $\text{C}_{12}\text{H}_{30}\text{S}_3\text{Cl}_3\text{Ru}$ requires C, 30.1; H, 6.3; Cl, 22.3%; M , 477.6].

Trichlorotris(diethyl sulphide)rhodium(III).¹—A solution of diethyl sulphide (2.5 ml.) and rhodium trichloride trihydrate (1 g.) in ethanol (100 ml.) was heated under reflux for 1½ hr. Solvent was removed under a high vacuum until the orange-yellow crystals formed. These were collected, washed with ice-cold ethanol, and dried, m. p. 126° (1.5 g.) (Found: C, 30.3; H, 6.1; Cl, 22.3%. Calc. for $\text{C}_{12}\text{H}_{30}\text{S}_3\text{Cl}_3\text{Rh}$: C, 30.2; H, 6.3; Cl, 22.3%).

Tribromotris(diethyl sulphide)rhodium(III).—The complex was prepared as in ref. 1. The dark brown crystals melted at 112–113° (Found: C, 25.2; H, 5.2; Br, 38.6. Calc. for $\text{C}_{12}\text{H}_{30}\text{S}_3\text{Br}_3\text{Rh}$: C, 23.5; H, 4.9; Br, 39.2%).

Tri-iodotris(diethyl sulphide)rhodium(III).—The violet-black crystalline compound was prepared as in ref. 1 (Found: C, 19.4; H, 4.4; I, 49.8. Calc. for $\text{C}_{12}\text{H}_{30}\text{S}_3\text{I}_3\text{Rh}$: C, 19.2; H, 4.0; I, 50.6%).

Trichlorotris(diethyl sulphide)iridium(III).—The complex was prepared as in ref. 4, and the benzene-soluble *cis*-complex, recrystallised from aqueous acetone, had m. p. 129–130° [Found: C, 25.95; H, 5.6; Cl, 17.8%; M (cryoscopic in benzene), 590. Calc. for $\text{C}_{12}\text{H}_{30}\text{S}_3\text{Cl}_3\text{Ir}$: C, 25.4; H, 5.3; Cl, 18.7%; M , 578.5].

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