Contribution from the Department of Chemistry
University of Canterbury, Christchurch, New Zealand

Neutral Ligand Complexes of Rhenium(III) Chloride

J. E. Fergusson and J. H. Hickford

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Complexes of the trinuclear chloride Re_3Cl_9 have been formed with the ligands diethylsulphide, o-phenylenebisdimethylarsine and α,α',α''-terpyridyl. These together with a previously reported 1,2-bis-(diphenylphosphino)ethane complex have been studied to determine their formulation.

Introduction

The versatility of the trinuclear entity Re_3X_3, existing in the trivalent chloride and bromide of rhenium, to donor atoms has been demonstrated a number of times.[1-4] Such properties as the wide range of donor atoms that coordinate and the coordination of polydentate as well as monodentate ligands show this. We wish to report the isolation of certain compounds which emphasise this versatility. The list of compounds prepared is given in Table I together with a certain number of their properties. The diphosphine complex has been reported previously.[2] However, we wish to report additional information on its properties which could alter the formulation previously made.

Results and Discussion

Diethylsulphide Complex. Whereas the majority of complexes of Re_3Cl_9 with monodentates form rapidly this is not so for the *diethylsulphide complex* $[Re_3Cl_9(Et_2S)_2H_2O]$. In addition the complex is not the sole product of the reaction; a blue-black gum which is not trinuclear also forms. The spectral and magnetic evidence together with the formation of the anion $Re_3Cl_{12}^{3-}$ from the action of hydrochloric acid on the red-brown bis(diethylsulphide) complex, indicates that it is definitely a trinuclear complex. The formulation with one molecule of coordinated water making it a «12» complex, *i.e.* a total of 12 ligands coordinated around the rhenium triangle, is supported by the presence of both the (O–H) stretch and HOH bend in the infrared. The tendency to fill all twelve positions where possible seems a general feature as indicated by the previously reported complexes $Cs[Re_3Cl_3Br_72H_2O]$ [5] and $Ph_4As[Re_3Cl_{11}(Ph_3P)]$.[1] Why the twelfth ligand is water rather than a third diethyl sulphide is not clear but may be related to the greater difficulty of making the sulphide complex.

Diarsine Complex. A *complex* of Re_3Cl_9 with *o*-phenylenebisdimethylarsine (diarsine) can be obtained by reaction in ethanol at room temperature. The complex of stoichiometry, $[Re_3Cl_9(diarsine)_2]$ contains the trimeric unit on the basis of its electronic spectrum and magnetism. In dimethylformamide (DMF) the complex has a conductivity typical of a 1:1 electrolyte suggesting the formulation $[Re_3Cl_8(diarsine)_2]Cl$ in which the rhenium triangle is twelve-

Table I.

Compound	Colour	Conductivity ohm^{-1} mole^{-1} cm^2	Magnetic Moment BM per Re	Electronic Spectral Bands, λ in mμ (intensities in parentheses)
$[Re_3Cl_9(Et_2S)_2H_2O]$	Red-brown	4.4 [a]	0.93	505 (1540), 740 (440) [a]
$[Re_3Cl_9(diarsine)_2]$	Pink-red	57 [b]	0.8	516 (1150), 770 (370) [b] 630 shoulder
$[Re_3Cl_9(diphosphine)_{1.5}]$	Pink-red	80 [b]	0.63	518 (1600), 770 (625) [b] 625 shoulder 540 830 [c] 648 shoulder
$[Re_3Cl_9(terpyridyl)]$	Blue-purple	70 [b]	0.48	525 (1100), 790 (350) [b]
$[Re_3Cl_9(terpyridyl)_2]$	Pink-red	176 [b] decomposes in solution	0.56	520 (1090), 750 (415) [b] 615 shoulder
$[Re_3Cl_9(terpyridyl)_{1.33}]$	Purple	93 [b] 80 [d]	0.51	555 (1800), 825 (550) [b] 620 shoulder

[a] Acctone. [b] Dimethylformamide. [c] Solid state (reflectance spectrum). [d] Dimethylsulphoxide.

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(1) B. H. Robinson and J. E. Fergusson, *J. Chem. Soc.*, 5683 (1964).
(2) F. A. Cotton and R. A. Walton, *Inorg. Chem.*, 5, 1802 (1966).
(3) F. A. Cotton and S. J. Lippard, *J. Amer. Chem. Soc.*, 88, 1182 (1966).
(4) F. A. Cotton, S. J. Lippard, and J. T. Mague, *Inorg. Chem.*, 4, 4508 (1965).
(5) M. Elder and B. R. Penfold, private communication.

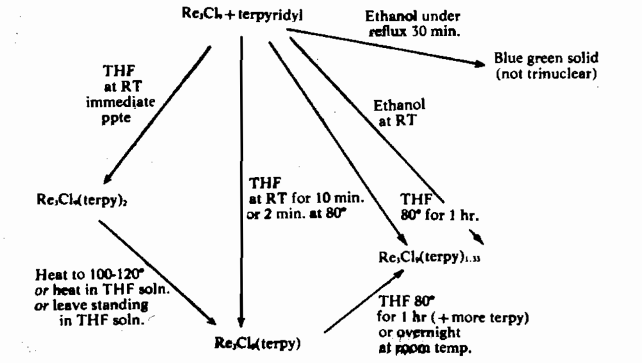
coordinate. The conductivity values are obtained at $10^{-3}\,M$ and are a rough guide of the extent of ionization.

The mother liquor of the original reaction mixture when warmed for a short period loses its red colour and turns yellow from which yellow crystals of the mononuclear diarsine complex[6] $[Re(diarsine)_2Cl_2]Cl$ can be isolated (evidence from X-ray powder photographs). To our knowledge diarsine is the first neutral ligand that readily breaks down the triangular structure. Slow decomposition of the red trinuclear complex in DMF also gives rise to some of the mononuclear species.

Diphosphine Complex. A 1,2-bis(diphenylphosphino)ethane (diphosphine) complex of stoichiometry $Re_3Cl_9(diphosphine)_{1.5}$ has been reported earlier.[2] In view of the relative simplicity of the coordination of diarsine (to be discussed below) we investigated this compound again and while agreeing on its trinuclear nature found it to have a conductivity close to that of a 1-1 electrolyte in DMF (based on the empirical formula) from which it could be recovered unchanged by precipitating with petrol ether. We therefore suggest the complex, at least in solution, could be formulated as a dimeric trinuclear complex $[(Re_3Cl_8)_2(diphosphine)_3]Cl_2$ and as a 2-1 electrolyte. However, it is quite probable that greater complexity exists in the solid state as indicated by the relatively big shifts in the electronic spectral bands from solution to solid (Table I).

From the mother liquor remaining after removing the diphosphine complex a small quantity of crystals can be obtained which are identified by X-ray powder photography as the mononuclear complex $[Re(diphosphine)_2Cl_2]Cl$.[7] However, the trinuclear complex remains unchanged even in heated DMF. These results suggest that while the diphosphine can break up the rhenium triangle it does so much less readily than diarsine. If this can be related to any factor it is probably the greater electron acceptor property of the diarsine.

Table II.



Terpyridyl Complexes. Three α,α',α''-terpyridyl complexes have been isolated which all contain the triangle of rhenium atoms; they are $Re_3Cl_9(terpy)_2$ and $Re_3Cl_9(terpy)$ produced from tetrahydrofuran (THF) solution in the above order and $Re_3Cl_9(terpy)_{1.33}$ formed in THF and exclusively in ethanol. The first two compounds are not isolated from ethanol solution due to some solubility in that solvent. The preparative reaction scheme for the three compounds is given in Table II. The $Re_3Cl_9(terpy)_{1.33}$ compound made a number of times is not a mixture of the other two complexes as demonstrated by X-ray powder photography.

On the basis of the initial conductivity the bis(terpyridyl) complex can be formulated as $[Re_3Cl_6(terpy)_2]Cl_3$, the compound being a «12» salt. The compound decomposes slowly in solution with rising conductivity (5% in 10 minutes). The mono(terpyridyl) compound's electrolytic behaviour is typical of a 1-1 salt indicating a formulation in solution of $[Re_3Cl_8(terpy)]Cl$ which is an «11» salt. The presence of a molecule of water filling the twelfth position is not confirmed by infrared spectroscopy. The latter compound is the more stable of the two (see Table II). The electrolytic conductivity of the complex $Re_3Cl_9(terpy)_{1.33}$ is something between a 1-1 and 1-2 electrolyte. It is difficult to imagine a formulation for this compound, but the simplest is three times the analytical stoichiometry, *viz.* $(Re_3Cl_9)_3(terpy)_4$ or $[(Re_3Cl_8)_3(terpy)_4]Cl_3$.

Mode of Attachment of the Polydentate Ligands. The environment around each rhenium is such that there are three bonding places X_1X_2 and X_3 lying in one plane as shown in Figure 1.[8] Some or all of these positions in the complexes of the halides can be filled, and in complexes of the type $Re_3X_9L_3$ the neutral monodentate ligands L fill the in-plane terminal positions X_2.[9] Bidentate ligands (assuming all donor atoms are used) could readily fill positions X_1 and X_2 or X_2 and X_3 and this is what we propose for the complex $[Re_3Cl_8(diarsine)_2]Cl$ as in Figure 2a. Bond angles subtended at the metal by diarsine are around 86°[10] not too different from the X_1ReX_2 angle (Figure 1).

It could be expected that the diphosphine would coordinate in a similar fashion, with perhaps greater

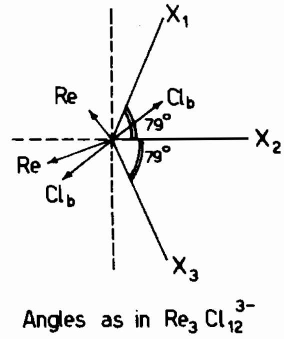


Figure 1.

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[6] J. E. Fergusson and J. H. Hickford, unpublished observations.
[7] J. Chatt and G. A. Rowe, *J. Chem. Soc.*, 4019 (1962).
[8] J. A. Bertrand, F. A. Cotton, and W. A. Dollase, *Inorg. Chem.*, 2, 1166 (1963).
[9] F. A. Cotton and J. T. Mague, *Inorg. Chem.*, 3, 1094 (1964).
[10] F. W. B. Einstein and G. A. Rodley, *J. Inorg. Nucl. Chem.*, 29, 347 (1967).

difficulty due to the presence of two bulky phenyl groups on each phosphorus atom. In view of the conductivity of the diphosphine complex we suggest the bonding as in Figure 2b with one diphosphine bridging two triangles as suggested earlier.[2] With this arrangement each triangle of rhenium atoms is eleven coordinated. Bridging triangles by chlorine seems unrealistic in view of the ease with which the inter-triangle chlorine bridging present in solid Re_3Cl_9 [11] is destroyed in solution.

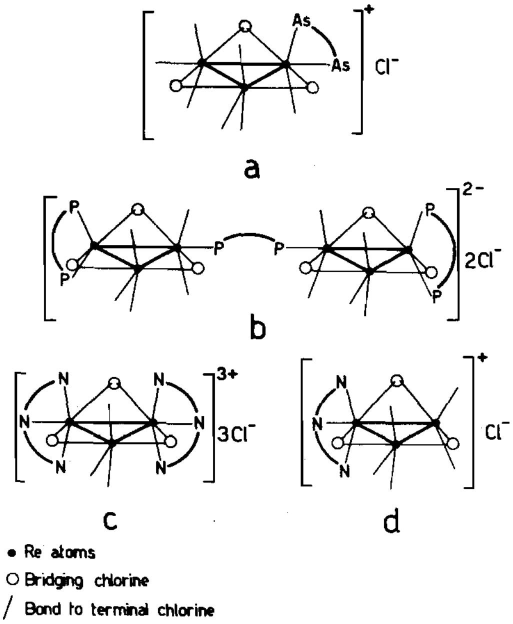

Figure 2.

The positions $X_1X_2X_3$ around a rhenium (Figure 1) are ideally situated to coordinate a planar tridentate ligand like α,α′,α″-terpyridyl. The N metal N″ bond angle in the complexes $ZnCl_2(terpy)$[12,13] and $[(CH_3)_2SnCl(terpy)][(CH_3)_2SnCl_3]$ [14] are 145° and 142° respectively. Hence we propose the structures (in solution) given in Figure 2c and 2d on the basis of conductivity for $[Re_3Cl_6(terpy)_2]Cl_3$ and $[Re_3Cl_8terpy]Cl$. Speculation as to the polymerisation of $Re_3Cl_9(terpy)_{1.33}$ would be fruitless at this stage. Terpyridyl is to our knowledge the first planar tridentate ligand that coordinates to the rhenium triangle in this way. The other reported tridentate ligand AsO_4^{3-} [3] due to its stereochemistry coordinates differently.

Experimental Section

Tri-μ-chloromonoaquohexachlorobis(diethylsulphide)-trirhenium(III). A solution of rhenium trichloride (0.25 g. in acetone, 30 ml.) and diethylsulphide (0.8 ml) was heated under reflux for 4 hours. The dark red solution was evaporated to dryness *in vacuo.* Addition of diethyl ether to the remaining gum gave a red-brown solution and left a blue-black residue. The ethereal solution was evaporated to dryness and the gum obtained was triturated using petroleum ether (3×10 ml. of 50-70° boiling range solvent). A red-brown powder formed. Red-brown needles could be obtained by treating the compound with benzene and then petroleum ether. Yield, 0.12 g., 40%.

Anal. Calcd. for $C_8H_{22}Cl_9OReS_2$ Re, 51.9; Cl, 29.7; C, 8.93; H, 2.05%. Found: Re, 50.8; Cl, 30.6; C, 8.8; H, 2.4%

Tri-μ-chloropentachlorobis-(o-phenylenebisdimethylarsine)-trirhenium(III) Chloride. To a solution of rhenium trichloride (0.1 g. in ethanol, 25 ml.) was added *o*-phenylenebisdimethylarsine (0.2 ml. in ethanol, 10 ml.) and hydrochloric acid (0.05 ml. of 11.3 *M*). A pink-red powder was precipitated out. This was collected, washed with ethanol and ether and dried *in vacuo.* Yield 0.14 g., 75%.

Anal. Calcd. for $C_{20}H_{32}As_4Cl_9Re_3$ Re, 38.5; Cl, 22.02; C, 16.6; H, 2.21%. Found Re, 38.2; Cl, 22.0; C, 16.8; H, 2.3%.

After the removal of the complex, the mother liquor was evaporated down on a water bath; its colour soon changed to yellow and crystals of dichlorobis-(*o*-phenylenebisdimethylarsine)-rhenium-(III) chloride were isolated from it.

Tris-1,2-bis(diphenylphosphino)ethane-bis(tri-μ-chloropentachlorotrirhenium(III) dichloride.[2] To a solution of rhenium trichloride (0.15 g in ethanol, 30 ml) was added bis(diphenylphosphino)ethane (0.29 g in ethanol, 40 ml). A pink-red precipitate was formed, which was collected, washed with ethanol, acetone and ether and finally dried *in vacuo.*

Anal. Calcd. for $C_{39}H_{36}Cl_9P_3Re_3$ Re, 37.9; Cl, 21.7; C, 32.8; H, 2.44%. Found: Re, 36.4; Cl, 20.9; C, 32.2; H, 2.0%.

From the mother liquor (after removal of the red trinuclear complex), crystals of dichlorobis-(bis-diphenylphosphino)ethane-rhenium(III) chloride were obtained.

Tri-μ-chloro-bis-(α,α′,α″-terpyridyl)trichlorotrirhenium(III) trichloride. Rhenium trichloride (0.3 g) in tetrahydrofuran (30 ml) was added to α,α′,α″-terpyridyl (0.35 g in tetrahydrofuran 15 ml). A red-pink precipitate formed immediately in the cold, this was collected, washed with tetrahydrofuran and dried immediately *in vacuo.* Yield 0.12 g, 26%.

Anal. Calcd. for $C_{30}H_{22}Cl_9N_6Re_3$: Re, 41.5; Cl, 23.7; C, 26.75; H, 1.64; N, 6.25%. Found: Re, 40.8; Cl, 23.5; C, 26.2; H, 2.3; N, 5.3%.

Tri-μ-chloro-(α,α′,α″-terpyridyl)pentachlorotrirhenium(III) chloride. The mother liquor from the above reaction gave a further precipitate after standing in the cold for 5 to 10 min. or heating to 80° for 2 min. The blue-purple powder was collected, washed with tetrahydrofuran and dried *in vacuo.*

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(11) F. A. Cotton and J. T. Mague, *Inorg. Chem.*, *3*, 1402 (1964).
(12) D. E. C. Corbridge and E. G. Cox, *J. Chem. Soc.*, 594 (1956).
(13) F. W. B. Einstein and B. R. Penfold, *Acta Cryst.*, *20*, 294 (1966).
(14) F. W. B. Einstein and B. R. Penfold, private communication.

Table III. " d " Spacings of strongest X-ray Powder Lines

$[Re_3Cl_9(Et_2S)_2H_2O]$	$[Re_3Cl_9(diphosphine)_{1.5}]$	$[Re_3Cl_9(terpy)_{1.33}]$	$[Re_3Cl_9(terpy)_2]$	$[Re(diarsine)_2Cl_2]Cl$	$[Re(diphosphine)_2Cl_2]Cl$
7.81 s	10.65 vs	4.11 s	7.43 mw	11.42 m	12.32 w
6.99 s	9.41 m	3.71 w	7.01 s	9.97 w	9.02 s
6.12 s	7.46 s	3.21 s	6.37 mw	7.46 w	7.90 s
5.38 m	6.48 md	2.77 s	4.79 bd	6.31 s	6.10 w
4.61 m	5.68 m	2.36 m	4.29 w	5.72 vw	5.17 m
4.03 m	5.22 m	2.04 w	3.99 w	4.96 vw	4.35 s
3.17 m	4.57 w	1.96 m	3.56 w	3.71 md	4.16 m
2.96 m	4.13 w	1.67 w	3.32 w	3.29 m	3.74 m
2.66 m	3.66 w	1.60 w		3.14 m	3.55 w
2.44 m	2.98 m				3.03 w
2.02 ms	2.82 w				
	2.62 w				
	2.45 w				
	2.40 w				

s, strong; m, medium; w, weak; d, diffuse; b, broad; v, very.

Anal. Calcd. for $C_{15}H_{11}Cl_9N_3Re_3$: Re, 50.2; Cl, 28.75; C, 16.25; H, 1.0; N, 3.8%. Found: Re, 50.6; Cl, 28.2; C, 17.1; H, 1.0; N, 3.7%.

The compound was also obtained by heating the bisterpyridyl complex to 100-120°.

Tri-μ-chloro one-and-a-third (α,α′,α″-terpyridyl)hexachlorotrirhenium(III). When ethanol was used as solvent a purple compound precipitated out in the cold which was collected, washed with ethanol and dried *in vacuo.*

Anal. Calcd. for $C_{20}H_{15}Cl_9N_4Re_3(Re_3Cl_9(terpy)_{1.33})$: Re, 47.0; Cl, 26.9; C, 20.2; H, 1.3; N, 4.7%. Found: Re, 46.4; Cl, 26.7; C, 20.3; H, 2.0; N, 4.5%.

The compound can also be isolated from a suspension of the mono(terpyridyl) complex in tetrahydrofuran heated to 80° for 1 hr or left overnight at room temperature.

Conductivities were measured in a dip type cell with bright platinum electrodes using a Philips type PR 9500 conductivity bridge.

Magnetic moments were measured by the Gouy method.

Powder photographs were taken with a Phillips Debye-Scherrer camera (radium 57.3 mm) using CuKα radiation. Table III contains the " d " values of the strongest lines of the X-ray powder photographs of a number of the compounds where photographs were obtainable.

Electronic Spectra were measured on a Beckman DK2A self recording spectrometer using solution cells or the diffuse reflectance attachment.

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