Structural Conclusions concerning Compounds with Rhenium–Rhenium Multiple Bonds

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The preparation of complexes of the form $(Re_2Cl_xBr_{8-x})^{2-}$ are reported (where x = 2, 3, and 6). The structures of these complexes have been investigated by infrared spectroscopy and it is suggested that, in appropriate cases, the absorptions arising from $\nu(Re\equiv Re)$ may be detected. This use is then confirmed by a study of $Re_2Cl_5(dth)_2$ (where dth = 2,5-dithiahexane). The paper then goes on to make use of these observations to assign structures to $[ReX_3(dth)]_2$ (where X = Cl and Br) and $[ReBr_2(dth)]_2$ which are then compared with the known structure of $(ReX_3Ph_3P)_2$.

SINCE the discovery and formulation of the $(Re_2X_8])^{2-}$ ions[1] and the structurally related carboxylates[2] this type of dimeric system with a very strong metal–metal bond has been identified for several other metals (*e.g.*, Mo,[3] Rh,[4] Cr,[5] Tc,[6] and Ru[7]) and a wide variety of

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[1] F. A. Cotton and C. B. Harris, *Inorg. Chem.*, 1965, **4**, 330.

[2] M. J. Bennett, W. K. Bratton, F. A. Cotton, and W. R. Robinson, *Inorg. Chem.*, 1968, **7**, 1570.

[3] J. V. Brencic and F. A. Cotton, *Inorg. Chem.*, 1969, **8**, 7.

[4] F. A. Cotton, B. G. De Boer, M. D. La Prade, J. R. Pipal, and D. A. Ucko, *Acta Cryst.*, 1971, **B27**, 1664.

[5] J. Krausse, G. Marx, and G. Schoell, *J. Organometallic Chem.*, 1970, **21**, 159.

[6] W. K. Bratton and F. A. Cotton, *Inorg. Chem.*, 1970, **9**, 789.

[7] M. J. Bennett, K. G. Caulton, and F. A. Cotton, *Inorg. Chem.*, 1969, **8**, 1.

ligands (*e.g.*, carboxylates,[2,4,7,8] halides,[1,3,6] thiocyanate,[9] and alkyls [5]) by *X*-ray structural determination. Previously [10] we reported empirical assignments for the metal–metal and metal–halogen stretching frequencies in the $(Re_2X_8)^{2-}$ ions (X = Cl and Br) and a series of their carboxylate derivatives in an attempt to identify such strong metal–metal bonding by means of vibrational spectroscopy. At the same time Cotton and his co-workers [11] also concluded that i.r. and Raman spectroscopy were valuable techniques to provide support for the quadruple bond in these systems. We have since extended this study [12] to structurally related compounds of Mo^{II} and Rh^{II} and demonstrated the wide applicability, ease, and sensitivity of Raman spectroscopy not only as a method of identifying strong metal–metal bonds but also highlighting variations in bond strength not observed by *X*-ray techniques.

Despite continuing advances in laser Raman spectroscopy there remain compounds which cannot be studied by this technique. These are either compounds which are totally absorbing or decompose on exposure to the laser radiation. The compounds obtained by treatment of $(Re_2X_8)^{2-}$ ions (X = Cl and Br) with 2,5-dithiahexane have this disadvantage, being either dark brown or black and decomposing rapidly when an attempt is made to record their Raman spectra. We required to see if i.r. spectroscopy could also be usefully used to identify the metal–metal stretching mode in species of lower symmetry than those previously studied and thereby extend the use of low-frequency vibrational spectra to identify metal–metal multiple bonds.

To this end it was initially decided intentionally to lower the symmetry of the $(Re_2X_8)^{2-}$ ions whose metal–metal stretching frequency was already identified from Raman spectroscopy and to look for the appearance of ν(Re–Re) in the infrared spectrum.

RESULTS AND DISCUSSION

We now report the preparation of mixed halogen compounds of the type $(Bu^n_4N)_2Re_2Cl_xBr_{8-x}$ (where x = 2, 3, and 6) by the addition of stoicheiometric quantities of 48% aqueous HBr to methanolic solutions of $(Bu^n_4N)_2Re_2Cl_8$. Although treatment with excess of hydrobromic acid has long been a recognised method of preparing $(Re_2Br_8)^{2-}$ species from $(Re_2Cl_8)^{2-}$, the isolation of intermediate mixed halogen species has not been reported. The low-frequency vibrational spectra of these compounds are in Table 1 with the previously assigned frequencies for $(Bu^n_4N)_2Re_2Cl_8$ and $(Bu^n_4N)Re_2Br_8$ for comparison.

The low-frequency i.r. spectra of the compounds formulated by Cotton *et al.*[13] as $Re_2Cl_5(dth)_2$, $[ReCl_3(dth)]_2$, $[ReBr_3(dth)]_2$, and $[ReBr_2(dth)]_2$ are in Table 2.

TABLE 1

Observed frequencies/cm⁻¹ of $(Re_2X_8)^{2-}$ salts (200—400 cm⁻¹)

$(Bu^n_4N)_2Re_2Cl_6Br_2$			$(Bu^n_4N)_2Re_2Cl_3Br_5$			$(Bu^n_4N)_2Re_2Cl_2Br_6$		$(Bu^n_4N)_2Re_2Cl_8$		$(Bu^n_4)_2Re_2Br_8$		
I.r.			I.r.									
MeCN solution	Solid	Raman Solid	MeCN solution	Solid	Raman Solid	I.r. Solid	Raman Solid	I.r. Solid	Raman Solid	I.r. Solid	Raman Solid	Assignment
216m			215w			215w					211w	ν(Re–Br)
	220m	218w		221sh	219m	222sh	219m			220m		
229w	229w			229sh		229sh						
238m	239m		236s	238s		234vs				232vs		
274m	274m	275vs	274m	274m	274vs	274m	274vs		275vs		277vs	ν(Re–Re)
		291m			291m		291m					
309m	310m		315wsh	316sh		316sh						ν(Re–Cl)
				324sh		324sh						
336vs	332vs		336s	334s		328sh		332vs				
	337sh					333s		338sh				
								348m				
									360w			

TABLE 2

Observed frequencies of 2,5-dithiahexane and triphenylphosphine complexes (200—400 cm⁻¹)

	Assignment					
Compound	ν($ReCl_{ax}$)	ν($Re–Br_{eq}$)	ν(Re–Re)	ν(Re–S)	ν($Re–Cl_{eq}$)	
$Re_2Cl_5(dth)_2$	229s		259m	285m	301sh, 314s, 328s, 339m	
$Re_2Cl_6(dth)_2$				281sh	301sh, 313sh, 328vs	
$Re_2Br_6(dth)_2$		230vs		287w		
$Re_2Br_4(dth)_2$		232m		279m		
$Re_2Cl_6(Ph_3P)_2$			278s (R)		309m, 347vs, 359s (R)	413m
$Re_2Br_6(Ph_3P)_2$		225w (R) 229s 244s	285s (R)			413m

(R) Raman bands.

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[8] D. Lawton and R. Mason, *J. Amer. Chem. Soc.*, 1965, **87**, 921.

[9] F. A. Cotton, W. R. Robinson, R. A. Walton, and R. Whyman, *Inorg. Chem.*, 1967, **6**, 929.

[10] C. Oldham, J. E. D. Davies, and A. P. Ketteringham, *Chem. Comm.*, 1971, 572.

[11] W. Bratton, F. A. Cotton, M. Debeau, R. A. Walton, *J. Co-ord. Chem.*, 1971, **1**, 121.

[12] A. P. Ketteringham and C. Oldham, in the press.

[13] F. A. Cotton, C. Oldham, and R. A. Walton, *Inorg. Chem.*, 1967, **6**, 214.

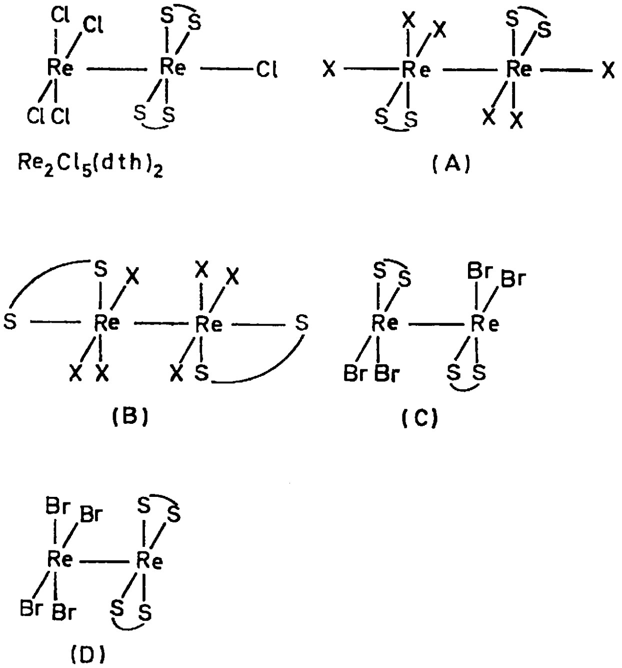
Mixed Halogen Species.—Elemental analyses of these compounds agree well with the statistical formulations $(Bu^n{}_4N)_2Re_2Cl_xBr_{8-x}$, where $x = 2, 3$, and 6. However, analysis will not uniquely differentiate between (*a*) a physical mixture of $(Re_2Br_8)^{2-}$ and $[Re_2Cl_8]^{2-}$ or (*b*) a mixture of complexes of different halogen stoicheiometries, *e.g.*, $(Re_2Cl_6Br_2)^{2-}$ may well contain substantial amounts of $(Re_2Cl_7Br)^{2-}$ and $(Re_3Cl_5Br_3)^{2-}$ as well as small quantities of species with higher Br content. The spectra eliminate (*a*) as the recorded spectrum of $(Re_2Cl_3Br_5)^{2-}$ is not a superposition of the spectra of $(Re_2Cl_8)^{2-}$ and $(Re_2Br_8)^{2-}$. We have not attempted to isolate an individually pure chloride- and bromide-containing species, as for our purposes it was sufficient that a reduction in symmetry from the essentially D_{4h} $(Re_2X_8)^{2-}$ species was achieved. We shall now show that such a reduction in symmetry has occurred.

The metal–metal stretching mode at 275 cm^{-1} and 277 cm^{-1} in $(Re_2Cl_8)^{2-}$ and $(Re_3Br_8)^{2-}$ respectively is a totally symmetric vibration and therefore Raman-active and infrared-inactive. In our mixed halide complexes we feel that the reduction in symmetry is demonstrated by the observation that the metal–metal stretching mode observed in the Raman spectra at 274 cm^{-1} also appears as a medium-intensity i.r. band at 274 cm^{-1}. New i.r. absorption bands appear in the regions previously associated [10] with equatorial * ν(Re–Cl), *ca.* 330 cm^{-1} and (Re–Br), *ca.* 230 cm^{-1}. As expected from simple coupling considerations some bands in these regions are shifted to slightly lower or higher frequencies respectively compared with the parent halide.

When the spectra are considered in conjunction with the analyses it is clear that we are dealing with discrete new mixed halogen compounds. It is also apparent that the expected ability to use i.r. spectroscopy to identify metal-to-metal multiple bonds in these systems with appropriate symmetry has been confirmed. Accordingly the following work is a description of this use of i.r. spectroscopy in the 200—500 cm^{-1} region to the problem of assignment of structures to a series of dimeric rhenium complexes unsuitable for Raman studies because of their colour.

2,5-*Dithiahexane Complexes.*—Re_2Cl_5(dth). The compounds $[ReX_3(dth)]_2$ (where X = Cl and Br; dth = 2,5-dithiahexane) were prepared by Cotton and his coworkers [13] by reaction of $(Re_2X_8)^{2-}$ with 2,5-dithiahexane under mild conditions. With more forcing conditions the (dth) acts as a reducing agent and $Re_2Cl_5(dth)_2$ and $[ReBr_2(dth)]_2$ were isolated. Of these compounds only the structure of $Re_2Cl_5(dth)_2$ has been determined by *X*-ray crystallography,[14] which shows the complex to contain both Re^{II} and Re^{III} (Figure). It can be seen that both rhenium atoms in the dimer have completely different environments and the metal–metal stretching mode is thus predicted to be i.r.-active.

The low-frequency i.r. absorption bands of $Re_2Cl_5(dth)_2$ are in Table 2. This Table shows the presence of both 'axial' and 'equatorial' chlorine atoms in accord with their previously established characteristic frequencies.[10] There are also two absorption bands at 285 cm^{-1} and 259 cm^{-1}. As all the complexes reported here, which contain sulphur ligands, have an absorption at 283 ± 4 cm^{-1} we associate this with the Re–S stretching mode. Efforts to prepare 1,2-dimethoxyethane derivatives [*i.e.*, the oxygen analogue of (dth)] to confirm this have been unsuccessful. The reported Re–Re bond length in this complex is 229 ± 1 pm [*cf.* 224 pm in $(Re_2Cl_8)^{2-}$]. This longer bond has been interpreted [14] together with the staggered configuration of the complex as indicating a reduction in bond order from four for $(Re_2Cl_8)^{2-}$ to three, with loss of the δ bond. Approximate calculations [10] based upon the 128 cm^{-1} band in $Re_2(CO)_{10}$ predict a lowering of *ca.* 40 cm^{-1} when one moves from bond-order 4 to bond-order 3 rhenium systems (four bonds of equal strength being assumed). As in $(Re_2Cl_8)^{2-}$ the stretching due to the metal–metal bond in the Raman is observed at 275 cm^{-1} one might expect the i.r. Re–Re absorption in $Re_2Cl_5(dth)_2$ to be in the region of 259 cm^{-1}, as the δ bond which is lost is the weakest of the four.[15] Thus metal–metal bonds in suitable asymmetric environments are again readily observed in the i.r. region.



FIGURE

$[ReX_3(dth)]_2$ *and* $[ReBr_2(dth)]_2$. The dark brown colour of these complexes made it impossible for us to observe their Raman spectra. The most likely structures [13] of $[ReX_3(dth)]_2$ (where X = Cl or Br) were considered to be either (A) or (B) shown in the Figure. I.r. spectra might be expected not only to differentiate between (A) and (B) (in the rhenium–chlorine stretching

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* The halogen atoms in $(Re_2X_8)^{2-}$ are, for convenience, called 'equatorial' while those in $Re_2(O_2CPh)_4Cl_2$ are called 'axial.'

[14] M. J. Bennett, F. A. Cotton, and R. A. Walton, *Proc. Roy. Soc.*, 1968, *A*, **303**, 175.

[15] F. A. Cotton, *Inorg. Chem.*, 1965, **4**, 334.

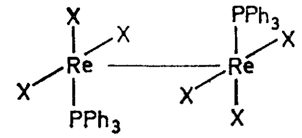
region) but also the presence or absence of any more unsymmetrical species should be apparent from their i.r. spectra. The i.r. spectra below 400 cm^{-1} are in Table 2. From this the characteristic 'equatorial' rhenium–chlorine can be seen at 328 cm^{-1} which is absent from the bromide, but there is no evidence of absorption in the region of 230 cm^{-1}, *i.e.*, the region where all 'axial' chlorine rhenium links have been found to absorb.[10] Additionally we have been unable to observe any absorption band in either the chlorine- or bromine-containing complexes which we could associate with the presence of an i.r.-active rhenium–rhenium stretching mode. Thus from these observations structure (B) is considered to be the most likely for $[ReX_3(dth)]_2$. Such a structure is most readily conceived under the reaction conditions of $(Re_2Cl_8)^{2-}$ with 2,5-dithiahexane as initial co-ordination of the sulphur into the 'vacant' co-ordination position along the Re–Re axis seems to be the most logical step in the complex formation.

$[ReBr_2(dth)]_2$ is a complex of Re^{II} and few complexes of this oxidation state have previously been reported and no *X*-ray structural data are available. Cotton and his co-workers[13] who prepared this complex suggested, from diffuse reflectance spectra, that the most likely structures are as shown for (C) and (D) in the Figure.

There must be a reduction in bond order in going from $(Re_2Br_8)^{2-}$ to $[ReBr_2(dth)]_2$ as the two extra electrons are accommodated in antibonding orbitals. This is particularly relevant to the reduced bond order found in $Re_2Cl_5(dth)_2$: indeed structure (D) strongly resembles that of $Re_2Cl_5(dth)_2$. Accordingly one should be able to differentiate between (C) and (D) by the absence from or presence in the i.r. spectrum of bands associated with the Re–Re stretching mode.

The i.r. evidence (Table 2) that no absorption capable of being assigned to the stretching mode of a rhenium–rhenium bond is observed rules out a structure such as (D). The absorption at 232 cm^{-1} which has previously been associated with equatorial bromine[10] and the band at 279 cm^{-1} [ν(Re–S)] are both consistent with a structure such as (C).

Phosphine Complexes.—$(ReX_3Ph_3P)_2$ (where X = Cl or Br) have structures[16] which only differ from that which we suggest for $[ReX_3(dth)]_2$ in the absence of axial substituents, *i.e.*, (I). Thus, as the *X*-ray crystal structure of the chloro-complex is known we feel that a brief discussion of their i.r. and Raman spectra is relevant to the foregoing conclusion. These low-frequency spectra are in Table 2. The expected ν(Re–X equatorial) and Raman-active ν(Re–Re) bands are observed but, more significant in the present context, there is no i.r. activity of the ν(Re–Re) band. Thus we have spectrally a similar situation to that of $[ReX_3(dth)]_2$ and further confidence in our present use of low-frequency i.r. spectra as an added useful tool in the understanding of dimeric Re_2 species.



(I)

EXPERIMENTAL

Complexes analysing as $(Bu^n{}_4N)_2Re_2Cl_2Br_6$, $(Bu^n{}_4N)_2Re_2Cl_3Br_5$, and $(Bu^n{}_4N)_2Re_2Cl_6Br_2$ were prepared by adding the calculated volume of 48% aqueous HBr to methanol solutions of $(Bu^n{}_4N)_2Re_2Cl_8$. The volume of the solutions was reduced on a steam-bath until crystals started to appear. The solutions were then cooled and the green crystalline products filtered off, washed with absolute ethanol and dry ether and dried *in vacuo*. The 2,5-dithiahexane complexes were prepared by the methods of Cotton, Oldham and Walton.[13] The triphenylphosphine complexes were prepared by the method of Cotton, Curtis, and Robinson.[17] All analyses are in Table 3.

TABLE 3

Analyses

	Found (%)			Calc. (%)		
Formula	C	H	Hal	C	H	Hal
$(Bu^n{}_4N)_2Re_2Cl_2Br_6$	26·9	5·2	39·4	27·3	5·2	39·1 *
$(Bu^n{}_4N)_2Re_2Cl_3Br_5$	28·5	5·3	36·7	28·2	5·3	37·1
$(Bu^n{}_4N)_2Re_2Cl_6Br_2$	31·2	5·8	30·1	31·2	5·9	30·3
$C_8H_{20}Cl_5Re_2S_4$	12·1	2·6	22·1	12·1	2·5	22·4
$C_8H_{20}Cl_6Re_2S_4$	12·4	2·4	25·3	11·6	2·4	25·6
$C_8H_{20}Br_6Re_2S_4$	9·2	1·9	43·0	8·8	1·8	43·7
$C_8H_{20}Br_4Re_2S_4$	9·8	2·2	32·8	10·3	2·2	34·1
$(Ph_3P)_2Re_2Cl_6$	38·5	2·8	19·5	39·0	2·7	19·2
$(Ph_3P)_2Re_2Br_6$	31·7	2·3	34·8	31·4	2·2	34·8

* Found: N, 2·1. Calc.: N, 2·2%.

I.r. spectra were recorded for Nujol nulls on a Perkin-Elmer 225 spectrometer. Solution i.r. spectra were recorded by the Physico-Chemical Measurements Unit, Harwell. Raman spectra were recorded for powdered samples on a Cary 81 Raman spectrometer.

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[16] F. A. Cotton and B. M. Foxman, *Inorg. Chem.*, 1968, **7**, 2135.

[17] F. A. Cotton, N. F. Curtis, and W. R. Robinson, *Inorg. Chem.*, 1965, **4**, 1696.