

Low Frequency Vibrational Spectra of Some Rhenium(III) Dimeric Complexes

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Summary An empirical low-frequency spectral assignment of both Raman and i.r. active modes for complexes containing an $\text{Re}\equiv\text{Re}$ unit is presented and a Raman active band at *ca.* 285 cm^{-1} is assigned to an Re-Re stretching mode.

OCTAHALOGENODIRHENATE(III) anions $(\text{Re}_2\text{X}_8)^{2-}$, form dimeric complexes¹ of the type $\text{Re}_2(\text{O}_2\text{CR})_x\text{X}_y$ ($x = 4$ or 2 when $y = 2$ or 4), with strong Re-Re interactions. Apart from a brief mention² of rhenium-chlorine derived bands in the i.r. spectrum of $(\text{Re}_2\text{Cl}_9)^{2-}$, molecular vibrations in these dimeric complexes have not been studied. We now report the vibrational frequencies of bands due to multiple Re-Re bonds in some halogeno-derivatives. The Raman

than two halogen atoms have i.r. absorptions at $332 \pm 1\text{ cm}^{-1}$ (Cl) or $230 \pm 2\text{ cm}^{-1}$ (Br). (iv) For complexes containing rhenium-oxygen bonds, two strong i.r. absorptions are observed in the region $350\text{--}540\text{ cm}^{-1}$.

Structurally the most important feature of the complexes is the quadruple bond between the rhenium atoms.¹ The stretching mode of such a bond would be expected to be Raman active and accordingly we assign the intense Raman band at $285 \pm 11\text{ cm}^{-1}$ to this metal-metal stretching mode. In the absence of polarisation data we base our assignment on the following reasoning: such a metal-metal vibration is expected to give rise to a high intensity band such as the one we observe. Secondly, although suitable compounds for comparison are few, in $\text{Re}_2(\text{CO})_{10}$ a Raman-active metal-metal (bond order 1)

TABLE
Raman and i.r. absorption spectra (frequencies in cm^{-1})

Compound	$\nu(\text{Re-X})$	$\nu(\text{Re}\equiv\text{Re})$	$\nu(\text{Re-X})$	$\nu(\text{Re-O})$
$\text{Re}_2(\text{O}_2\text{CMe})_4\text{Cl}_2$	220s	224w ^a	288vs ^a	356s 391s
$\text{Re}_2(\text{O}_2\text{CMe})_4\text{Br}_2$			281vs ^a	356s 391s
$\text{Re}_2(\text{O}_2\text{CET})_4\text{Cl}_2$	224s	234m ^a	288vs ^a	356s 457s
$\text{Re}_2(\text{O}_2\text{CET})_4\text{Br}_2$			277vs ^a	356s 455s
$\text{Re}_2(\text{O}_2\text{CPr})_4\text{Cl}_2$	232s	234w ^a	289vs ^a	368s 475s
$\text{Re}_2(\text{O}_2\text{CPr})_4\text{Br}_2$			280vs ^a	370s 480s
$\text{Re}_2(\text{O}_2\text{CC}_6\text{H}_{11})_4\text{Cl}_2$ ^c	233s	246m ^a	293s ^a	390m 462s
$\text{Re}_2(\text{O}_2\text{CC}_6\text{H}_{11})_4\text{Br}_2$			278s ^a	389m 462s
$\text{Re}_2(\text{O}_2\text{CPh})_4\text{Cl}_2$	240s	248s ^a	295s ^a	416s 523s
$\text{Re}_2(\text{O}_2\text{CPh})_4\text{Br}_2$	223m		280s ^a	416m 522s
$\text{Re}_2(\text{O}_2\text{CMe})_4\text{Cl}_2\cdot 2\text{H}_2\text{O}$			274s ^a	352s 366s
$\text{Re}_2(\text{O}_2\text{CMe})_4\text{Br}_2\cdot 2\text{H}_2\text{O}$	232s		278s ^a	351s 362s
$(\text{Bu}^n\text{N})_2\text{Re}_2\text{Cl}_8$			274s ^b	332s
$(\text{Ph}_4\text{As})_2\text{Re}_2\text{Cl}_8$			275s ^b	333s
$(\text{Bu}^n\text{N})_2\text{Re}_2\text{Br}_8$ ^d	229s			
$(\text{Ph}_4\text{As})_2\text{Re}_2\text{Br}_8$	232m		278 ^a	

^a Raman bands which were recorded on a Cary 81 spectrometer, using Kr 6471 Å excitation. ^b Bands similarly recorded using Kr 4762 Å excitation. ^c No Raman above 350 cm^{-1} (fluorescence). ^d No Raman obtained.

spectra were measured for powders and the i.r. spectra for Nujol mulls (see Table). The general features of the spectra are as follows: (i) An intense, remarkably constant, Raman band is observed in all complexes studied at $285 \pm 11\text{ cm}^{-1}$. (ii) The i.r. absorption band at $230 \pm 10\text{ cm}^{-1}$ found for all chloride-containing tetracarboxylates is absent in the bromo-analogues. The appearance of this band may also be associated with a weaker Raman-active band at slightly higher wave numbers. (iii) Complexes containing more

stretching mode is observed³ at 128 cm^{-1} . A rough calculation using the harmonic diatomic approximation indicates that, for a bond order of four, the frequency would be *ca.* 260 cm^{-1} . Thirdly both the position and intensity of this Raman band suggest that coupling occurs between the metal-metal stretching mode and metal-chlorine stretching modes in some compounds.

The limited structural data available for such compounds suggest that there are two, perhaps even three, distinct

rhenium-halogen bonds. Low frequency i.r. spectroscopy is able to distinguish two Re-Cl stretching modes. The axial† chlorine is associated with the $230 \pm 10 \text{ cm}^{-1}$ band (note expected Raman activity) and the equatorial† chlorine with the $332 \pm 1 \text{ cm}^{-1}$ absorption. As the i.r. spectra were recorded on a Perkin-Elmer 225 spectrometer only the

equatorial Re-Br stretching modes at $230 \pm 2 \text{ cm}^{-1}$ were observed.

The remaining low frequency absorptions (*i.e.* above 350 cm^{-1}) are coincident with the presence of a carboxylic acid group and must be associated with rhenium-oxygen bonds. A full analysis will be published elsewhere.

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† The halogen atoms⁴ in $(\text{Re}_2\text{Cl}_8)^{2-}$ and $(\text{Re}_2\text{Br}_8)^{2-}$ are for convenience called 'equatorial' while those⁵ in $\text{Re}_2(\text{O}_2\text{CPh})\text{Cl}_2$ are called 'axial,' (bridging or non-bridging).

¹ F. A. Cotton, C. Oldham, and W. R. Robinson, *Inorg. Chem.*, 1966, 5, 1798 and refs. therein.

² F. Bonati and F. A. Cotton, *Inorg. Chem.*, 1967, 6, 1353.

³ H. M. Gager, J. Lewis, and M. J. Ware, *Chem. Comm.*, 1966, 616; F. A. Cotton and R. M. Wing, *Inorg. Chem.*, 1965, 4, 1328.

⁴ F. A. Cotton and C. B. Harris, *Inorg. Chem.*, 1965, 4, 330; F. A. Cotton, B. G. DeBoer, and M. Jeremic, *Inorg. Chem.*, 1970, 9, 2143.

⁵ M. J. Bennett, W. K. Bratton, F. A. Cotton, and W. R. Robinson, *Inorg. Chem.*, 1968, 7, 1570.