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THE NATURE OF "$Re(CO)_3Cl$": EVIDENCE FOR A TETRANUCLEAR STRUCTURE

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Summary

The compound of empirical formula, $Re(CO)_3Cl$, has been shown by mass spectrometry to be tetranuclear in the vapour phase. Vibrational spectroscopic measurements did not provide unequivocal evidence for the molecular geometry, but it is suggested that the most likely structure is one consisting of a tetrahedral array of $Re(CO)_3$ units with chlorine atoms triply bridging each face of the tetrahedron.

Introduction

The rhenium pentacarbonyl halides, $Re(CO)_5X$ and the dimeric compounds, $[Re(CO)_4X]_2$ have been known for many years, but Colton [1] recently reported the new class of halide complexes of empirical formula $Re(CO)_3X$ (X = Cl, Br, I). These complexes have a minimal solubility in a wide range of noncoordinating solvents, thus precluding molecular weight measurements. However, the presence of two bands in the infrared spectrum of the chloro complex which could be assigned to Re—Cl stretching modes is consistent with a trimeric structure of D_{3h} symmetry in which a triangular arrangement of $Re(CO)_3$ units are bridged by halogen atoms.

Results and discussion

Presented in Table 1 is the mass spectrum of the chloro complex. This shows that the base peak of the spectrum corresponds to the ion $[^{185}Re_4{}^{35}Cl_4(CO)_{12}]^{+}$ (*m/e* 1216). No ions above this mass value are observed and on this basis it is suggested that this is the molecular ion of a tetranuclear complex. Further discussion of the mass spectral data will be presented later in the paper. In the light of these findings the carbonyl vibrational spectrum of the complex was reexamined. Although the compound has only minimal solubility in non-

TABLE 1

MASS SPECTRUM OF $[ReCl(CO)_3]_4$ [a]

m/e	Rel. abd.	Assignment	*m/e*	Rel. abd.	Assignment
1216	100	$Re_4Cl_4(CO)_{12}$	625	13	Re_3Cl_2
1188	3	$Re_4Cl_4(CO)_{11}$	615	8	$Re_2Cl_3(CO)_5$
1160	9	$Re_4Cl_4(CO)_{10}$	608	27	$Re_2Cl_2(CO)_6$
1132	11	$Re_4Cl_4(CO)_9$	590	8	Re_3Cl
1104	18	$Re_4Cl_4(CO)_8$	587	17	$Re_2Cl_3(CO)_4$
1076	25	$Re_4Cl_4(CO)_7$	580	12	$Re_2Cl_2(CO)_5$
1048	10	$Re_4Cl_4(CO)_6$	559	23	$Re_2Cl_3(CO)_3$
1020	13	$Re_4Cl_4(CO)_5$	552	17	$Re_2Cl_2(CO)_4$
992	12	$Re_4Cl_4(CO)_4$	531	34	$Re_2Cl_3(CO)_2$
964	18	$Re_4Cl_4(CO)_3$	524	5	$Re_2Cl_2(CO)_3$
936	22	$Re_4Cl_4(CO)_2$	510	6	Re_2Cl_4
908	86	$Re_4Cl_4(CO)$	503	14	$Re_2Cl_3(CO)$
880	72	Re_4Cl_4	496	3	$Re_2Cl_2(CO)_2$
845	21	Re_4Cl_3	475	38	Re_2Cl_3
826	37	$Re_3Cl_3(CO)_6$	468	3	$Re_2Cl_2(CO)$
814	1	$Re_3Cl(CO)_8$	440	18	Re_2Cl_2
800	36	$Re_3Cl_3(CO)_5$	405	8	Re_2Cl
772	44	$Re_3Cl_3(CO)_4$	330	5	$Re_3Cl_3^{2+}$
744	26	$Re_3Cl_3(CO)_3$	304	21	$ReCl(CO)_3$
730	5	$Re_3Cl(CO)_5$	290	4	$ReCl_3$
716	27	$Re_3Cl_3(CO)_2$	276	17	$ReCl(CO)_2$
688	20	$Re_3Cl_3(CO)$	248	17	$ReCl(CO)$
674	2	$Re_3Cl(CO)_3$	220	17	$ReCl$
660	20	Re_3Cl_3	185	14	Re
646	1	$Re_3Cl(CO)_2$			
643	28	$Re_2Cl_3(CO)_6$			

[a] All *m/e* values are based on ^{185}Re and ^{35}Cl. The relative intensities of isotopic clusters were checked against those predicted by a computer simulation procedure.

coordinating solvents, it was possible to obtain satisfactory infrared spectra in dichloromethane employing a cell of path length 1.0 mm. Two bands were observed at 2140 and 1925 cm^{-1} in the C—O stretching region. However, although the lower frequency band showed a well defined maximum and no shoulders, it was nevertheless broad (band width at half height = 40 cm^{-1}) and could thus contain more than one peak maximum in the envelope. The complex was insufficiently soluble in dichloromethane to obtain Raman data and attempts to obtain such data in the solid state using either blue (488 nm) or green (514 nm) exciting light led to photolytic decomposition of the sample. Thus no definite conclusions can be drawn concerning the geometry of the complex on the basis of the vibrational spectroscopic results. It is however, worthy of note that the two most likely structural possibilities for this tetranuclear complex are one involving a square planar arrangement of metal atoms with bridging chlorine atoms (D_{4h} symmetry; 3 IR active C—O stretching modes) and one involving a tetrahedral array of metal atoms with chlorines triply bridging each face of the tetrahedron (T_d symmetry; 2 IR active C—O stretching modes). In both of these structures all carbonyl groups are terminally bonded, there being no indication of vibrational frequencies in the bridging region [1]. Thus the infrared data are consistent with the structure of T_d symmetry, but the results are not unequivocal. Previous vibrational spectroscopic studies [2] of $[Re(CO)_3SPh]_4$ have shown this complex and some manganese analogues to exhibit infrared active carbonyl stretching fundamentals very similar in both position and intensity to those discussed above. A detailed consideration of overtone and combination bands observed for these compounds showed them to have structures of T_d symmetry. However, a similar approach to vibrational assignment of the chloro complex was prohibited by its low solubility.

Further consideration of the mass spectrum shows that the Re_4Cl_4 unit is of high stability. This is evidenced by the fact that ions of the type $[Re_4Cl_4(CO)_n]^+$ (n = 0—12) carry almost 40% of the total ion current. Although no metastable ions are observed in the spectrum, all other ions can be accounted for in terms of fragmentation by simple cleavage rather than rearrangements and it is noteworthy that although only of low intensity, ions of the type $[Re_3Cl(CO)_n]^+$ are observed, as might be predicted from a structure of T_d symmetry.

Finally, it is worthy of mention that only in the case of the tetrahedral structure can each metal atom achieve the inert gas configuration and that the related complexes, $M_4X_4(CO)_{12}$ (M = Mn, Re, X = SR [2—4]; M = Re, X = H [5]) have been suggested as having tetrahedral arrangements of $M(CO)_3$ units with X groups triply bridging each of the tetrahedral faces. An X-ray crystallographic study of one of these complexes, $[Re(CO)_3SMe]_4$ [6] has shown that such a structure is adopted by this molecule.

Experimental

The complex, $Re_4Cl_4(CO)_{12}$, was prepared by the method of Colton [1]. It was found that great care had to be taken to ensure that all the $Re(CO)_5Cl$ was taken up by the heptane prior to commencement of the reflux procedure. This was necessary to ensure that the final product was free from a black impurity (presumably rhenium metal) formed by total thermal decomposition of undissolved $Re(CO)_5Cl$. (Found: C, 12.6; Re, 59.5. $C_{12}Cl_4O_{12}Re_4$ calcd.: C, 11.8, Re, 60.9%.)

Infrared spectra were recorded on a Perkin—Elmer 457 spectrometer. Raman spectra were recorded on a JEOL JRS-S1. Mass spectra were recorded on an AEI MS9 operating with an electron beam energy of 70 eV and an accelerating potential of 6000 volts.

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