Raman Spectra of Multiply Bonded Metal Species

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The Raman and i.r. spectra of a series of dimeric molybdenum and rhodium compounds are reported. The metal–metal stretching frequencies are found to fall in the region 400 ± 4 cm^{-1} for the molybdenum carboxylates $Mo_2(O_2CR)_4$ (R = Me, CF_3, Et, Pr^n, Ph, and C_6H_{11}) and 342 ± 8 cm^{-1} for the $(Mo_2X_8)^{4-}$ containing species (X = Cl and Br) indicating a difference in metal–metal bond strength between the two series of compounds which has not previously been recognised from *X*-ray data. The metal–metal stretching frequency of the dimolybdenum tetrakis-(perfluoroacetate) is lowered by the attachment of donor ligands along the metal–metal axis. The metal–metal stretching frequencies for the rhodium carboxylates $Rh_2(O_2CR)_4$ and $Rh_2(O_2CR)_4,2L$ (R = Me and Et, L = MeOH, H_2O, Me_2SO, and Ph_3P) fall in the region 288—351 cm^{-1} and decrease with increasing donor strength of the attached ligands.

$\{Re_2Cl_8\}^{2-}$ was one of the first compounds in which metal–metal multiple bonds were recognised. Since then, Re_2 entities with bond lengths similar to that of $\{Re_2Cl_8\}^{2-}$ have been recognised with a variety of ligands, *e.g.*, carboxylates,[1] halides,[2] SCN,[3] *etc.* More recent work has also established that multiply bonded diatomic units can be found in Mo^{II},[4,5] Rh^{II},[6] and Ru^{II} complexes.[7]

X-Ray structural work has provided the main source of evidence used to establish the bonding patterns in these complexes. A comparison of the experimentally determind bond length with the sum of the covalent radii allows short metal–metal distances to be recognised unequivocally. Empirical molecular orbital calculations are consistent with a bond order of 4 for many of these systems.

In favourable instances evidence for metal–metal bonding may also be indicated by magnetic susceptibility measurements. Frequently reductions in magnetic moments can be associated with the pairing of electron spins on the metal in bond formation, *e.g.*, $Cr_2(OAc)_4$.[6] Magnetic measurements of this type, while more experimentally convenient, suffer from a rather limited applicability and factors other than M–M bond formation can often be invoked to rationalise reductions in magnetic moment, *e.g.* antiferromagnetism.

We successfully applied[8] Raman spectroscopy to many Re_2 species in an attempt to find a more readily accessible method of identifying such systems. The Raman bands observed were generally strong and the spectra relatively simple, thus allowing a ready identification of the dimeric species from the Re–Re stretching mode around 285 cm^{-1}. A combination of the Raman spectra with the low-frequency i.r. spectra also allowed empirical assignments of Re–Cl and Re–O stretching modes to be made.

We have now extended our studies to the structurally closely related molybdenum(II) compounds in an effort to determine how these multiply bonded metal systems are affected by (*a*) changing the metal and (*b*) changing the attached ligands. The Raman spectra can be used as readily to demonstrate the presence of multiply bonded atoms in molybdenum chemistry as rhenium. However, the wide range of the Mo–Mo stretching frequencies for a similar series of complexes to that studied in the rhenium case demonstrates the caution needed in empirically correlating stretching frequency directly with bond order. Apart from a mention of the Raman spectra of molybdenum trifluoroacetate[9] and its adducts the Raman spectra of these dimeric complexes have not been studied.

RESULTS AND DISCUSSION

The principal i.r. and Raman frequencies together with their relative intensities are in Table 1. The most striking observation from the Raman spectra is the relatively wide range of the most intense band. This is in sharp contrast to the analogous rhenium case. There appear to be two quite distinct wavenumber values; *i.e.*, 400 ± 4 cm^{-1} for the non-axially substituted carboxylate complexes and 342 ± 8 cm^{-1} for the halide species. In all cases the strongest Raman band is assumed to be associated with the Mo–Mo stretching mode. The doublet at *ca.* 340 cm^{-1} and the i.r. band at 366 cm^{-1} in $Mo_2(OAc)_4$ were assigned (similarly to other workers[10]) to the molybdenum–oxygen stretching modes as were the absorptions at 330 cm^{-1} and 380 cm^{-1} in the spectrum of $Mo_2(O_2C{\cdot}CF_3)_4$. The increased complexity of the i.r. spectra of the other carboxylates precludes all but the most tentative assignment that ν(Mo–O) is to be found in the region 330—480 cm^{-1}.

For the $\{Mo_2X_8\}^{4-}$ ions two M–X stretching and three M–X bending modes are predicted in the i.r. spectrum.

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[2] F. A. Cotton, N. F. Curtis, B. F. G. Johnson, and W. R. Robinson, *Inorg. Chem.*, 1965, **4**, 326.

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

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

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

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[9] F. A. Cotton and J. G. Norman, *J. Coord. Chem.*, 1971, **1**, 161.

[10] L. Dubicki and R. L. Martin, *Austral. J. Chem.*, 1969, **22**, 1571.

ν(Mo–Cl) are observed at the expected region,[11] *i.e.*, 303 cm^{-1} and 273 cm^{-1} with ν(Mo–Br) at 251 cm^{-1} and 223 cm^{-1}. The bending modes are presumed to occur below 200 cm^{-1} and could not be observed with our instrument. Of the nine predicted Raman bands only four were observed with certainty for $\{Mo_2Cl_8\}^{4-}$. The most intense was taken (see below) to be ν(Mo–Mo), and the remainder to be associated with the Mo–Cl band. In this particular case preliminary calculations show that the ν(Mo–Mo) and ν(Mo–Cl) stretching modes are strongly coupled while ν(Mo–Mo) in $\{Mo_2Br_8\}^{4-}$ is essentially a pure vibration. The effect of this coupling in the $\{Mo_2Cl_8\}^{4-}$ species is that the true ν(Mo–Mo) lies below 350 cm^{-1}, *i.e.*, the apparent ν(Mo–Mo) is higher than the actual ν(Mo–Mo).

TABLE 1

$Mo_2(OAc)_4$		$Mo_2(O_2C{\cdot}Et)_4$		$Mo_2(O_2C{\cdot}Pr^n)_4$		$Mo_2(OBz)_4$		$Mo_2(O_2C{\cdot}C_6H_{11})_4$		$Mo_2(O_2C{\cdot}CF_3)_4$		Assignment
I.r.	R[a]	I.r.	R[a]	I.r.	R[a]	I.r.	R[a]	I.r.	R[a]	I.r.	R[a]	
		587s	596s					594m	592m			
573w		577sh		577w				587m		523sh	523s	
565w	567w			570w		490w	497s	520s	526s	517s	515s	
										509s	502s	
548w						481s	483s			494s		
				440sh		454w		454m	450m			
		434m		432s	434m			445m	439m			
		417m						415s	414s			
	404vs		400vs		402vs		404vs		397vs		398vs	ν(Mo–Mo)
						386s						
366s						364m	364w			380s	365w	
345sh				357sh				355s	357w			
334s		333s		347s	347w					330s		
	322s	322s										
	313w		312w		310w			310m	308w			
	301s		301w				306w				306w	
			290w	280m		282m						
			270w			274m		264s				
223m	202m	251m							194w	244s	206m	
	188m						186s		185w	228s	189w	

$Mo_2(O_2C{\cdot}CF_3)_4,2MeOH$		$Mo_2(O_2C{\cdot}CF_3)_4(Ph_3P)_2$		$K_4Mo_2Cl_8$		$K_4Mo_2Cl_8,2H_2O$		$Cs_4Mo_2Br_8$		$(enH_2)_2Mo_2Cl_8,2H_2O$		Assignment
I.r.	R[a]	I.r.	R[a]	I.r.	R[b]	I.r.	R[b]	I.r.	R[b]	I.r.	R[b]	
	518s	519s	516s									
	507s	508s	507s									
		496s	488m									
		458w	409w									
		444m	400w									
	386vs		377vs		350s		349s		335m		349s	ν(Mo–Mo)
380s		380s										
330s		330s			320s		320s					
											315w	
			301w	303vs		300vs				301vs		
		294s										
		260w	257s	273s	281m	273s	280m	251s		275s		
	199w	240s						223s				
	188w	232s			193w		194m					

[a] Raman bands recorded by use of Kr 5682 Å excitation. [b] Raman bands recorded by use of Kr 6471 Å excitation.

In order to obtain a suitable molybdenum species for comparison, we prepared $\{(h^5C_5H_5)Mo(CO)_3\}_2$, which *X*-ray structural data showed to have a single metal–metal bond distance of 322 pm.[12] The most intense band in the Raman spectrum of this complex is at 193 cm^{-1}. If this is assumed to arise from the Mo–Mo stretching mode then calculations by use of the harmonic diatomic approximation indicate that for a bond order of four the expected Mo–Mo frequency would be *ca.* 400 cm^{-1} and for a bond order of three *ca.* 330 cm^{-1}. So the expected high intensity and position of the Raman band for the molybdenum carboxylates studied here would seem to be acceptable for strongly multiply bonded molybdenum atoms. The halide complexes still contain the dimeric Mo_2 unit although a weaker Mo–Mo bond is indicated by the lower Mo–Mo stretching region.

The two distinct wavenumber regions require further comment. It is appropriate to compare, where possible, the Mo–Mo stretching frequencies with the reported bond-length data. For example in $K_4Mo_2Cl_8$[5] and $Mo_2(OAc)_4$[4] the appropriate figures are 350 cm^{-1} in a species with bond length 211 pm and 404 cm^{-1} with a bond length of 214 pm. The observed spectral difference of 54 cm^{-1} is unequivocal while according to the published standard deviations the small bond-length difference of *ca.* 3 pm is also significant and real. No such spectral difference was observed for the rhenium complexes.

It has been observed that *X*-ray structural techniques are not the most discerning to use in studies on complexes, such as these, with high bond orders. For example, it has been estimated that a narrow range of

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[11] J. Lewis, R. S. Nyholm, and G. A. Rodley, *J. Chem. Soc.*, 1965, 1483.

[12] F. C. Wilson and D. P. Shoemaker, *J. Chem. Phys.*, 1957, **27**, 809.

20 pm could well contain bond orders two to four. Consequently we feel that Raman spectroscopy offers a much more discerning method of studying such compounds. It appears that in these multiply bonded molybdenum species the Raman spectra have highlighted a difference not unequivocally demonstrated by other techniques.

TABLE 2

Compound	ν(Rh≡Rh)	ν(Rh–O)		
$Rh_2(OAc)_4$	351s [a]	350s	381s	392s
$Rh_2(OAc)_4,2MeOH$	336s [a]	340s	378s	388s
$Rh_2(OAc)_4,2H_2O$	320s [a]	336s	372s	383s
$Rh_2(OAc)_4,2Me_2SO$	311s [a]	331s	374s	382sh
$Rh_2(OAc)_4(Ph_3P)_2$	289vs [a]	320w	374m	379sh
$Rh_2(O_2C{\cdot}Et)_4$	347s [a]	354s	411m	436m
$Rh_2(OBz)_4(Ph_3P)_2$	288s [a]	334m	415m	440m

[a] Raman bands recorded by use of Kr 5208 Å excitation.

One possible explanation of the differences between these multiply bonded molybdenum atoms is that of a diminution in metal–metal bond strength. Chemically different types of ligand are associated with the different spectral regions. Unidentate halide ligands are associated with the lower wavenumbers whereas when the bridging carboxylate ligand is present frequencies around 400 cm^{-1} are observed. As these ligands are at 90° to the Mo–Mo axis, these ligands are most likely to perturb the π or δ bonding between the molybdenum atoms. However, this perturbation is insufficient to cause the eclipsed structure of the molecule to be destroyed. Thus at the moment we see the Raman data as indicating a difference in the degree of metal–metal bonding, rather than any fundamental change in the kind of bonding pattern previously established. The foregoing discussion does assume that coupling effects will be small [in all save $\{Mo_2Cl_8\}^{4-}$ species]. For the heavier rhenium atom this appeared to be so; in the case of molybdenum we expected coupling effects to be more apparent. However, the close similarity of the most intense Raman line within the two series suggests that coupling effects are insufficient to account for the two distinct areas of absorption.

TABLE 3

Analyses (%)

Compound	Calc.				Found			
	C	H	N	X	C	H	N	X
$Mo_2(OAc)_4$	22·1	2·9			22·4	2·9		
$Mo_2(O_2C{\cdot}Et)_4$	29·3	4·1			28·8	3·9		
$Mo_2(O_2C{\cdot}Pr)_4$	35·6	5·2			35·4	5·2		
$Mo_2(OBz)_4$	49·1	2·9			48·3	2·6		
$Mo_2(O_2C{\cdot}C_6H_{11})_4$	48·8	6·3			48·0	6·3		
$Mo_2(O_2C{\cdot}CF_3)_4$	14·9				14·9			
$Mo_2(O_2C{\cdot}CF_3)_4,2MeOH$				Unstable; loses methanol				
$K_4Mo_2Cl_8$				44·9				45·0
$K_4Mo_2Cl_8,2H_2O$				42·5				42·8
$[(CH_2NH_4)_2]_2Mo_2Cl_8,2H_2O$	7·5	3·8	8·7	44·3	8·1	3·7	8·4	42·4
$Cs_4Mo_2Br_8$				46·9				47·3
$[(\pi\text{-}C_5H_5)(CO)_3Mo]_2$	40·2	2·4			39·2	2·1		
$Rh_2(OAc)_4$	21·7	2·7			21·6	2·8		
$Rh_2(OAc)_4,2MeOH$				Unstable; loses methanol				
$Rh_2(OAc)_4,2H_2O$	20·1	3·3			20·1	3·4		
$Rh_2(OAc)_4,2Me_2SO$	24·1	4·0			24·0	3·9		
$Rh_2(OAc)_4(Ph_3P)_2$	54·7	4·3			55·3	4·6		
$Rh_2(O_2C{\cdot}Et)_4$	28·9	4·0			30·2	4·3		
$Rh_2(O_2C{\cdot}Et)_4(Ph_3P)_2$	56·3	4·9			56·6	4·9		

All the structural studies reported have been on solid samples so possible lattice effects cannot be ignored. Unfortunately attempts to obtain solution spectra on this series of complexes have not yielded spectra of sufficient definition to allow useful conclusions to be made.

Rhodium.—Rhodium(II) carboxylates are isostructural with the dinuclear molybdenum(II) and rhenium(III) carboxylates and the published Rh–Rh distance of 240 pm suggests considerable Rh–Rh bonding. This short rhodium–rhodium distance prompted empirical molecular orbital calculations which suggested a bond order of three for the metal–metal bond.[7] Dubicki and Martin,[10] from studies of u.v. spectra, favour a bond order of unity.

The principal Raman and i.r. spectral data for a limited number of rhodium carboxylates are in Table 2. A very intense Raman line was detected for each compound at *ca.* 350 cm^{-1}. This was again assumed to arise primarily from the Rh–Rh stretching mode. Ligand attachment along the axis of the Rh–Rh bond results in a lowering by between 10 cm^{-1} (for H_2O) and 60 cm^{-1} (for triphenylphosphine). This lowering was expected as all axial donors share the same metal orbitals as those used to directly bond the rhodium atoms together. This lowering can be correlated with the increased donor strength of axial ligand.

Suitable spectroscopic data for comparative use in these systems are not yet available and we have been unable to obtain any ourselves. This means that one can only qualitatively relate these Raman spectra to a discussion of the nature of the metal–metal bond. If we use the Raman data available[14] for $Rh_4(CO)_{16}$ and $Rh_3(CO)_{12}$ then the region of 190 cm^{-1} seems acceptable for a Rh–Rh bond order of unity. The simple

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

[14] W. P. Griffith and A. J. Wickham, *J. Chem. Soc.* (*A*), 1969, 834.

harmonic oscillator model then confirms that these rhodium carboxylates are indeed examples of multiply bonded rhodium atoms. Predictions of a Raman line at *ca.* 340 cm^{-1} for a bond-order three system would be more consistent with the theoretical calculations of Cotton than with the work of Martin. Further definitive interpretation of these rhodium systems must await the outcome of difficult preparative work.

Thus while some of the numerically based discussions presented are necessarily crude, Raman spectroscopy has demonstrated that it is a particularly useful tool in the instant detection of multiply bonded metal–metal systems.

EXPERIMENTAL

Molybdenum Compounds.—Dimolybdenum tetrakis(trifluoroacetate) was prepared by the method of Cotton and Norman.[9] All the other molybdenum carboxylates were prepared by the method of Bannister, Wilkinson, and Stephenson.[15] $K_4Mo_2Cl_8$, $K_4Mo_2Cl_8,2H_2O$, and $(enH_2)_2Mo_2Cl_8,2H_2O$ were prepared by the method of Brencic and Cotton.[16,17] $\{(h^5C_5H_5)(CO)_3Mo\}_2$ was prepared by the method of Hayter.[18] Analyses are in Table 3.

$Cs_4Mo_2Br_8$.—The preparation was carried out under nitrogen. Freshly prepared dimolybdenum tetra-acetate (0·192 g) was dissolved in 48% aqueous HBr (5 cm^3) containing caesium bromide (0·135 g). On standing at 0 °C for 4 h a purple precipitate was obtained which was filtered off, washed with ethanol and then dry ether, and dried *in vacuo* at 20 °C.

The rhodium carboxylates were prepared by the method of Johnson, Hunt, and Neuman.[19]

I.r. spectra were recorded on Nujol mulls with a Perkin-Elmer 225 spectrometer.

Raman spectra were recorded on powdered samples with a Cary 81 spectrometer.

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[16] J. V. Brencic and F. A. Cotton, *Inorg. Chem.*, 1970, **9**, 351.

[17] J. V. Brencic and F. A. Cotton, *Inorg. Chem.*, 1969, **8**, 2698.

[18] R. G. Hayter, *Inorg. Chem.*, 1963, **2**, 1031.

[19] S. A. Johnson, H. R. Hunt, and H. M. Neuman, *Inorg. Chem.*, 1963, **2**, 960.