713. *The Stretching Frequencies of Metal–Oxygen Double Bonds.*

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The infrared spectra of a number of compounds containing metal–oxygen double bonds have been measured. It is concluded that the presence of a metal=O bond can be correlated with a stretching frequency in the range 900—1100 cm.$^{-1}$. The potential diagnostic value of this band in inorganic chemistry is discussed, with particular reference to metal–oxygen systems wherein more than one type of bonding occurs.

The rapid, and even occasionally the positive, detection of a metal–oxygen double bond in metal complexes is difficult. If we exclude those cases where the oxygen atom is also attached to a lighter atom (*e.g.*, M–O–H or M–O–C$\leqslant$ as in metal alkoxides which can be identified through O–H or O–C stretching frequencies), the two main kinds of metal–oxygen bond in metal complexes are (1) M=O and (2) M–O–M.

One of the major problems in a study of these systems is the difficulty of obtaining model compounds in which the presence of an M=O bond has been unambiguously established by structural investigations (*e.g.*, *X*-ray or electron diffraction). Unfortunately, many compounds which are normally written as monomers with an M=O link are polymers with a chain structure, *i.e.*, M–O–M–O–M–. For instance, $TiOSO_4$ has recently been found to be polymeric [1] with such a chain structure.

A number of compounds have been studied whose spectra contain the M=O stretching frequency, to ascertain how it varies in different circumstances. The compounds are conveniently divided into three groups (Table 1). Class A contains those compounds in

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[1] Lundgren, *Arkiv Kemi*, 1957, **10**, 397.

which there is only one metal–oxygen bond per metal atom, this bond having a high double-bond character. Class B is similar except that there are two such M=O bonds per metal atom. Class C contains all compounds with more than two M–O bonds, including complex oxides in which there may be a noteworthy decrease in double-bond character.

In Class A we have included those compounds containing one oxygen atom per metal atom and which *probably* contain metal–oxygen bonds with a high degree of double-bond character. Of these titanyl bisacetylacetone is a non-electrolyte in nitrobenzene and is monomeric in benzene;[2] hence it is one of the few compounds in which the titanyl group (Ti=O) may be considered to be present. Comparison of the spectrum of this compound with that of trisacetylacetonetitanium(III), shows the presence of a new band at 1087 cm.$^{-1}$ which is strong and sharp, and this is considered to be the Ti=O stretching frequency. In the majority of titanyl complexes one or more very broad absorption bands are normally observed in the 800—900 cm.$^{-1}$ region, which may be associated with the lower bond order and high degree of degeneracy of the vibrations to be expected in a system of the type (–Ti–O–Ti–O–Ti–O–). Thus $TiOSO_4$ shows very broad bands at 820 and 920 cm.$^{-1}$, and potassium titanyl oxalate, generally written as $K_2TiO(C_2O_4)_2$, has broad bands at 800 and 900 cm.$^{-1}$.

A closely related compound to the titanium complex is vanadyl bisacetylacetone which has recently been shown by *X*-ray diffraction to be a monomer [3] with a tetragonal-pyramidal arrangement of the five bonds about the metal atom. The absorption band at 995 cm.$^{-1}$ is taken as corresponding to the (V=O) stretching frequency. Vanadyl chloride has a monomeric molecule with a tetrahedral structure and shows a strong, sharp band at 1035 cm.$^{-1}$ which corresponds to the metal–oxygen stretching vibration.[4] For the other compounds listed in Class A the structures have not been unambiguously established. However, their formulation as monomeric molecules would involve a similar type of bonding, and in the cases of the vanadyl bisoxalate and potassium pentachloro-oxychromate and pentachloro-oxymolybdate complexes a sharp band is observed in a similar region of the spectrum. The magnetic moments of the last two compounds [$\mu_{\text{eff.}} = 1{\cdot}82$ B.M. for $(NH_4)_2CrOCl_5$; $\mu_{\text{eff.}} = 1{\cdot}73$ B.M. for K_2MoOCl_5] agree with their formulation as monomers. For vanadyl sulphate and the bismalonatovanadyl complex only one band would be expected on the basis of a simple structure, and the splitting of the bands may arise from a solid-state effect or alternatively the complexes may be polymeric. In the case of vanadyl sulphate pentahydrate the *X*-ray structure [5] has established an octahedral arrangement of five water molecules and one oxygen atom around each vanadium atom. The compound examined in Table 1, however, was the anhydrous form as it was not found possible to obtain a satisfactory spectrum of the hydrated species. The vanadyl bisoxalate and bismalonate complexes have been formulated as dimers involving two bridging oxygen groups [6] but no direct evidence for this formulation has been obtained.

It has been suggested [7] that the V=O stretching frequency in some vanadyl chelates of tetraphenylporphin derivatives occurs at 1337 cm.$^{-1}$, but this gives a force constant of approximately 12 millidynes/Å, as mentioned by Ueno and Martell.[7] This is well outside the ranges given in Table 2.

For the molecules containing two oxygen atoms per metal atom in Class B an electron-diffraction study of chromyl chloride shows the molecule to be tetrahedral and it is reasonable to assign a similar structure to CrO_2F_2. The spectra show two strong bands in the 1000 cm.$^{-1}$ region and these have been assigned to the two metal–oxygen stretching modes expected for molecules of this type.[8]

[2] Cox, unpublished work.
[3] Dodge, *Univ. California Rad. Lab. Publ.*, 8225.
[4] Miller and Cousins, *J. Chem. Phys.*, 1957, **26**, 329.
[5] Lundgren, *Rec. Trav. chim.*, 1956, **75**, 585.
[6] Palmer, "Experimental Inorganic Chemistry," Cambridge Univ. Press, 1954, p. 320.
[7] Ueno and Martell, *J. Phys. Chem.*, 1956, **60**, 934.
[8] Hobbs, *J. Chem. Phys.*, 1958, **28**, 1220.

The three oxides listed in Class C are of special interest and will be considered in more detail. Vanadium pentoxide is polymeric but the *X*-ray data [9] show that the structure may be regarded as distorted VO_5 trigonal-bipyramids sharing four corners and leaving one oxygen atom bonded effectively only to one vanadium atom. It seems reasonable to interpret the spectrum by considering the sharp band at 1020 cm.$^{-1}$ as representing stretching vibrations of the independent V=O groups, while the broader and weaker band at 825 cm.$^{-1}$ represents vibrations of the vanadium–oxygen layer lattice. The V–O distance of the isolated oxygen atom is 1·54 Å, similar to that in $VOCl_3$ (V–O = 1·56 Å [10]) and also to that in vanadyl bisacetylacetone (V–O = 1·59 Å [3]).

Chromium trioxide is described [11] as distorted CrO_4 tetrahedra sharing two corners to form chains, with only weak van der Waals forces operating between the chains. The band at 969 cm.$^{-1}$ in the spectrum is considered to represent the stretching frequency of the two free Cr–O groups, while the much broader band at 893 cm.$^{-1}$ represents vibrations of the continuous chromium–oxygen chain. The structure of molybdenum trioxide has been given by Anderson and Magnelli.[12] It may be regarded as containing distorted MoO_6 octahedra in which three of the oxygen atoms are common to three MoO_6 octahedra, two of the oxygen atoms are common to two octahedra, and the sixth oxygen atom is unshared, *i.e.*, bound to only one molybdenum atom. As in the previous two cases the strong band at 985 cm.$^{-1}$ is regarded as being due to stretching vibrations of the independent Mo–O groups while the two much broader bands at longer wavelengths are attributed to the two different (Mo–O–Mo) continuous structures.

The data in Table 1 show that most of the metal–oxygen stretching frequencies fall within the range 900—1100 cm.$^{-1}$. However even for a particular metal the frequencies can vary widely as the bond order changes. For example, Jones [13] quotes the uranyl group as giving asymmetric stretching frequencies between 850 and 1000 cm.$^{-1}$ depending upon the nature of the compound. It is of interest to consider the information which is available on stretching force constants and these results are quoted in Table 2.

TABLE 1. *Metal–oxygen stretching frequencies.*

Compound *	State	Frequency (cm.$^{-1}$) †	Compound *	State	Frequency (cm.$^{-1}$) †
Class A			Class C		
TiO(acac)$_2$	Nujol mull	1087	V_2O_5	Nujol mull	825 m, b, 1020 s
$VOSO_4$	,,	987, 1003, 1020	CrO_3	,,	893 m, b, 969 s
VO(acac)	,,	995 s, sh	MoO_3	,,	813 m, b, 870 s, br, 985 s
$(NH_4)_2[VO(ox)_2,2H_2O]$	,,	976 s, sh	$KMnO_4$	,,	900 s, br
$(NH_4)_2[VO(mal)_2,4H_2O]$	,,	967, 977	$KReO_4$	,,	913 s, br
K_2MoOCl_5	,,	967	K_2CrO_4	Soln. in formamide	880 s, br
K_2CrOCl_5	Soln. in formamide	952	K_2CrO_3Cl	,,	906 w, 951 s
$VOCl_3$	Liquid	1035 [a] s, sh	$K_2Cr_2O_7$	,,	906 w, 951 s
Class B					
CrO_2Cl_2	Gas	990, 1000 [b]			
CrO_2F_2	,,	1006, 1016 [b]			

* acac = acetylacetone, mal = malonate, ox = oxalate.
† s = strong, sh = sharp, b = broad, m = medium, w = weak.
[a] Ref. 4. [b] Ref. 8.

The results fall into two groups. One corresponds to compounds generally regarded as containing double bonds, and the other consists of tetrahedral anions in which the bond order is intermediate between 1 and 2. The vibrational mode observed in tetrahedral anions is not a simple metal–oxygen stretching frequency but is triply degenerate, and any

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[9] Byström, Wilhelmi, and Brotzen, *Acta. Chem. Scand.*, 1950, **4**, 1119.
[10] Palmer, *J. Amer. Chem. Soc.*, 1938, **60**, 2360.
[11] Byström and Wilhelmi, *Acta. Chem. Scand.*, 1950, **4**, 1131.
[12] Andersson and Magnelli, *Acta. Chem. Scand.*, 1950, **4**, 793.
[13] Jones, *Spectrochim. Acta*, 1958, **10**, 395.

slight distortion from tetrahedral symmetry could lead to the broad bands actually observed. The values of the force constants are surprisingly constant and support the idea that a characteristic frequency is to be expected for each group, especially as the changes in reduced mass of an (M–O) group are also small, going from 12·3 for a Ti–O group to 15·0 for a U–O group. Treatments in terms of group frequencies are necessarily approximate but we feel that this work will be of diagnostic value in metal compounds. At least, if there is no band in the 900—1100 cm.$^{-1}$ region, one can be confident that there is no Metal=O bond in the compound; on the other hand when a band is observed in this region, it is good evidence for a Metal=O link, provided that there is not present in the molecule any other atom (*e.g.*, nitrogen) of similar atomic weight, which might give rise to a similar frequency.

TABLE 2. *Stretching force constants.*

Bond	V–O	V–O	U–O	Cr–O	Cr–O	Mo–O	Mn–O	V–O
Compound	$VOCl_3$	$VOSO_4$	$UO_2(ClO_4)_2$	CrO_2F_2	CrO_4^{2-}	MoO_4^{2-}	MnO_4^-	VO_4^{3-}
Force constant (mdynes/Å)	7·55	7·25	7·75	7·5	5·48	5·66	5·50	4·86
Ref.	*a*	*b*	*c*	*d*	*e*	*f*	*g*	*h*

[a] Eichhoff and Weigel, *Z. anorg. Chem.*, 1954, **275**, 267. [b] Calc. from a frequency of 987 cm.$^{-1}$ for the diatomic ion VO^{2+}. [c] Jones and Penneman, *J. Chem. Phys.*, 1953, **21**, 542. [d] Calc. from data in ref. 8. [e] Stammreich, Bassi, and Sala, *Spectrochim. Acta*, 1958, **12**, 403. [f] Siebert, *Z. anorg. Chem.*, 1954, **275**, 225.

Experimental.—Samples were laboratory reagents or were prepared according to published methods. The spectra were recorded on a Grubb-Parsons G.S.2A double-beam spectrometer.

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