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OXYGEN BONDING IN COORDINATION COMPOUNDS

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Some atoms are particularly capable of combining with other atoms of higher electronegativity. Oxygen and hydrogen atoms are known frequently to appear in that role. Hydrogen bridges between atoms of high electronegativity, such as oxygen and fluorine, have for a long time been considered as a kind of chemical bond. The hydrogen in a bridge is an electron and orbital acceptor and binds atoms which are electron and orbital donors. The nature of the hydrogen bond has for a long time been subject to studies and discussions and it's significance both in the liquid and solid phases is being increasingly appreciated. Oxygen in a bridge, in contrast to hydrogen is an orbital and electron donor—therefore, it acts between atoms of lower electronegativity. The oxygen atom can bind both atoms of the non-transition elements Si, Ge, P and transition metals Cr, Mo, Re etc. The bond strength of the oxygen bridge is at least one order higher than that of the hydrogen bridge. Hence, oxygen bonds do not occur in the intermediate products but rather in the final products of chemical processes. The silicates, alumino-silicates and silica are being accumulated in the earth's crust as final products in the formation of rocks. Hydrolysis, alcoholysis, solvolysis and polymerization processes in aqueous or alcoholic solutions are often accompanied by the formation of oxygen bonds. The dimers and polymers then being formed could be bound either by means of one or two oxygen bridges, or, most frequently, by two bydroxyl bridges. The two hydroxyl bridges may be reversibly changed into the oxygen bridge $2\,OH^- \leftrightarrow -O^{2-}- + H_2O$

The role of the oxygen bond in the hydrolysis process is emphasized in Sillen's "core-link" hypothesis which explains the expansion of the hydrolysis products by the effect of oxygen bridges.

The hydrolysis products may sometimes be separated from solution as dimers with a M–O–M nucleus, bent or linear, or as trimers and polymers M–O–M–O–M or, generally speaking, as μ-oxycomplexes. If compounds containing paramagnetic cations are subjected to hydrolysis then the dimers or polymers exhibit a decrease in paramagnetism.

The decrease of paramagnetism discovered by Mulay and Selwood[1] in ferric perchlorate solutions may be ascribed to the formation of dimers in solution $[(H_2O)_5\,Fe\text{–}O\text{–}Fe\,(H_2O)_5]^{4+}$ as was suggested by Sillen[2]. A similar decrease of paramagnetism was found during the hydrolysis of molybdenum(V) compounds[3,4,5,6] $MoOCl_5^{2-}$ and $MoOBr_5^{2-}$. A similar effect was found by us in chlororhenate solutions in hydrochloric acid. In this case it was also possible to investigate the mechanism of formation of the oxygen bridge.

$$[ReCl_6]^{2-}+H_2O \leftrightarrow [ReCl_5OH]^{2-}+H^++Cl^-$$

$$[Cl_5ReOH]^{2-}+[HOReCl_5]^{2-} \rightarrow$$

$$[Cl_5Re-\overset{H}{O}-H-O-ReCl_5]^{4-}$$

$$\underset{\text{dimer I}}{[Cl_5ReO(H_2O)ReCl_5]^{4-}} \rightleftarrows \underset{\text{dimer II}}{[Re_2OCl_{10}]^{4-}}+H_2O$$

Both compounds I and II, being diamagnetic dimers with oxygen bridges, have been separated in the solid phase.

The formation of a dimer may be roughly presented as follows:

$$2[ReCl_5OH^{2-}] \rightleftarrows [Re_2OCl_{10}]^{4-}+H_2O$$

Knowledge of the magnetic susceptibilities of all the compounds participating in the reaction allowed the determination of the equilibrium constants at various temperatures by the magnetic method. Enthalpies, entropies and free energies were also obtained[7].

In a similar hydrolysis reaction of the paramagnetic $RuCl_6^{2-}$ ion having 2 electron spins, a diamagnetic dimer $[Ru_2OCl_{10}]^{4-}$ is formed[8]. The osmium(IV) dimer $[Os_2OCl_{10}]^{4-}$ is also diamagnetic[3]. In solution, however, the dimer-monomer equilibrium is shifted towards the paramagnetic, high-spin monomer. Monomeric iron(III) complexes with organic bases are of a high-spin character whereas the oxygen bridged, dimeric complex with ō-phenanthroline $[Fe_2O(\text{ō-phen})_4Cl_2]Cl_2$ has a paramagnetism corresponding to one electron spin per Fe^{III} atom[10].

It is worth while mentioning that the diamagnetic dimers exhibit no paramagnetic effect even at liquid air temperature. It may then be assumed that the electrons are delocalized over the whole M–O–M nucleus and can not be assigned to particular metal nuclei.

Special attention should be paid to the hydrolysis and polymerization of the molybdenum(V) compound $MoOCl_5^{2-}$[5,6,11,12]. Dimers with two oxygen bridges are the predominant products in solution. In the solid phase we have obtained[5,6] dimers with two oxygen bridges $Mo{<}^{O}_{O}{>}Mo$ and with hydroxyl bridges $Mo{<}^{OH}_{OH}{>}Mo$ which show a marked decrease in magnetic susceptibility. In addition we have also prepared the diamagnetic monobridged dimer Mo–O–Mo.

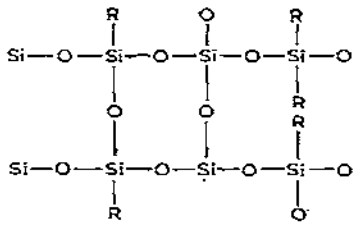
The change in magnetic properties resulting from dimerization allows the determination of the dimerisation constants, enthalpies, entropies and free energies even in the more complex systems. A change in paramagnetic properties has also been observed in chromium(III) complexes when the hydroxyl bridge, or NH_2

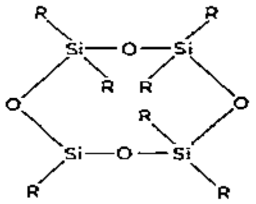
bridge in dimeric ammines, is substituted by the oxygen bridge. The chromium(III) complex $[Cr_2O(NH_3)_{10}]Cl_4$ has a very weak paramagnetism at room temperature and at 120 °K it becomes diamagnetic[13,14].

The magnetic criterion thus enables us to investigate the dimerization of transition metal compounds. No such criterion exists, however, for dimerization or polymerization of non-transition metal compounds. For determination of the bridge character at least, spectroscopic criteria and X-ray structural analysis may be applied.

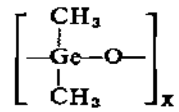
Silicon-containing inorganic polymers, silicones and others, are formed as a result of Si–O–Si bond formation and the silicon atom tending to reach tetrahedral hydridization. Polymerization is often accompanied by intermolecular water evolution, for instance in diols, resulting in the formation of a polymer $OH\ H_2\ Si-(OSiH_2)_n-OSiH_2OH$.

As a result of polymerization occuring during the hydrolysis of alkyl-or aryl-halogenosilanes, chain, ring and spatial silicones are formed.





Similar polymers are formed by the higher homologues of silicon, *e.g.* germanium. Methyl derivatives of germanium with oxygen, being dimers, trimers and ring tetramers have been prepared as well as larger polymers in which the group



$$\left[-\overset{CH_3}{\underset{CH_3}{Ge}}-O- \right]_x$$

is a structural polymerization element.

Oxygen bonds occuring in compounds of non-transition group IV elements are very stable as the above examples show. The fourth group elements are usually in the tetrahedral initial valence state whereas the transition d electron elements are mainly in the octahedral initial valence state. The d^0 configuration is an exception since it also favours the tetrahedral valence state. The formation of oxygen bridges obviously results in the distortion of the octahedral state and lowering of the symmetry.

Octahedral coordination is also possible in heavier non-transition elements, for example, tin forms some complexes in which oxygen combines two atoms of tin being the centre of distorted octahedra *e.g.* $[F_5Sn–O–SnF_5]^{4-}$.

Similarly, the germanium compound $K_4[Ge_2OF_{10}]$, a product of thermal dimerization of the hydroxy compound K_2GeF_5OH is an analogue of the transition element dimers. The Sn–O–Sn and Ge–O–Ge bonds in these compounds are less stable and longer than those in the analogous tetrahedral systems. This is because in tin and germanium the sp^3d^2 orbitals participate in octahedral hydridization, *i.e.* the excited d orbitals, 4d or 5d, of higher energy than s and p are used which results in lower bond stability.

Oxygen bridges bonds in the various polyphosphates, chain or ringtype, pyrosulphates etc., may be regarded as oxygen bonds in tetrahedral systems.

Transition elements of a d° configuration form compounds with oxygen bridges between tetrahedral structures as in, for example, the dichromates, polychromates, polymolybdates and polytungstates.

OXYGEN BRIDGE BONDING IN THE LIGHT OF VALENCE BOND AND MOLECULAR ORBITAL THEORIES

Let us consider two atoms linked by oxygen, X–O–X, as a molecular structural unit. This structural unit may be either linear or bent. This will later be called a linear or bent oxygen bond. The oxygen bond is always linear between hexacoordinated atoms. The symmetry of the entire molecule (XOX) is D_{4h}.

The linear bond occurs in transition elements where the d orbitals are accessible or in non-transition elements which can use excited d orbitals The transition elements may, however, possess some other type of initial symmetry of the atoms linked by oxygen and then the compound with the XOX nucleus molecule has another symmetry, usually lower than D_{4h}.

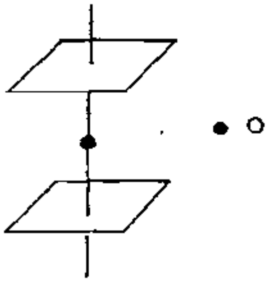


Fig. 1. The structural unit of D_{4h} symmetry.

Oxygen bonds between tetracoordinated atoms with tetrahedral symmetry are usually bent, Table 1.

Such bonds are formed between atoms of non-transition elements which use s and p orbitals or between atoms of transition elements with the d° configura-

TABLE 1

Compound	*Bond*	*Angle*	*ref.*
$HS_2O_7^-$	S–O–S	114°	(15)
$P_2O_7^{4-}$	P–O–P	134	(16)
P_4O_{10}	P–O–P	121	(15)
$Si_3O_3H_6$	Si–O–Si	130	(15)
As_4O_8	As–O–As	126	(15)
Sb_4O_6	Sb–O–Sb	130	(15)

tion. Unpopulated d orbitals have higher energy and are less capable of overlapping with the bridge atom orbitals.

Let us first consider the most typical oxygen bonds, the linear bonds occurring in transition elements where the magnetic properties give information about the quenching through the oxygen atom of the electron spins of the two metal nuclei.

The oxygen atom with its first electron affinity being positive and its second being negative has strong donor properties as a binegative ion. Some of the oxygen electrons are easily shifted towards the electron clouds of the acceptor cations where they form one or two σ bonds. If all the electron pairs of the oxygen ion are involved then the oxygen forms two σ bonds and two π bonds.

In order to form π bonds between oxygen and bound atoms the latter should possess a free d or p orbital.

Hexacoordinated central ions form 6 σ bonds, one of which is to the bonding oxygen.

Nine orbitals in each metal atom are available, namely 5 d orbitals, 3 p orbitals and one s orbital. These are used to house the six σ orbitals or the ligands. Moreover one orbital from each atom is used for the formation of the π bond with oxygen. The remaining two free orbitals each central ion are populated by the electrons belonging to these ions. From the point of view of valence bond theory, this suggests that each central ion could possess at most 4 electrons. According to the discussion presented below, MO theory allows an increase in that number of electrons in agreement with experiment.

Valence bond theory does not explain all the known examples of diamagnetic dimers even if it is assumed that the oxygen atom forms two σ bonds and two π bonds with the metal atoms. On the basis of that theory dimers with metal nuclei configurations d^3–d^3 *e.g.* Re^{IV} and d^1-d^1, Mo^V should always be paramagnetic. The decrease in paramagnetism of the iron dimers d^5-d^5 could not be explained on the basis of VB theory. A full elucidation of the magnetic properties may only be given by a molecular orbital interpretation of the delocalization of electrons, that is their belonging to the entire X–O–X nucleus. Let us consider which electrons should be regarded as delocalized over the entire nucleus.

The electrons which form the σ bonds may be considered as localized between the two nuclei. The electrons from the π bonds and the valence electrons, that is, d electrons from each central atom may first be delocalized. These electrons should be placed in the molecular orbitals of the X–O–X nucleus which are formed from the p π orbitals of oxygen and the valence orbitals of the central ions not used in σ bonding.

In our molecular orbital calculation[17,18] we took into account the linear combination of p_x and p_y orbitals of the oxygen atom and d_{xy}, d_{xz} and p_z orbitals from each central atom, Table 2.

TABLE 2

C_{4v}	a_1	d_{z^2}	s p_z
	b_1	$d_{x^2-y^2}$	
	b_2	d_{xy}	
	e	d_{xz}	p_x
		d_{yz}	p_y
D_{4h}	a_{1g}	d_{z^2}	s
	b_{1g}	$d_{x^2-y^2}$	
	a_{2u}	p_z	
	b_{2g}	d_{xy}	
	e_u	p_x	p_y
	e_g	d_{xz}	d_{yz}

We have thus assumed that the σ bonds are formed in d^3sp^2 hybridization.

The calculated energies of the π orbitals are arranged in the following sequence, (fig. 2).

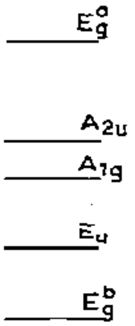


Fig. 2. Energy levels in XOX system of D_{4h} symmetry.

$$E_g{}^b < E_u < A_{1g} < A_{2u} < E_g{}^a$$

The maximum number of electrons which can go into these orbitals is 16.

Since four electrons are from the bridging atom, this means that each central atom could have at most 6 electrons of its own. The central ion-oxygen bond order is equal to 1.5. These considerations allow us to draw some conclusions about the type of central ion electronic configuration most suited to forming stable systems with X–O–X bonding. The MO theory states that the bond is strongest if there are no electrons in the anti-bonding orbitals. The bond gets weaker as that orbital is being populated with electrons. If the number of electrons on the anti-bonding orbital becomes equal to that on the bonding orbital, then the bond order amounts to zero.

The complexes in question in which the coordination number of the central ions is 6 show that the dimers formed by the central ions of d^1, d^2, d^3, d^4 configurations are the most stable. If the central ions have a d^5 configuration, the oxygen bond is weaker. If the central ions have a d^6 configuration, the bridge M–O–M involves only σ bonds.

In such a case the bond would be very weak. No oxygen bridge dimers with d^6 central ions are known. The existence of dimers in which the number of electrons on each central ion is higher than 6 is still less probable as these electrons would be placed in the anti-bonding σ orbitals resulting in further weakening of the bond.

The magnetic properties of these complexes will depend on two factors:

1. the number of d electrons donated to the molecular orbital system by the metal ions.
2. the symmetry of the entire complex.

The molecular orbital system given below refers to dimeric complexes of D_{4h} symmetry. The orbital diagram indicates that complexes with the X–O–X bond and D_{4h} symmetry are diamagnetic if there are 4,8, 10, 12 or 16 electrons in the molecular orbitals of the nucleus, Table 3.

TABLE 3

Nucleus	*Number of electrons in the nucleus*	*Distribution of electrons in the molecular orbitals*
Re—O—Re	10	$(E_g{}^b)^4\ (E_u)^4\ (A_{1g})^2\ (A_{2u})^0\ (E_g{}^a)^0$
Cr—O—Cr	10	$(E_g{}^b)^4\ (E_u)^4\ (A_{1g})^2\ (A_{2u})^0\ (E_g{}^a)^0$
Ru—O—Ru	12	$(E_g{}^b)^4\ (E_u)^4\ (A_{1g})^2\ (A_{2u})^2\ (E_g{}^a)^0$
Os—O—Os	12	$(E_g{}^b)^4\ (E_u)^4\ (A_{1g})^2\ (A_{2u})^2\ (E_g{}^a)^0$
Fe—O—Fe	14	$(E_g{}^b)^4\ (E_u)^4\ (A_{1g})^2\ (A_{2u})^2\ (E_g{}^a)^2$

If the orbitals of the XOX nucleus possess 6 or 14 electrons then paramagnetic compounds should be formed. An example is the Fe^{III} complex mentioned above with phenanthroline. In agreement, Mo^V also forms paramagnetic dimers in solution. Dimeric complexes with an odd number of electrons whose XOX nuclei possess metal cations in different valence states are also paramagnetic and their moments correspond to one or three electron spins.

The complex $[Cr_2O(NH_3)_{10}]Cl_4$ is weakly paramagnetic at room temperature and has the energy interval between the A_{1g} and A_{2u} orbitals of the order of kT^{14}. This results in a Boltzmann distribution of electrons in these orbitals and causes the paramagnetism of that compound. Even a slight increase of the energy interval between the energy levels results in diamagnetism at low temperatures.

The sequence of molecular orbitals calculated by us explains the magnetic properties of all known complexes of D_{4h} symmetry with oxygen bridges.

In order to characterize the bridge resulting from the sharing of electrons in the molecular orbitals, it is important to find experimental evidence that any disturbance of that orbital system results in a change in magnetic properties. Such a disturbance is produced by the protonating of the oxygen bridge, *i.e.* transformation of the —O— bridge into an $\overset{\displaystyle\mathrm{H}}{\overset{|}{-\mathrm{O}-}}$ bridge or its oxidation to $\overset{\displaystyle\mathrm{O}}{\overset{|}{-\mathrm{O}-}}$.

Chromium(III) complexes with one "olic" bridge show a normal paramagnetism and paramagnetic absorption[14].

The peroxy complex of rhenium(IV) $[Re_2O_2Cl_{10}]^{4-}$ which is formed by oxidation of the diamagnetic $[Re_2OCl_{10}]^{4-}$ is also paramagnetic[19,20].

The effect of symmetry on the magnetic properties is evident in the molybdenum(V) complexes. Blake, Cotton and Wood[21] have discussed the structure and properties of the Mo^V complex $[(C_2H_5OCS_2)_2MoO]_2O$ on the basis of MO theory. This compound has a linear group Mo–O–Mo They have discussed its properties in D_{2h} and D_{2d} symmetries, taking into account the formation of π bonds between the bridging oxygen and Mo^V ions.

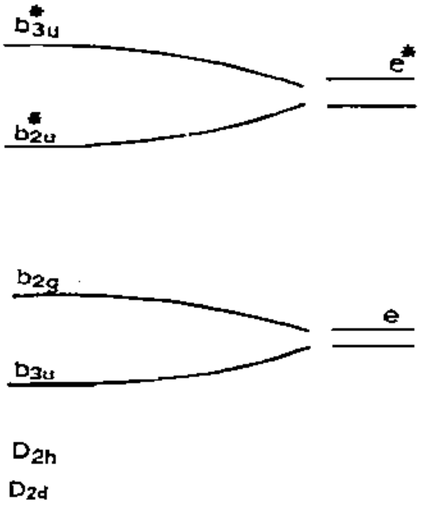


Fig. 3. Energy levels in XOX system of lower symmetry.

In the case of D_{2d} symmetry, two d orbitals of the Mo^V ions transform into the bonding E molecular orbital and the p_x and p_y orbitals of oxygen transform into the anti-honding E* molecular orbital. In the Mo–O–Mo nucleus four electrons are placed into the bonding E orbital and two into the anti-honding E* orbital, two of these electrons come from the Mo^V ions and four electrons from the bridging oxygen atom.

The electron distribution in these orbitals shows that in this symmetry the Mo–O–Mo nucleus would be paramagnetic with one electron spin per central ion.

In changing to D_{2h} symmetry, the E molecular orbital in D_{2d} correlates with the B_{3u} and B_{2g} orbitals and the E* orbital in D_{2d} symmetry corresponds to the B^*_{2u} and B^*_{3u} orbitals in D_{2h} symmetry. When six electrons are placed into these orbitals

$$(B_{3u})^2\,(B_{2g})^2\,(B^*_{2u})^2\,(B^*_{3u})^0$$

the Mo–O–Mo grouping becomes more stable and diamagnetic. Some attempts were made to apply the superexchange[22–30] and double exchange[31,32] theories to explain the magnetic properties of the magnetic systems M–O–M. The application of these theories to such molecular systems as two metal ions interacting through the oxygen atom inside the same molecule is not satisfactory as these theories pertain to the crystalline state in which the M–O–M systems exist. However, the description of the M–O–M nucleus above may be regarded as a particular super-exchange model.

In order to explain the magnetic properties of dimers with two O or OH bridges which show a decreased magnetic moment, one should assume a direct spin–spin interaction between the metal atoms. This interaction is so prevailing over the interaction through the oxygen atom that the latter may be neglected.

The magnetic susceptibilities for these compounds are given by the equation[33–35]

$$\chi = N\frac{g^2\beta^2}{kT}\sum_S \sum_{M_S=-S}^{S} M_S^2 \exp\left[-E^0(S)/kT\right] \Big/ \sum_S \sum_{M_S=-S}^{S} \exp\left[-E^0(S)/kT\right]$$

By comparing the experimental magnetic susceptibility curves (susceptibility versus reciprocal temperature) with theory, it is possible to determine the magnitude of the exchange integral J between the two ions. This integral assumes a value from 2–12 cm^{-1} for most compounds.

Let us now consider the structure and properties of binuclear compounds consisting of two tetragonal pyramids joined through their apices[36]. To that type of compound belong the dichromates, pyrosulphates, pyrophosphates etc. The central ion in these compounds is surrounded by four oxygen atoms and each of them may form both π and σ bonds. Such compounds may have D_{3d}, D_{3h} or C_{2v} symmetries.

In the case of D_{3d} symmetry the X–O–X bond is linear. The bridging oxygen is sp hydridized. The two bonding a_{2u} molecular orbitals form the σ bonds with the central ions. The remaining σ bonds are formed with a_{1g}, e_g, a_{2u} orbitals.

Group theory considerations have shown that in the case of compounds with that type of symmetry the bridging oxygen atom could form no π bonds with the central ions. These bonds could be formed only between the central ions and the remaining oxygen atoms by means of the a_{1g}, a_{2g}, $2e_g$, a_{1u}, a_{2u} and $2e_u$ orbitals.

Similar results have been obtained in considering the formation of π and σ bonds in complexes with D_{3h} symmetry [22]. In this case there are no π bonds in the X–O–X nucleus. The σ bonds of the bridging oxygen form two bonding molecular orbitals a_1.

Complexes with C_{2v} symmetry are of considerable interest. This type of symmetry may incur two possible hydridizations of the bridging oxygen, sp^2 and sp^3. The σ bonds of the bridging oxygen atom are formed by means of the a_1 and b_2 orbitals. The remaining σ bonds arise from the a_2 and b_1 orbitals, two a_1 orbitals and two b_2 orbitals. The bonds of the non-bridging oxygen atoms, form the following molecular orbitals: $2a_1$, $3a_2$, $2b_1$, $3b_2$. If the bridging oxygen undergoes sp^2 hybridization, the molecular orbital a_1 is formed which corresponds to the formation of one π bond between this oxygen and the central ions. In the case of sp^3 hybridization the two orbitals a_1 and b_1 correspond to the formation of two π bonds, one from each central ion.

The stability of complexes with a C_{2v} structure is explained by this possibility of π bond formation.

The oxygen bond has some characteristic frequencies in the infra-red. There are certain differences between linear and bent bonds. In the case of linear oxygen bonds which appear in compounds of the d electron elements the symmetric frequencies are observed at about 220 cm^{-1} and the asymmetric frequencies at about 850 cm^{-1}. It is important to note that these frequencies depend only to a slight extent on the atomic weight and type of the central ions, Table 4.

TABLE 4

Compound	$\nu_s(cm^{-1})$	$\nu_{as}(cm^{-1})$
$K_4Ru_2OCl_{10}$	226[37]	885[37,39]
$K_4Ru_2OBr_{10}$	222[37]	860[37,39]
$(NH_4)_4Os_2OCl_{10}$	–	850[37,39]
$K_4Re_2OCl_{10}$	230[37]	855[37,39]

Symmetric frequencies for the bent oxygen bonds are higher than in the case of the linear bonds. For instance, in group IV the vibrational energies increase with decreasing atomic weight, from Sn to C. The energy of the asymmetric vibration is much higher for carbon, above[40] 1000 cm^{-1}, and suddenly decreases in germanium and tin indicating that the oxygen bond in principal carbon group elements is much stronger than in its successors[41], Table 5.

This is no doubt due to decreasing covalency in the central atom-oxygen bond. A similar change of bond strength is observed in group V, on transition from phosphorus to arsenic and antimony[42], Table 6.

TABLE 5

1200–1225 cm^{-1}	ν_{as} C–O–C
840–1100 cm^{-1}	
1000–1100 cm^{-1}	ν_{as} Si–O–Si
830– 880 cm^{-1}	ν_{as} Ge–O–Ge
735– 775 cm^{-1}	ν_{as} Sn–O–Sn
813–1270 cm^{-1}	ν_s C–O–C
510– 530 cm^{-1}	ν_s Si–O–Si
– 458 cm^{-1}	ν_s Ge–O–Ge
465– 490 cm^{-1}	ν_s Sn–O–Sn

TABLE 6

Compound	ν_s	ν_{as}
$(P_2O_3Cl_4)n$	705 cm^{-1}	962 cm^{-1}
$(PO_2Cl)_n$	735 ,,	995 ,,
$(AsO_2Cl)_n$	640 ,,	778 ,,
$Cl_4Sb–SbO_2Cl_4–SbCl_4$	559 ,,	692 ,,
$(SbO_2Cl)_n$	562 ,,	725 ,,

TABLE 7

Compound	ν_s	ν_{as}	ν
$S_2O_5F_2$	323 cm^{-1}	814 cm^{-1}	157 cm^{-1}
$S_2O_5Cl_2$	298 ,,	760 ,,	147 ,,
S_2O_5Cl	313 ,,	802 ,,	154 ,,
$H_2S_2O_7$	328 ,,	809 ,,	155 ,,
HS_2O_6F	325 ,,	794 ,,	140 ,,
HS_2O_6Cl	310 ,,	803 ,,	148 ,,
$K_2S_2O_7$	321 ,,	800 ,,	–
$Na_2S_2O_7$	346 ,,	805 ,,	–
$S_2O_5(CH_3)_2$	329 ,,	770 ,,	–
SF_5OSF_5	256 ,,	808 ,,	125 ,,
$(CH_3O)Se_2O_5$	555 ,,	687 ,,	229 ,,
$H_2Se_2O_7$	557 ,,	690 ,,	230 ,,
$D_2Se_2O_7$	555 ,,	690 ,,	230 ,,
$Na_2Se_2O_7$	556 ,,	696 ,,	
$K_2Se_2O_7$	557 ,,	668 ,,	236 ,,
$(NH_4)_2Se_2O_7$	555 ,,	670 ,,	
$(NO)_2Se_2O_7$	560 ,,	673 ,,	

The oxygen bond strength to sulphur in group VI is less than to silicon and decreases with atomic weight from sulphur to selenium[43,44], Table 7.

Transition metal compounds involving bent bridge bonds exhibit asymmetric vibrational frequencies close to those observed in sulphur and selenium derivatives. The symmetric vibration energies are also similar to those observed for selenium.

A typical feature of non-transition metal complexes containing oxygen bridges is the considerable variation in the X–O–X bridge frequencies. These frequencies are practically constant in the case of the transition elements which is additional evidence that the M–O–M– system is linear.

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