

# THE NATURE AND SPECTROSCOPIC CHARACTER OF THE METAL-OXYGEN BONDING OF SOME HEAVY METALS. PART III\*. METAL-OXYGEN $\pi$ -BONDING AND ITS INFLUENCE ON THE STRUCTURE OF OXY-COMPLEXES ON THE BASIS OF INFRA-RED SPECTROSCOPY

BY J. HANUZA, M. BAŁUKA AND B. JEŻOWSKA-TRZEBIATOWSKA

Institute of Low Temperature and Structure Research, Polish Academy of Sciences, Wrocław\*\*

(Received December 14, 1971)

The present work contains certain general statements pertaining to  $\pi$ -interactions in the oxy-complexes of  $d$ -electron metals. The conclusions presented here are based upon the results obtained by the spectroscopic IR methods and reported in our previous papers.

## 1. Introduction

The formation of multiple bondings is a common effect encountered in both inorganic and organic compounds. From the standpoint of the molecular orbital approach the multiple bonding may be formed in a diatomic molecule if orbitals of adequate energies and symmetries overlap, yielding regions of maximum "electron densities" both along the line interconnecting the two nuclei ( $\sigma$  bonding) and beyond it (see Fig. 1 (I)). Simultaneously, the number of electrons in bonding orbitals is greater than that in anti-bonding orbitals. Overlapping beyond the internuclear axis usually takes place in a single nodal plane passing through both these nuclei (Fig. 1 (III)–(VI)) and leads to the formation of  $\pi$ -bondings which correspond to the orbital moment unit ( $\lambda h/2\pi$  at  $\lambda = 1$ ) with respect to the internuclear axis. The overlapping in two perpendicular nodal planes is less frequent (for instance, if two  $d_{x^2-y^2}$  or  $d_{xy}$  orbitals overlap "face to face") and results in a  $\delta$ -bonding with orbital angular momentum  $\lambda = 2$ . In polyatomic molecules the same nomenclature is employed and  $\sigma$  and  $\pi$  characterize a spatial orbital distribution. Such an approach explains many properties of multiple bonding (e. g., the lack of rotation and symmetry) but requires two entirely different bondings,  $\sigma$  and  $\pi$ , to appear in the molecule. In the

\* Part II: *Acta Phys. Polon.*, A42, 537 (1972); Part I: *Acta Phys. Polon.*, A38, 563 (1970).

\*\* Address: Instytut Niskich Temperatur i Badań Strukturalnych PAN, Wrocław, Pl. Katedralny 1, Poland.

case when a molecule has no planes or axes of symmetry, an accurate definition of the  $\pi$ -bondings is not possible. In such considerations individual pairs of atoms are usually isolated from the rest of the molecule.

In the valence bonding approximation the atoms which may engage only the  $s$  and  $p$  orbitals in the bonding usually give tetrahedral groups in  $sp^3$  hybridization. This leads to a minimization of the repulsion between the four paired electrons of the octet or to a correlation of two electron quartets of opposite spins. The double boelnding may be

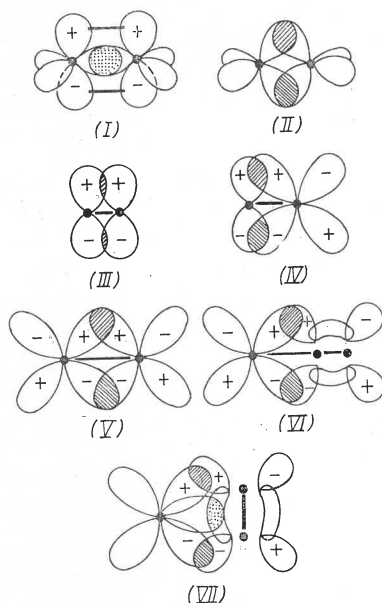


Fig. 1. Orbital overlap diagram: (I) — definition of the  $\sigma+\pi$  bond in the Molecular Orbital Theory; (II) — definition of the double bond in the Valence Bond Theory; (III) —  $p-p_\pi$  interaction; (IV) —  $d-p_\pi$  interaction; (V) —  $d-d_\pi$  interaction; (VI) —  $d-\pi_\pi^*$  interaction; (VII) —  $d-\pi_\mu^*$  interaction

then considered as a common edge of two tetrahedra (Fig. 1 (II)) while the triple bonding may be considered as a common plane. Such a model may be generalized for studies on multiple bondings resulting from interaction between the  $d$ ,  $s$  and  $p$  orbitals by applying an octahedral or cubic cell instead of the tetrahedron. Such models provide a qualitative explanation of a majority of the properties exhibited by the multiple bondings, with the advantage that they do not require any rigorous discrimination between the  $\sigma$  and  $\pi$ -bondings. One should instead assume a possibility that two or more angular bondings may appear, as in Fig. 1 (II). From the mathematical point of view, two angular bondings are equivalent to the  $\sigma+\pi$  combination and in a full, quantitative approach both these formalisms lead to certain differences in interpretation which are, in fact, correct and insignificant, as shown by Pople [1]. The  $\pi$ -bonds are formed as a result of overlapping between various orbitals (Fig. 1).

The most frequent are the  $p-p$  (Fig. 1. (III)),  $d-p$ (IV),  $d-d$  (V) and  $d-\pi^*$ ((VI) and (VII)) interactions. Analogous interactions with the  $f$  orbitals may be considered

from a similar viewpoint. The bonds resulting from overlapping of orbitals which are directed towards the centre of the multiple bonding, their origin being a hybrid and not a single atom (*e. g.*, the hybrid  $sp-\pi$  interaction is diagrammatically shown in Fig. 1 (VII)) are called  $\mu$ -bonds. In order to distinguish between both types of  $d-\pi^*$  interaction shown in Fig. 1 (VI) and (VII), the symbols  $d-\pi_\pi^*$  and  $d-\pi_\mu^*$ , respectively, are used in the nomenclature.

When the orbitals having accessible electrons combine, yielding molecular orbitals, the energy of the bond formed is approximately proportional to the overlap integral. Since this overlapping is much more effective along the internuclear axis than beyond it, the  $\pi$ -bond will be weaker than the  $\sigma$ -bond. The formation of  $\pi$ -bonds, however, leads to bringing the nuclei together and, in consequence, to an increase of  $\sigma$  overlapping and further — to an increase of total bond energy. An increase of bond energy resulting from shorter  $\sigma$ -bonding and formation of  $\pi$ -bonds takes place simultaneously with the reduction of mutual repulsion between non-bonding electrons. With the presence of the  $\pi$ -bonding these electrons appear in bonding  $\pi$ -orbitals, which leads to shorter and stronger bonds.

A comparison of bond lengths is the most useful method for identifying multiple bonds. The angles between bonds in some cases also provide information on the orbitals which may effectively overlap each other. The bond strength manifested quantitatively by the vibrational-spectroscopic data, that is, stretching frequencies or force constants, is a measure of this bond length and many authors have suggested empirical relationships between the force constants and bond order. Finally, the interpretation of UV, VIS and ESR spectra also enables multiple bonds in the molecule to be revealed. The same applies to other properties related to the appearance of such  $\pi$  interactions, namely, the dipole moment, NMR spectra, complex formation constants or magnetic susceptibility.

## 2. Results and discussion

Vibrational-spectroscopy is, besides *X*-ray structural analysis, one of the best methods for identifying  $\pi$ -bonds. A very promising subject of studies on this problem are the oxy-compounds in which there is observed a greater or lesser contribution of  $p_\pi-d_\pi$  interactions in the overall bonding effect, depending on the amount of oxygen atoms per metal atom. The occurrence of these interactions is manifested directly in the data obtained by means of infra-red spectroscopy.

The main "vibrational arguments" employed are as follows. First of all, the energy level of a given vibration in the infra-red or Raman spectrum provides considerable information on the existence and distribution of  $\pi$ -bonds in an oxy-compound. The force constants, and especially the bond length and order, are a direct measure of such  $\pi$ -interactions.

Certain indirect conclusions regarding the  $\pi$ -bonds in a complex may also be drawn by comparing the vibrations resulting from the ligands occupying the other co-ordination positions in a complex. The appearance of a short metal-oxygen bond, *e. g.*, in the  $MOL_5$  type complexes, leads to certain structural phenomena designated a "trans-effect", which show up in the vibrational spectrum.

The vibrational spectra also exhibit a reversible effect of ligands on the metal-oxygen bonds in the complex, and this effect depends on the ligand position in the spectrochemical series.

Now, we shall discuss these effects in detail. The first effect has been extensively described in our earlier papers [2-3]. The infra-red spectra of a number of mononuclear oxy-compounds of rhenium, technetium, osmium and ruthenium of the general formula  $MO_nL_{6-n}$ , and hydroxy-compounds and binuclear complexes containing a bridging  $M-O-M$  group, have been presented. Theoretical considerations based upon group theory enabled us to assign a definite range of vibrational absorption to each oxygen system. These absorption ranges were used for calculating the force constants of metal-oxygen bonds [2] which, in turn, were employed in estimations of the bond order, determinations of the contribution of  $p_\pi-d_\pi$  interactions to this bond, and in calculations of the lengths of oxy-bonds [3]. A full correlation of the results obtained by us by means of infra-red spectroscopic methods are presented in Table I.

TABLE I  
Correlation between vibration frequency, force constant, length and bond order of the metal-oxygen bonding

Type of compound	Vibration frequency of the metal-oxygen bonding in $cm^{-1}$	Stretching force constant $f$ [Md/Å]	Bond order	Metal-oxygen distance [Å]
$MO_5$	950-995	7.41-8.36	2.41-2.68	1.72-1.73
$MO_4^n$	800-920	5.56-8.05	1.89-2.56	1.71-1.75
$MO_3L_3$	890-950	6.95-7.47	2.22-2.40	1.74-1.76
$MO_2L_4$	775-912	5.50-6.68	1.86-2.19	1.75-1.78
$M_2OL_{10}$	830-885	3.37-4.15	1.33-1.64	1.85-1.91
(M-O-M)	200-250			
M-OH	440-580	2.82-2.99	1.11-1.19	1.90-1.95

The numerical values of bond order, which are a measure of the overall binding effect ( $\sigma + \pi$ ), indicate a considerable contribution of  $\pi$ -electrons to the metal-oxygen bond.

This contribution decreases in the series:

$$N_{MO} > N_{MO_3} > N_{MO_2} > N_{MOM} > N_{M-OH}$$

where  $N$  is bond order. Maximum saturation of the metal-oxygen bond with  $\pi$ -electrons appears in mono-oxycomplexes in which the overall bond order is close to 2.6. On the other hand, a "pure" metal-oxygen  $\sigma$ -bond appears in  $M(H_2O)_xL_{6-x}$  type *aquo*-complexes, since in hydroxy-compounds the bond order is 1.1 to 1.2.

An equally important argument revealing the existence of  $p_\pi-d_\pi$  interactions in oxy-compounds is the trans-effect. A transition from the  $ML_6^{n\pm}$  complex ion of regular octahedral structure to a  $MO_5$  ion yields two essential types of deformation:

- change of  $OML_{cis}$  angles,
- change of  $M-L_{trans}$  length (trans-effect).

The first self-contained type of deformation was found in the  $K_2[Ru(NO)Cl_5]$  [4] and  $K_2[Fe(NO)(CN)_5]$  [5] structures. Non-equivalency (kinetic trans-effect) of cyanide groups in the latter complex was found by Jeżowska-Trzebiatowska and Ziółkowski [6] by means of radioisotopic exchange. In crystal structures  $K_2[ReOCl_5]$  and  $K_2[MoOCl_5]$  [7] two types of deformation were found, most frequently appearing together. A similar deformation is also observed in  $K_2[NbOF_5]$  and  $K_2[OsNCl_5]$  [4]. Except for  $K_2[OsNCl_5]$ , in all other complexes the metal-ligand bond in the trans position with respect to oxygen was found to be elongated in comparison with identical ligands in the  $ML_4$  plane. An opposite effect was originally observed in  $K_2[OsNCl_5]$ , for which a shorter bond with the trans ligand was allegedly observed. A paper published by the same authors [4] a few

TABLE II

Trans-effect in the  $MOL_5$  type complexes

Electronic state	Complex	Distances in Å			$\nu(MO)$ [cm <sup>-1</sup> ]	$\nu(M-L_{trans})$ [cm <sup>-1</sup> ]	$\nu(M-L_{cis})$ [cm <sup>-1</sup> ]	$\Delta\nu(M-L)$ [cm <sup>-1</sup> ]	Ref.
		M-O	M-L <sub>cis</sub>	M-L <sub>trans</sub>					
$d^2$	$K_2[ReOCl_5]$	1.66	2.39	2.47 [7]	993-988	316	330	14	[2]
	$Cs_2[ReOCl_5]$				955	310	327	17	[2]
	$K_2[TcOCl_5]$				992-986	325	342	17	[2]
	$Cs_2[TcOCl_5]$				956	323	339	16	[2]
$d^1$	$OsOF_5$	1.74	1.72	1.78 [8]	690	640	705	63	[2]
	$K_2[MoOCl_5]$	1.67	2.40	2.63	967	—	—	—	[7]
	$Cs_2[MoOCl_5]$				952	320	329	9	[9]
	$K_2Na[VOF_5]$				943	383	525	142	[10]
	$Rb_2[WOCF_5]$				960	317	339	22	[9]
	$Cs_2[CrOCl_5]$				945	320	340	20	[11]
$d^0$	$K_2[NbOF_5]$	1.68	1.84	2.06	926	—	—	—	[7]
	$Cs_2[NbOCl_5]$				930	327	339	12	[12]
	$K_2Na[TiOF_5]$				920	379	530	144	[10]
	$Rb_2Na[TiOF_5]$				900	337	487	150	[10]
	$IOF_5$		1.75	1.86	927	640	680	40	[13]

years later corrected these results, however. They then stated that inaccurate measurements resulted from the fact that the compound studied previously contained a water molecule instead of a chlorine atom in the trans-position, contrary to the implication of the formula  $K_2[OsNCl_5]$ . The  $Re = Cl_{trans}$  bond length in  $K_2[ReOCl_5]$  is slightly longer than the  $Re - Cl_{cis}$  bond length. A short metal-oxygen bond appears in this ion, the presence of which leads to a change in the  $O - M - L_{cis}$  angles and to a slight increase in the metal-chlorine (trans) bond length, *i. e.* the so-called trans-effect. This results in a lowering of the central ion symmetry. The magnitude of the trans-effect in oxy-complexes depends on several factors:

- the number of  $d$ -electrons in the central ion,
- the extent of the screening effect for the valence electrons (period),

the type of the ligands, and  
the type of the cation.

The most important are the first two factors, as is evident from a comparison of the X-ray structural data with the results of infra-red studies for a number of *d*-electron metal-oxy-complexes (Table II).

On the basis of a comparison of lengths and stretching vibration frequencies for the metal-ligand bonds, one may stipulate the following sequence of increasing oxygen trans-interactions according to the electronic structure of the central ion:

$$M(d^2) < M(d^1) < M(d^0).$$

This relationship is intuitively obvious, for with a decrease of the number of *d*-electrons in the central ion to zero, the reverse oxygen-ligand trans-interaction barrier (which is the metal atom) disappears. A similar conclusion is reached by Głowiak [7] on the basis of X-ray structural analysis of some rhenium oxy-compounds.

The difference in frequencies of stretching vibrations  $\nu(M-L_{cis})$  and  $\nu(M-L_{trans})$  reveal the effect of  $\pi$  interactions between metal and oxygen on the other part of the oxy-compound. The ligands adjacent to the oxygen atom in the oxy-compound do not behave identically. This may be observed by comparing the frequencies of the stretching vibrations  $\nu_{as}(MO_2)$  in the dioxy-group over the range of one element, *e. g.*, rhenium (the spectroscopic data have been published by us previously [2]). Such a comparison is given below:

Complex	$ReO_2(CN)_4^{3-}$	$ReO_2 en_2^+$	$ReO_2 py_4^+$	$ReO_2(NH_3)_4^+$
$\nu_{as}(ReO_2)$	775	819	822	825 $cm^{-1}$

The differences in the  $\nu_{as}(ReO_2)$  vibrational frequencies occurring for specific complexes result from the nature of other ligands. If these ligands are  $\pi$ -acceptors, then the metal-oxygen bond becomes weakened, and *vice versa*, if they are  $\pi$ -donors, then the bond order, *i. e.* the metal-oxygen bond strength, increases. The increase in bond strength is accompanied by an increase in frequency. The arrangement of the series according to the increasing  $\nu_{as}(ReO_2)$  frequency,  $CN < en < py < NH_3$ , corresponds, therefore, to the increase in  $\pi$ -donor properties of ligands. The  $CN^-$  ion has the  $\pi$ -acceptor properties and forms weak  $\pi$  bonds with the metal  $d_{xz}$  and  $d_{yz}$  orbitals, which also results in a weakening of the rhenium-oxygen bonds. This series is identical with that formed on the basis of charge transfer transition band positions in the electron spectra of the complexes examined by us, and at the same time gives a sequence which is the ligand spectrochemical series [14] in reverse. In this case these are the oxygen-metal transitions from the molecular  $e^b$  orbital to a delocalized  $e^*$  orbital.

### 3. Summary

Taking into account all conclusions pertaining to the metal-oxygen  $\pi$ -interactions in oxy-compounds, the distribution of  $\pi$ -electrons in the complex may be found to be labile. Their distribution among the oxygen atoms in the complex is symmetrical, while the other

ligands strengthen or weaken the metal-oxygen bond owing to their  $\pi$ -donor or acceptor properties. It is worthwhile to emphasize the fact that these effects are quantitatively revealed in infra-red spectra, IR spectroscopy being the most sensitive method of studying multiple bonds in oxy-compounds and chemical compounds in general.

## REFERENCES

- [1] J. A. Pople, *Quart. Rev.*, **11**, 273 (1957).
- [2] B. Jeżowska-Trzebiatowska, J. Hanuza, M. Bałuka, *Acta Phys. Polon.*, **A38**, 563 (1970); *Spectrochim. Acta*, **27A**, 1753 (1971); *Bull. Acad. Polon. Sci., Ser. Sci. Chim.*, **20**, 271 (1972).
- [3] J. Hanuza, M. Bałuka, B. Jeżowska-Trzebiatowska, *Acta Phys. Polon.*, **A42**, 537 (1972).
- [4] T. S. Khodashova, G. B. Bokii, *Zh. Strukt. Khim.*, **1**, 151 (1960); *Dokl. Akad. Nauk USSR*, **128**, 78 (1959); L. O. Atovmian, G. B. Bokii, *Zh. Strukt. Khim.*, **1**, 501 (1960); **11**, 933 (1970).
- [5] P. T. Manoharan, W. C. Hamilton, *Inorg. Chem.*, **2**, 1043 (1963).
- [6] B. Jeżowska-Trzebiatowska, J. Ziólkowski, *Proceedings of the Conference on Some Aspects of Phys. Chem.*, Budapest 1966.
- [7] T. Głowiak, *Proceedings of the XIIIth International Conf. on Coordination Chemistry*, Kraków-Zakopane 1970; Doctor's Dissertation, University of Wrocław 1970, Poland; to be published.
- [8] N. Farlett, J. Trotter, *J. Chem. Soc. A*, 543 (1968).
- [9] B. J. Brisdon, D. A. Edwards, *Inorg. Chemistry*, **7**, 1898 (1968).
- [10] K. Dehnicke, G. Pausewang, W. Rüdorff, *Z. anorg. allgem. Chem.*, **366**, 64 (1969).
- [11] O. V. Zierbarth, J. Selbin, *J. Inorg. Nucl. Chem.*, **32**, 849 (1970).
- [12] A. Sabatini, J. Bertini, *Inorg. Chem.*, **5**, 204 (1966).
- [13] D. F. Smith, G. M. Begun, *J. Chem. Phys.*, **43**, 2001 (1965).
- [14] M. Bałuka, Doctor's Dissertation, Institute of Low Temperature and Structure Research, Polish Academy of Science, Wrocław 1971, Poland.