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The Electronic Structure of Transition Metal Cluster Complexes with Weak- and Strong-field Ligands

G.P.Kostikova and D.V.Korol'kov

A systematic account and a survey of the results of quantum-chemical and spectroscopic studies of the electronic structure of transition metal cluster complexes are presented. In terms of the theory of canonical molecular orbitals and the theory of weak- and strong-field ligands, the concept of the structure and stability of the clusters taking into account the influence of the ligands and transition metal atoms on the characteristics of the M-M bonds has been formulated. The characteristic features of the delocalisation of the valence electrons of the M atoms in the M_n groups, the intercluster interaction, the density of the M atoms in the clusters, and the effects of cluster formation in the optical and X-ray spectra are discussed.
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I. INTRODUCTION

In the modern chemistry and physics of clusters, one of the main taks is to create a general theoretical conept concerning the structure and stability of clusters whereby one can account for the existence of these complexes and formulate the principles governing their structure as a function of the position of the transition metal in the Periodic System, the formal valence of the M atoms, and the individual nature of the ligands; such a concept would constitute a general solution of the problem of the mutual influence of the nature of the transition metal and the ligands on the stability of cluster structures. The knowledge of the electronic structure of the clusters is undoubtedly a basis for the understanding of their structure, stability, and reactivity. The electronic structure of transition metal cluster complexes has been the subject of numerous theoretical studies in the last twenty years. The present review is devoted to the discussion of the results of these investigations and also the results of experimental studies of the spectroscopic properties of cluster compounds which supplement and refine the quantum-chemical calculations of the electronic structure.

II. THE ELECTRONIC STRUCTURE OF CHLORIDE AND CARBONYL CLUSTERS

Non-empirical and semi-empirical methods of the theory of delocalised molecular orbitals,[1-6] the electron gas method,[7] topological methods,[8,9] and the ligand field theory[10] are used in the quantum chemical calculations of the electronic structures of isolated cluster complexes. The references quoted above refer to review papers which have been published during the last decade. The results of spectroscopic and theoretical studies of the nature of the M-M bonds in transition metal cluster complexes (with the exception of dinuclear complexes) with strong M-M interactions are described in a recent review.[11]

The cluster chlorides and carbonyls of transition metals have been investigated most fully both experimentally and theoretically at the present time; attention is in fact concentrated on these substances in the present review. Weak π-donors (Cl atoms) and strong π-acceptors (CO molecules) occupy positions at the opposite ends of the general series of ligands and the study of clusters incorporating precisely these ligands is therefore most fruitful for the solution of the problems mentioned above in the most general form.

Table 1. Electronic structure parameters of clusters.

Cluster	Symmetry	R_{M-M}, Å	B_{M-M}	Bonding "M-M" MO	N_{M-M}	n_{M-M}	P_{M-M}	Refs.
$Mo_2Cl_8^{4-}$	D_{4h}	2.14	1	$a_{1g}eb_{2g}$	8	8	$4(\sigma+2\pi+\delta)$	[1,6,14]
$W_2Cl_9^{3-}$	D_{3h}	2.41	1	$a_1'e'$	6	6	$3(\sigma+2\pi)$	[2-4]
$Re_3Cl_{12}^{3-}$	D_{3h}	2.47	3	$a_1'a_2''e'e''$	12	4	$2(\sigma+\pi)$	[2-4]
$Nb_6Cl_6^{6-}$	C_{2h}	2.86	5	$a_ua_gb_ua_gb_g$	10	2	$1(\sigma)$	[2]
$Mo_5Cl_8^{3+}$	C_{4v}	2.58	8	$a_1a_1a_1ab_1eeb_2e$	19	2.4	$1.2(\sigma+[\pi])$	[4]
$Ta_6Cl_{12}^{3+}$	O_h	2.93	12	$a_{1g}t_{1u}t_{2g}a_{2u}$	15	1.2	$0.6(\sigma)$	[2,19]
$Re_2(CO)_{10}$	D_{4v}	3.02	1	a_1	2	2	$1(\sigma)$	[2-4]
$Os_3(CO)_{12}$	D_{3h}	2.88	1	$a_1'e'$	6	2	$1(\sigma)$	[2-4,11]
$Ir_4(CO)_{12}$	T_d	2.68	1	a_1el_2	12	2	$1(\sigma)$	[2-4,11]
$Mo_2(O_2CR)_4$	D_{4h}	2.11	1	$a_{1g}e_ub_{2g}$	8	8	$4(\sigma)$	[6,15]
$Ru_2(O_2CR)_4^+$	D_{4h}	2.28	1	$a_{1g}e_u$	6	6	$3(\sigma+2\pi)$	[4,17]
$Mo_3O_{13}^{14-}$	C_{3v}	2.52	3	a_1e	6	2	$1(\sigma)$	[4]
$Ru_3O_{12}^{12-}$	C_{3v}	2.55	2	a_1ee	8	4	$2(\sigma+\pi)$	[4]

Notation: R_{M-M} is the M-M distance, B_{M-M} the number of two-centre M-M bonds, N_{M-M} the total number of valence electrons in the M-M bonds, n_{M-M} the number of valence electrons per two-centre M-M bond, and P_{M-M} the multiplicity of the two-centre M-M bond.

The results of semi-empirical[1-6,11-15] and non-empirical[16-19] molecular-orbital calculations (some examples are presented in Table 1) revealed the most important features of the electronic structures of the chloride and carbonyl clusters and the fundamental differences between clusters containing ligands of different types.

In the chloride clusters the energy splitting of the valence *d* orbitals of the M atoms in the mononuclear fragment in the field of weak π-donor ligands (Cl atoms) is slight and much less pronounced than the corresponding splitting of these atomic orbitals (AO) following the appearance of M-M bonds, i.e. on formation of the cluster (Fig.1).

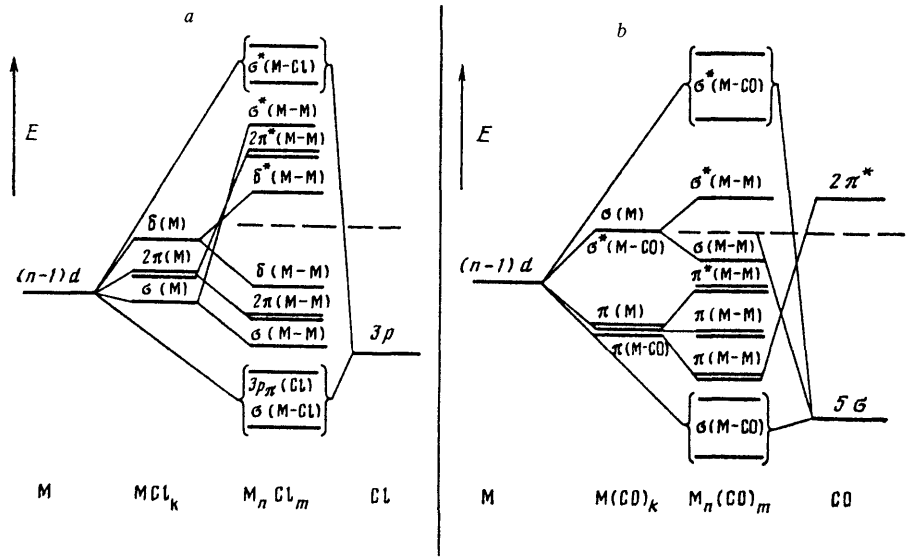


Figure 1. The molecular orbitals in the chloride and carbonyl clusters; the MO populated by electrons and the unoccupied MO are shown below and above the dashed lines respectively.[4]

The bonding and antibonding and sometimes also non-bonding molecular σ, π, and δ orbitals of the M–M bonds arise in the electronic structure of the chloride cluster under these conditions. The number and symmetry of these MO are rigorously individual for each chloride cluster, are determined by its stereochemistry, and are the most important characteristic of its electronic structure.[1,4]

A different picture is observed in the electronic structure of carbonyl clusters: the energy splitting of the valence *d* orbitals of the M atoms of the mononuclear fragment in the field of strong π-acceptor ligands (CO groups) is pronounced and greatly exceeds their energy splitting induced by the formation of the M–M bonds when the cluster is produced (Fig.1).[4,20,21]

This, the first important difference between the electronic structures of the chloride and carbonyl clusters, is caused by the fact that in the carbonyl clusters the two-centre M–L bonds are characterised by an enhanced multiplicity (M ← CO donor–acceptor σ interactions and M → CO dative π interactions) owing to the strong π-acceptor character of the CO groups, in contrast to the chloride clusters, where the two-centre M–L interactions represent virtually single two-electron bonds predominantly of the covalent σ-type. As a result of the different types of behaviour of the valence *d* orbitals of the M atoms in the fields of different ligands, the following situation arises: in the electronic structure of the chloride cluster, the molecular orbitals which are occupied by electrons and are responsible for the M–M interactions always constitute a single (and fairly isolated as regards energy) group, which incorporates in the general case σ, π_1, π_2, and δ MO (with increase of the number of valence *d* orbitals of the M atoms involved in the bonding with the Cl atoms and with the increase of the coordination number of each M atom in the cluster, initially the δ compound and then the π_1 and π_2 components are successively eliminated from the M–M interactions and only the σ component remains). In the vast majority of the known systems only the bonding molecular orbitals associated with the σ, π_1, π_2, or δ M–M interactions are occupied by electrons, while the corresponding antibonding MO are populated by only one–two electrons and in only rare instances.[1–4] On the other hand, in the electronic structure of the carbonyl cluster the electron-occupied MO of the M–M interactions are always clearly subdivided into two groups, which are not interconvertible in terms of energy: the first includes all the bonding and antibonding π molecular orbitals, while the second includes the bonding σ molecular orbitals of the M–M interactions. The electronic energies of the MO of the first group are appreciably reduced because these MO are simultaneously solely bonding orbitals in relation to the dative M → CO π-bonds; the electronic energies of the MO of the second group are greatly increased because they are simultaneously solely antibonding orbitals in relation to the M–CO σ-bonds. Insofar as all the molecular orbitals which are bonding in relation to the dative M → CO π-bonds and hence all the bonding and antibonding MO of the M–M π-bonds are fully populated by electrons in the electronic structure of the carbonyl cluster, only the highest (in terms of energy) occupied MO of the M–M σ-bonds are responsible for the M–M interactions in the carbonyl cluster.[4,20,21]

The above characteristics features of the electronic structure of the carbonyl clusters are the reason why the bonding and antibonding contributions to the M–M π-bonding approximately cancel out, while the π-contribution to the energy of the M–M interactions is either altogether absent or is slightly antibonding, the π-electron density being concentrated in the region of the M–CO bonds and mainly only single M–M σ-bonds, characterised by comparatively large internuclear distances and a reduced strength, are formed. The solution of the variational problem for the $Re_2(CO)_{10}$ cluster[22] showed that the decrease of the overall M–M bond energy is almost wholly responsible for the increase of the total energy of the cluster with decrease of the M–M distance below the equilibrium value of 3.02 Å; the decrease of the overall M–M bond energy is caused in its turn by the π-antibonding effects, by the energy destabilisation of the carbonyl cluster owing to the M–M π-interactions.

The electronic structure of the chloride clusters presupposes the bonding character of not only the σ- but also frequently the π- and even δ-interactions of the M–M type. For this reason, the multiplicity of the two-centre M–M bonds in such clusters varies within wide limits, reaching the limiting unique value $4(\sigma + 2\pi + \delta)$ for the M–M bonds in the $Re_2Cl_8^{2-}$, $Tc_2Cl_8^{3-}$, $Mo_2Cl_8^{4-}$, and similar dinuclear clusters. In the chloride clusters the multiple two-centre M–M bonds arise whenever this is allowed by the stereochemistry of the cluster group and the effective number of electrons involved in the M–M interactions. This is why the energies of the two-centre M–M bonds and the M–M distances in the chloride clusters vary within wide limits, ranging from weak interactions and long bonds in certain hexanuclear clusters to very strong interactions and extremely short bonds in the dinuclear groups.[23,24]

Thus M–M bonds with very high multiplicities and energies and sharply reduced M–M distances are formed only in the chloride clusters: such two-centre bonds involve σ-interactions, frequently π_1- and π_2-interactions, and sometimes even δ-interactions, whose electron densities concentrated in the region of the M–M bond hardly affect the ligands. The high stability of the chloride clusters of the formally low-valence 4*d* and 5*d* elements (Nb, Ta, Mo, W, Tc, Re), determined by the high M–M bond energies, is accompanied by the instability of the corresponding mononuclear anions ($TaCl_6^{4-}$, $MoCl_6^{4-}$, WCl_6^{3-}, $ReCl_6^{3-}$), which agrees with experimental findings.[25]

The second important difference between the electronic structures of the chloride and carbonyl clusters concerns the character of the M–M bonds. In the chloride clusters the main contribution to the MO of the M–M bond and to the overall orders of these bonds comes solely from the valence $(n-1)d$ orbitals of the M atoms and the bonds between the metal atoms are formed in the interaction of virtually only the $(n-1)d$ electrons of the M atoms.[1–4,26] In the carbonyl cluster also the valence *ns* and particularly *np* orbitals of the M atoms make a significant contribution together with the $(n-1)d$ orbitals, sometimes even the dominant contribution, to the σ-bonding M–M molecular orbitals and to the overall orders of the M–M σ-bonds.[21] This difference between the electronic structures is probably caused by the fact that in the chloride clusters the M atoms supply the *ns* and *np* electrons for the formation of bonds with ligands, such electrons being most suitable for this purpose in terms of symmetry and energy, while most of the $(n-1)d$ electrons are retained for the formation of various M–M bonds. On the other hand, owing to the high π-acceptor capacity of the ligands, in the carbonyl clusters a considerable proportion of the valence $(n-1)d$ electron density, which is more suitable as regards symmetry and energy than the *ns* and *np* states of the M atoms, is involved in the dative M → CO π-bonds; as a result of the formation of direct M–M σ-bonds, the number of the remaining $(n-1)d$ electrons is clearly insufficient and the use of the valence *ns* and particularly *np* electrons of the M atoms is necessary. The increased *np* character of the molecular orbitals of the M–M σ-bonds in the carbonyl clusters also entails (together with the antibonding character of these MO in relation to the donor–acceptor M–CO σ-bonds already mentioned), an increase of the energies of these MO, which accounts for the appreciably reduced energy of the two-electron two-centre M–M bonds in the cluster carbonyls compared with the cluster chlorides.[3,21]

This second difference is significant in the chemistry of cluster compounds in yet another respect. It is actually the decisive cause of the situation where 3*d* elements form cluster carbonyls but not cluster chlorides. In particular, the formation of the M–M bond in $Mn_2(CO)_{10}$ (i.e. the formation of a cluster) is associated with the involvement in this σ-bond of the valence 4*s* and 4*p* electrons of the Mn atoms not participating in the dative π-bonding with the ligands; on the other hand the participation of all the 4*s* and 4*p* electrons of the Cl atoms in the bonds with the ligand in $Cr_2Cl_9^{3-}$ explains the absence of any kind of M–M bond in this anion (i.e. the absence of a cluster), because, owing to the spatial contraction of their charge clouds, the valence 3*d* electrons of the M atoms cannot alone ensure the formation of any kind of strong M–M bond over the long M–M distances characteristic of both $Mn_2(CO)_{10}$ and $Cr_2Cl_9^{2-}$ (2.92 and 3.21 Å).[22,27]

The third difference lies in the fact that in the chloride clusters the molecular orbitals of the M–M bonds are of the purely "metallic" character and the contribution of the valence orbitals of the ligands to them is small; on the other hand, in the carbonyl clusters this contribution is appreciable. An important feature of the electronic structure of the chloride cluster is as follows: in the unique MO system of the cluster, the molecular orbitals responsible for the M–M interactions always constitute a distinct and isolated, in terms of energy and character, group and are predominantly of the $(n-1)d$ electron type: the isolation of these molecular orbitals is independent of either the energy and steric characteristics of the valence orbitals of the M atoms (i.e. of the nature of the transition element) or of the symmetry of the cluster group, which means that the M–M and M–L electronic interactions in the chloride clusters are to a large extent isolated from one another and their mutual influence is very weak, while the properties of the M–M and M–L bonds (in the first place their energies) are additive; in the cluster carbonyls everything is completely different and the characteristics of their M–M and M–L bonds are non-additive.

The isolation of the electronic M–M and M–L interactions in the chloride clusters makes it possible to solve the problem of their stability in a generalised form. The molecular orbitals of the M_n groups, which constitute the "metallic nuclei" of all the known chloride clusters of the 4*d* and 5*d* elements, have been calculated[2,28–30] (the symmetry of the point group of the cluster is indicated in brackets): M_2 for $M_2X_8(D_{4h})$, M_2 for $M_2X_9(D_{3h})$, M_2 for $M_2X_8(C_{2v})$, M_2 for M_3X_9 or $M_3X_{12}(D_{3h})$, M_2 for $M_3X_{12}(C_{3v})$, M_4 for $M_4X_{16}(C_{2h})$, M_4 for $M_4X_{16}(T_d)$, M_6 for M_6X_8 or $M_6X_{14}(O_h)$, and M_6 for M_6X_{12} or $M_6X_{18}(O_h)$. The electronic interactions arising in typical cases within the limits of each M_n group (direct M–N bonds) are represented by a characteristic set of bonding, non-bonding, and antibonding MO. These are in fact the molecular orbitals of the M–M bonds in the unique electronic structure of the M_nX_m chloride cluster as a whole. The number and character of such MO are determined not only by the number of M atoms in the M_n group but also by the number of ligands and the symmetry of their arrangement in the corresponding cluster group, i.e. by the detailed stereochemistry of the entire M_nX_m chloride cluster.[2,4,28,29]

There exist also chloride clusters, where, among the molecular orbitals responsible for the M–M interactions, only the bonding MO are populated (as a rule completely) by electrons (not involved in the M–L bonds), while the corresponding antibonding MO are unoccupied or in rare instances are populated by 1–2 electrons.[10] The stability of the M_nX_m chloride cluster as a whole and of its M_n group separately should therefore be attributed precisely to this (optimum) electron population of the molecular orbitals of the direct M–M bonds. The characteristic number of electrons ensuring the maximum stability of the M_n group when M–M bonds arise in it as a consequence of the complete population of all its bonding MO (and only the bonding MO) by electrons can be determined for each M_n group.

Thus it is possible to outline the limits of stability of each M_nX_m cluster taking into account its characteristic number of electrons and the individuality of the *d* element (the total number of valence electrons of the M atom) and its formal valence (the number of valence electrons of the M atom in the M–L bonds). Namely, by sorting through the transition metals of various Groups in the Periodic System, i.e. by scanning the number of valence electrons in their atoms, it is possible to outline the range of 4*d* and 5*d* elements (and at the same time indicate their formal valences), which can form stable chloride clusters.[4] It is then found that the clusters can be stable only in structures of the lowest chlorides of heavy Group V, VI, and VII *d* elements, since the total number of valence electrons in their atoms is such that it enables them to ensure the stability of one or (more frequently) several forms of clusters for a low oxidation state. On the other hand, the number of valence electrons in Group III and IV *d* elements is too small and that of the electrons of the M atoms (for any realistic oxidation states of the metal), not involved in the formation of bonds with the ligands, is clearly insufficient to populate the bonding orbitals of the M–M bonds in the M_n cluster of any form and hence for the formation of a more or less stable chloride cluster. In the atoms of Group VIII 4*d* and 5*d* elements the number of valence electrons is too large, which leads to the population by the electrons not involved in the M–L bonds not only of the bonding but also of the antibonding molecular orbitals of the M–M bonds in a cluster of any form and hence to a decisive destabilisation of the structure (and the absence of any cluster); for a low formal valence of M, whereupon a large number of the valence electrons of the M atoms are involved in the M–L bonds and whereupon a seemingly optimum number of electrons remains available for the formation of the M–M bonds, the possibility of the formation of such bonds and of the M_n cluster is sharply limited (owing to the large number of bonds of each M atom with the ligands) by purely steric factors.

The results of calculations of the molecular orbitals of both the M_n groups[2,28–30] and the M_nX_m cluster groups as a whole[2,3,11] indicate, firstly, the criteria of the stability of one or several forms of chloride clusters for a given formal valence of a specific *d* element. These results show that both dinuclear and trinuclear but not hexanuclear chloride clusters should be stable for Tc and Re; the dinuclear cluster should be relatively unstable for Nb and Ta and octahedral clusters should be most characteristic; almost all the known forms of cluster groups should be stable for Mo and W in different oxidation states (2–4). The above approach possesses predictive power in relation to almost all *d* elements.

Secondly, these results explain the stability of the integral oxidation states of some *d* elements ($MoCl$–Mo_6Cl_{12}, WCl_3–W_6Cl_{18}, $ReCl_3$–Re_3Cl_9, etc.) and the non-integral oxidation states of others ($NbCl_{2.33}$–Nb_6Cl_{14}, $NbCl_{2.67}$–Nb_3Cl_8, $TaCl_{2.50}$–Ta_6Cl_{15}, etc.), i.e. the causes of the non-stoichiometry of their lowest chlorides; in the presence of six (Mo, W) or seven (Tc, Re) valence electrons in the M atom, the maximum stability of particular chloride clusters is attained for an integral electronic configuration of the M atom (d^2, d^3), i.e. for an integral formal valence of the metal M characterising the number of its valence electrons in the bonds with the ligands. When five (Nb, Ta) valence electrons are present in the M atom, the cluster groups with a non-integral (between d^2 and d^3) electronic configuration of the M atoms are mainly stable, which accounts for their fractional formal valence in the corresponding non-stoichiometric chlorides.

Thirdly, the results of calculations reveal and explain the unique ability of the heavy Group VI *d* elements to produce the greatest number of stable clusters among almost all the known forms. It was found that all the oxidation states (2, 3, and 4) potentially suitable for cluster formation are thermodynamically stable for molybdenum and tungsten, because in these oxidation states the Mo and W atoms have the electronic configurations (d^4, d^3, d^2), which are most suitable in the sense that the number of valence *d* electrons in each M atom capable of participation in the M–M bonds ensures the stability of at least one or even several different forms of clusters by populating only the bonding (but not antibonding) M–M molecular orbitals.

These results made it possible to establish a distinct relationship between the stable form of the chloride cluster (and its stability in general), the formal valence of the transition metal, and its position in the Periodic System, and, finally, to explain why chloride clusters are stable in the main only for the heavy Group V, VI, and VII transition elements (Nb, Ta, Mo, W, Tc, Re) and are as a rule unstable for the Group III, IV, and VIII elements (La, Hf, Os, Ar, Pd, and their analogues).[3,4]

The characteristics of the electronic structure of the carbonyl clusters revealed by the calculation show that each M atom supplies (regardless of the stereochemistry of the cluster and its component mononuclear fragments) exactly six valence electrons for the formation of the necessary (for the existence of the carbonyl cluster) dative M–CO π-bonds. The molecular orbitals (bonding in relation to the dative M–CO π-interactions) occupied by these electrons are at the same time both bonding and antibonding in relation to the M–M π-interactions. The valence electrons of the M atoms involved in the dative M–CO π-bonds are therefore as a whole "frozen" in the M–L bonds and do not participate in M–M bonds. This is precisely the reason why the carbonyl clusters are stable only for those transition metals in the atoms of which the number of valence electrons is greater than six (i.e. at least seven). Only then do the σ-bonding M–M molecular orbitals which have higher energies and are responsible for the formation of the M–M bonds in the carbonyl clusters, become populated with electrons. This accounts for the known fact that the cluster carbonyls are formed mainly only by Group VII (Mn, Tc, Re) and particularly VIII (Fe, Co, Ru, Rh, Os, Ir) transition metals and are unstable for the metals in the first half of the transition series.[10]

It is of interest that hitherto no clusters have been found where each M atom would supply exactly six of its valence electrons for the formation of the M–M bond. On the one hand, these can be caused by the special stability of the spin-paired d^6 electronic configuration[31–33] and, on the other hand, it follows directly from the considerations described above: six electrons are too many for the formation of an energetically stable cluster with π-donor ligands (Cl) but are too few to ensure the occupation of the σ-bonding M–M molecular orbitals in the cluster with π-acceptor ligands (CO) and hence to impart energy stability to the latter.

III. DISTRIBUTION OF CLUSTERS IN THE PERIODIC SYSTEM

The isolated nature of the M–M and M–L interactions in the chloride clusters and, in contrast, the strong mutual influence of these interactions in the carbonyl clusters permit the conclusion that the main features of the clusters with π-donor ligands should be almost independent of the individual characteristics of ligands of this type and should remain almost unchanged on passing from one π-donor ligand to another. On the other hand, clusters with π-acceptor

ligands should be extremely sensitive to the individual characteristics of ligands of this type and their structure should change significantly on replacing one π-acceptor ligand by another.[4]

The available experimental facts confirm these ideas or at least do not conflict with them.[31-42] Indeed clusters with many different π-donor ligands have properties which are similar in broad outline (the replacement of these ligands does not influence greatly the structure and stability of the cluster) although there are no sufficient grounds for a fully unified approach to these clusters. On the other hand, the replacement of π-acceptor ligands leads to significant changes in the structure and stability of the clusters; one of the causes of this is probably that the π-acceptor ligands ensure to some extent the delocalisation of the valence electrons of the M atoms on formation of the dative M–L π-bonds as a function of the individual properties. Thus, in contrast to Tc, Re, Ru, Rh, Os, and Ir, "pure" carbonyl clusters are unknown for Pd and Pt, whose atoms have the maximum number (ten) of valence electrons, but instead either the molecular dinuclear cations of the type $[Pd_2(CO)_2]^{q+}$, with a reduced (owing to the ionisation of the complex) effective number of valence electrons in the M atoms[44] or the dinuclear compounds $Pd_2(PPh_3)_4(NO)_2$ and $Pt_2(PPh_3)_4(NO)_2$, where the ligands are NO molecules with π-acceptor properties even more pronounced than those of the CO groups, are stable.[44] New features in the electronic structure of M–M bonds can be observed in cluster groups with PR_3 ligands: $Ru_2(\mu\text{-}PPh_2)_2.(NO)_2$, $Rh(PPh_3)_4(CO)_2$, $Rh_2Cl_2(PF_3)_4$, $Ir_2Cl_2(PF_3)_4$, $Rh_2(PF_3)_8$, $Ir_2(PF_3)_8$, etc. Such compounds are known hitherto only for some of the elements of the platinum group.[45-50]

Thus the main conclusion which follows from the results of the study of the electronic structure of the clusters of *d* elements can be formulated thus: the M–M interactions in the clusters are determined not only by the nature of the *d* element but also depend significantly on the nature of the ligands, because the electronic structure of different M–L bonds has by no means the same influence on the electronic structure of the M–M bonds. In clusters with ligands of the first type fundamental differences are observed in the stereochemistry, energy, and multiplicity of the M–M bonds, in the stability of the clusters as a function of the position of the transition metal in the Periodic System, etc. However, one should note that, together with the natural similarity of the properties of the isoelectronic clusters within the limits of any one variety (for example, the 40-electron $MO_6Cl_8^{4+}$ and $Nb_6Cl_{12}^{2+}$ clusters or the 8-electron MO_2 cluster from $Mo_2Cl_8^{4-}$ and the Re_2 cluster from $Re_2Cl_8^{2-}$), there is evidence[4] indicating definite signs of similarity in the properties of isoelectronic clusters belonging to different categories [for example, the 72-electron $Mo_2Cl_8^{4-}$ and $Mo_2(O_2CR)_4$ clusters, the 108-electron $Re_2Cl_{12}^{3-}$ and $Ru_3O_{12}^{2-}$ clusters, or the 18-electron W_6 cluster from W_6Cl_{18} and the Rh_6 cluster from $Rh_6(CO)_{16}$]. This must be taken into account to avoid overestimating the differences between the structures of the chloride, carbonyl oxygen, carboxylate, and other clusters of 4*d* and 5*d* elements.

The mutual influence of the metal atoms and the ligands in the clusters is manifested mainly by the fact that a specific region in which the cluster structures of the *d* elements occur in the Periodic System is characteristic of each ligand. The discussion of the influence of the ligands on the character of the M–M interactions in the transition metal clusters and hence on the structure and properties of the clusters is on the whole treated in the present review in the nature of a survey, because the Cl atoms constitute a prototype of a whole series of comparatively weak π-donor ligands, while CO molecules serve as a prototype of a series of active π-acceptor ligands; this general approach helps in securing an answer to the main question: with which transition metals and with what ligands can stable cluster structures be formed?

Ligands of the π-donor type should promote the occurrence of cluster structures in compounds of heavy (4*d*, 5*d*) transition elements only in the first halves of the series for low oxidation states of the metal, whereupon the valence electrons of the M atoms not involved in bonds with the ligands can form strong M–M σ-, π-, and even δ-bonds. The formation of cluster structures in yttrium, lanthanum, zirconium, and hafnium compounds is most difficult because of the small number of valence electrons in their atoms. Cluster structures of π-donor ligands cannot arise in formally low-valence compounds of the remaining 4*d* and 5*d* elements owing to the critically large number of valence electrons in their atoms, which leads to an excess of electrons in the M–M bonds, as a result of which the antibonding M–M orbitals are effectively populated and the bonds between the metal atoms vanish.

Ligands of the π-acceptor type should promote the appearance of cluster structures in compounds of all (3*d*, 4*d*, 5*d*) transition elements only in the second halves of the series, whose atoms have a sufficient number of valence electrons also for the formation of the dative M–L π-bonds necessary to ensure the stability of the compounds and for the formation of M–M bonds. The appearance of cluster structures is most difficult in compounds of the elements of the copper subgroup and especially zinc owing to the supersaturation of their atoms by valence electrons. Cluster structures with π-acceptor ligands cannot appear in compounds of the *d* elements at the beginning of the transition series in connection with the small number of valence electrons in their atoms, which is frequently insufficient even for the formation of strong M–L bonds in the mononuclear complexes. Thus the limits of the stability of the transition metal cluster compounds in the Periodic System can be represented schematically as follows:

Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn
Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd
La	Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg

π-donor ligands | π-acceptor ligands

An analogous concept concerning the formation and structure of transition metal cluster complexes has been developed within the framework of the ligand field theory.[10]

Thus despite the fact that a detailed explanation of the similarity and differences between all the characteristics of clusters with ligands of different types is so far impossible, one can already achieve a reliable and simple interpretation of the fundamental features of the cluster theory—the question of the stability of clusters as a function of the nature of ligands and also the electronic state of the transition metal atoms and the position of the transition metal in the Periodic System, i.e. the nature of the *d* element.

IV. THE INFLUENCE OF THE TYPE OF LIGANDS ON THE STRUCTURE OF CLUSTERS

The influence of the nature of ligands on the properties of cluster compounds is manifested not only by the fact that the type of ligands (more precisely the character of the M–L bonds) determines in many respects the electronic structure of the M–M bonds and that a specific region of the occurrence of clusters in the Periodic System is characteristic of each type of ligand, but also by the fact that the key properties of some (for example, chloride) clusters are associated with

their "metallic nucleus" (the M_n group), while the properties of others (carboxylate, carbonyl, and oxygen clusters) are in many respects determined by the ligand environment.

Furthermore the character of the interaction of the clusters in crystals of different transition metal compounds is likewise determined in many respects by the nature of the ligands. The clusters differ appreciably in their capacity to enter or not enter into the intercluster interaction: some of these (chloride and related systems) usually remain crystal-chemically isolated in the form of "island complexes", while others (oxygen and similar groups) are involved as a rule in strong intercluster interactions and because of this all the cluster fragments throughout the crystal are drawn together into a kind of "supercluster". This influences the properties of cluster compounds and in the first place structure-sensitive properties such as the X-ray electronic and emission spectra, the chemical shifts of the lines due to the metal in such spectra, the optical electronic and vibrational infrared and Raman spectra, the magnetic properties of the crystal, its conductivity, etc.

1. Non-bridged Dinuclear Chloride Clusters

One of the most striking manifestations of the "non-interference" of the ligand environment in the formation of the electronic structure of the M–M bond is provided by the non-bridged dinuclear M_2L_8 clusters with D_{4h} symmetry (Fig. 2). Such clusters are formed by Group VI and VII 4*d* and 5*d* elements (Mo, W, Tc, Re) with participation of ligands of the type Cl^-, Br^-, I^-, SCN^-, etc.

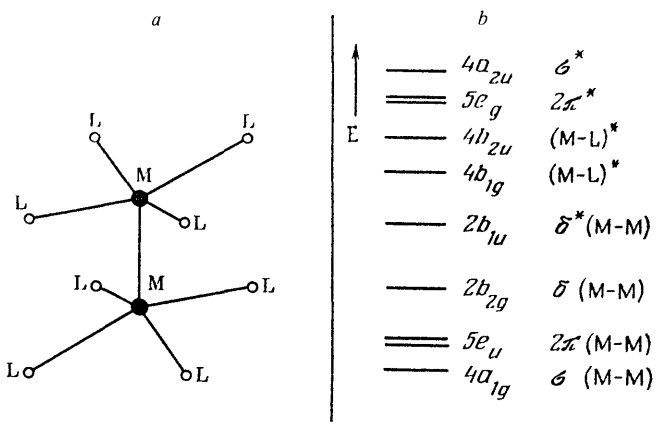


Figure 2. The molecular structure (*a*) and the one-electron energy diagram (*b*) of the highest occupied and lowest unoccupied molecular orbitals of the dinuclear M_2L_8 clusters with D_{4h} symmetry.[17]

The chloride clusters M_2Cl_8 have been most thoroughly investigated.[1,12,14,15,17,30,51–54] The unusual stereochemistry of the M_2Cl_8 clusters (the especially short M–M distance and the eclipsed orientation of the MCl_4 fragments linked to one another directly via an M–M bond without any bridging ligands), their extremely high thermodynamic stability, the specificity of the ligand substitution processes and oxidation-reduction processes, as well as many other properties—all these are factors which are undoubtedly directly related to the characteristics of the electronic structure of the multiple M–M bonds and can be accounted for at the electronic level by the formation of the quadrupole ($\sigma + 2\pi + \delta$) M–M bond.

Thus the two-centre M–M bonds with the maximum possible multiplicity (4) and the highest energy known hitherto among cluster compounds exist in the M_2Cl_8 clusters. Eight valence *d* electrons (four electrons from each M atom) are effectively involved in this strong bond and one (δ) component of this bond limits the mutual rotation of the two MCl_4 fragments about the line of the M–M bonds, i.e. about the rotational fourfold axis of the cluster, promoting thereby a significantly eclipsed (D_{4h}) but not crossed (D_{4d}) conformation of the dinuclear group. Precisely because the energy of the M–M δ-bond is sufficiently high, the M_2Cl_8 (D_{4h}) cluster is not converted into the D_{4d} form where the endo-effect of the interligand repulsion would have been sharply reduced but the M–M δ-bond would have been absent. The barrier to the internal rotation of M_2Cl_8, calculated as the difference between the total energies of the cluster for the eclipsed (D_{4h}) and crossed (D_{4d}) conformations, is close to the energy of the M–M δ-bond[12,30,54] and this result shows yet again that the unusual (D_{4h}) conformation of the M_2Cl_8 cluster arises due to the strong M–M δ-bond without which the observed D_{4h} form of the non-bridged chloride clusters would have been energetically unstable.

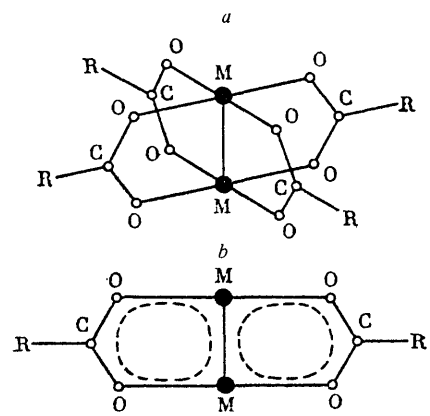


Figure 3. The molecular structure of the dinuclear $M_2(O_2CR)_4$ carboxylate clusters with D_{4h} symmetry (*a*) and the system of delocalised M–M and M–L π-bonds (*b*).[59]

2. Dinuclear Carboxylate Complexes

In contrast to the non-bridged chloride clusters M_2Cl_8, where the electronic structure of the M–M bond plays the main role, the dinuclear carboxylate clusters (clusters with O_2CR ligands) constitute an example of the active involvement of the ligand environment in the formation of the cluster complex as a whole. The $M_2(O_2Cr)_4$ cluster groups, which are characteristic mainly of heavy Group VI, VII, and VIII *d* elements,[55–58] also have the D_{4h} symmetry (Fig. 3), but, in contrast to M_2Cl_8, where the M–L bonds are predominantly of the single σ-character without an appreciable π-contribution and where the involvement of the valence electrons of the ligands in the M–M molecular orbitals is small, in the $M_2(O_2CR)_4$ carboxylate clusters the π-interaction also makes

an appreciable contribution to the M–L bond and the multiplicity of the latter is greater than unity; furthermore, the molecular orbitals of the M–M and M–L bonds do not differ in this instance quite so markedly in their one-electron energies and the contributions of the valence *d* orbitals of the metal atoms.

Compared with M_2Cl_8, the role of the ligands in the formation of M–M bonds in $M_2(O_2CR)_4$ is appreciably enhanced, particularly as regards the M–M π_1- and π_2-interactions.[15,59] In the $M_2(O_2CR)_4$ cluster the energy of the M–L π-interaction which ensures its additional stabilisation, is optimum when the cluster has the D_{4h} symmetry. Indeed, for bidentate ligands such as the O_2CR groups, the D_{4h} form does in fact ensure the most favourable conditions for the formation of a single system of delocalised π-bonds in the $M_2(O_2CR)_4$ cluster with participation of both M atoms in the ligands. Such a system of delocalised π-bonds is illustrated schematically in Fig.3 for each half fragment of the $M_2(O_2CR)_4$ cluster; this scheme can probably be extended also to the M–M and M–L π-bonds. The results of quantum-chemical calculations, on the basis of which the above conclusions have been reached, do not conflict with the X-ray electronic spectra of $M_2(O_2CR)_4$.[59–61]

Thus, for monodentate ligands (M_2Cl_8 dinuclear chloride clusters), the stabilisation of the D_{4h} form of the cluster is impossible without the formation of the M–M δ-bond. On the other hand, the stability of the D_{4h} form of the $M_2(O_2CR)_4$ carboxylate clusters must be accounted for by the bidentate character of the O_2CR ligands and the above characteristics of M–M and M–L π- and possibly σ-bonds in these dinculear clusters rather than by the presence of an M–M δ-bond.

The fact that the D_{4h} M_2Cl_8 chloride clusters exist only for M atoms with a d^4 electronic configuration, i.e. when eight valence electrons participate effectively in the M–M bond and when this two-centre bond is in fact quadruple (all the bonding σ, 2π, and δ molecular orbitals of the M–M bond are occupied by electrons, while the corresponding antibonding MO are unoccupied) with a strong δ-component constitutes convincing evidence for the above explanation. Even for a slight deviation of the electronic configuration of the M atom from the d^4 configuration to one side or another, i.e. for any change in the number of electrons involved in the M–M bond, the D_{4h} M_2Cl_8 chloride clusters are not as a rule formed. In this situation the formation of the δ-component of the M–M bond is impossible owing to the absence of valence electrons in the bonding δ molecular orbital of the M–M bond (when the total number of electrons in the two-centre M–M bond is less than eight) or owing to the appearance of electrons in the antibonding δ^* molecular orbital (when the total number of electrons is greater than eight).

On the other hand, the $M_2(O_2CR)_4$ carboxylate clusters exist in the D_{4h} form not only for the d^4 electronic configuration of the M atoms, when a quadruple M–M bond with a strong δ-component is formed, but also for large deviations from these configurations—for d^5, d^6, and even d^7 M atoms when the δ-component of the M–M bond is absent and the two-centre M–M interaction is as a whole significantly weakened. Indeed, the electronic structure of the two-centre M–M bond in the $M_2(O_2CR)_4$ clusters is quite varied: ranging from a quadruple M–M bond with a high energy in the molybdenum and rhenium clusters to the M–M bond with a reduced energy and multiplicity in the ruthenium and rhodium clusters, where the effective numbers of electrons in the M–M bonds are much greater than eight (Table 2).

The increase of the M–M distance and the paramagnetism of the complexes $Ru_2(O_2CC_3H_7)_4Cl$ and $Rh_2(O_2CCH_3)_4.2H_2O$ show that the M–M bonds in the complexes are significantly weakened; they are apparently triple ($\sigma + 2\pi$) and not quadruple ($\sigma + 2\pi + \delta$) and do not include a δ-component, because the excess (above eight) valence electrons in $Ru(O_2CC_3H_7)_4^+$ (eleven electrons) and $Rh_2(O_2CCH_3)_4$ (fourteen electrons) populate only the antibonding M–M δ^*-molecular orbital, i.e. they prevent the appearance of the δ-component in the M–M bonds; the remaining excess electrons populate the antibonding MO of the M–L bonds (Fig.2). The M–M antibonding $2\pi^*$ and σ^* MO still remain unoccupied under these conditions; this preserves the M–M triple ($\sigma + 2\pi$) bond in the cluster, which is apparently characteristic of $Ru_2(O_2CR)_4^+$ and $Rh_2(O_2CR)_4$.

Table 2. Electronic structure parameters of M–M bonds in the $M_2(O_2CR)_4$ clusters.

Parameter	Cluster			
	$Mo_2(O_2CR)_4$	$Re_2(O_2CR)_4^{2+}$	$Ru_2(O_2CR)_4^+$	$Rh_2(O_2CR)_4$
Electronic configuration of M atoms	d^4	d^4	d^5—d^6	d^7
M–M distance, Å	2.11	2.24	2.28	2.45
Multiplicity of M–M bond	$4(\sigma+2\pi+\delta)$	$4(\sigma+2\pi+\delta)$	$3(\sigma+2\pi)$	$3(\sigma+2\pi)$
No. of valence electrons in M–bond	8	8	11	14
References	[17, 59]	[17, 59]	[17, 59]	[17, 59]

A strong influence by the bidentate O_2CR ligands on the stereochemistry of the clusters is also manifested by the fact that the D_{4h} M_2Cl_8 chloride clusters are stable only for heavy (4*d*, 5*d*) elements, while the dinuclear D_{4h} $M_2(O_2CR)_4$ carboxylate groups are stable also in the case of light (3*d*) elements; an example of this is provided by the dimeric copper and chromium acetates.

3. The Conformational Transformations of Carbonyl Clusters

Transition metal chloride and carbonyl clusters have significantly different stereochemistries, particularly in the case of the heaviest (5*d*) transition elements: the differences consist in the fact that the ligands in the chloride clusters very often form bridge bonds with the M atoms, while in the carbonyl clusters all the ligands are always terminal.

One of the main stereochemical characteristics of the carbonyl clusters is their tendency towards the *trans*-disposition of the CO groups relative to the M–M bonds, i.e. approximately along the line of the two-centre M–M bonds. Owing to the absence of the π-component in the M–M bonds in the carbonyl clusters, such dispotion of the ligands is most favourable for the formation of strong dative M–CO π-bonds, i.e. for the maximum energy stabilisation of the carbonyl cluster as a whole.[21,22,62] In particular, such are the molecular and electronic structures of the $Ir_4(CO)_{12}$ tetrahedral carbonyl cluster with T_d symmetry[63,64] (Fig.4). However, steric factors prevent the ideal *trans*-disposition of the CO groups relative to the two-centre M–M bonds; these groups are "deflected" towards the centre of the Ir_4 tetrahedron and the C–Ir–Ir valence angle is 150°, i.e. much less than 180°. Such distortion of the molecular structure of the $Ir_4(CO)_{12}$ leads to some destabilisation of the dative Ir–CO π-bonds.

In the isoelectronic tetranuclear $Co_4(CO)_{12}$ carbonyl cluster the M–CO bonds are much shorter[40] and the steric limitations under discussion therefore increase so sharply that $Co_4(CO)_{12}$ with a tetrahedral structure becomes energetically unstable:

the CO groups in the tetrahedral $Co_4(CO)_{12}$ would have been too remote from the *trans*-disposition relative to the two-centre M–M bonds, for which the formation of strong dative M–CO π-bonds is possible. It is therefore likely that $Co_4(CO)_{12}$ has a conformation different from that of $Ir_4(CO)_{12}$ and in the energetically stable state assumes the C_{3v} molecular structure, where three out of the twelve ligands are of the bridging type (Fig.4).

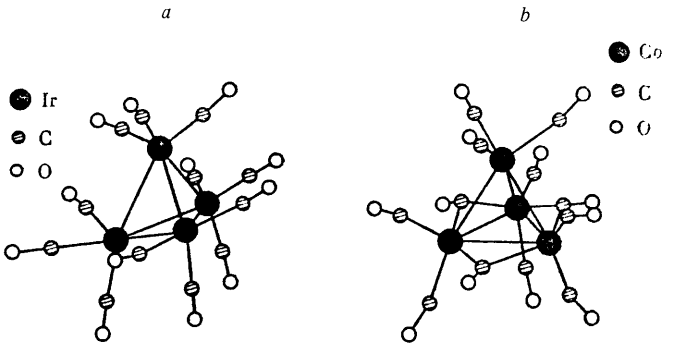


Figure 4. The molecular structure of tetranuclear carbonyl clusters: *a*) $Ir_4(CO)_{12}$ (T_d); *b*) $Co_4(CO)_{12}$ (C_{3v}).[62]

An analogous phenomenon for $Ir_4(CO)_{12}$ is hardly feasible. The appearance of bridging CO groups in the molecular structure of any carbonyl clusters requires that the M–M and M–CO bond lengths must meet severe requirements, rigorously specified by the extent and angular distribution of the virtual (unoccupied by electrons in free CO molecules) $2\pi^*$ MO of the CO groups, the only ones which can give rise to dative M–CO π-bonds necessary for the existence of the carbonyl cluster. Indeed in all the carbonyl compounds with bridging CO groups without exception, the M–C–M valence angle lies within very narrow limits (80–87°).[65] Clearly, on passing from atoms of 3*d* elements (Co) to those of 5*d* elements (Ir), which are characterised by a much greater extent of the valence orbitals, the necessity for the preservation of the angular distribution characteristic of the bridging M–C–M group would lead to such a marked deviation of the M–CO bond lengths from their normal values in the carbonyl cluster of a 5*d* element with bridging ligands that sufficiently strong M–CO bonds (primarily σ-bonds) could hardly exist at all.

However, on the whole, the bridging CO groups as a rule stabilise the carbonyl cluster and the only limitation is the "rigidity" of the valence electronic structure of the CO group. This is precisely the reason why carbonyl clusters with bridging ligands are formed mainly by 3*d* elements, while 5*d* elements produce carbonyl clusters solely with terminal ligands [$Os_3(CO)_{12}$, $Ir_2(CO)_8$, $Ir_4(CO)_{12}$, etc.[40]]. The clusters of 3*d* elements [$Fe_3(CO)_{12}$, $Co_2(CO)_8$, $Co_4(CO)_{12}$, etc.] can exist both in the form with bridging ligands (this is most characteristic of such clusters) and in the form incorporating only terminal ligands. In this sense the conformational transformations of carbonyl clusters constitute an entirely realistic physical process. The appearance of a carbonyl cluster of a 3*d* element in the form without a bridging ligand requires special conditions (high temperature, molecular solutions) ensuring the energy activation necessary for such a conformational transformation.[65]

The carbonyl clusters of 4*d* elements occupy a intermediate position in this respect: in some cases they incorporate bridging CO groups [$Rh_4(CO)_{12}$], while in others all the ligands are terminal [$Ru_3(CO)_{12}$, $Rh_2(CO)_8$].

The inability of the 5*d* elements to form carbonyl clusters with bridging CO groups has an important consequence: the 3*d* and 4*d* elements in a particular Group in the Periodic System form carbonyl clusters of a kind which are absent for the heaviest (5*d*) transition metals. As an example, we may point to the stability of $Fe_2(CO)_9$, $Co_6(CO)_{16}$, $Rh_6(CO)_{16}$ and the absence of analogous derivatives of osmium and iridium.[40,42]

The causes of the preferential existence of the chloride clusters of 5*d* elements in a form involving bridging ligands and the absence of bridging ligands from molecular structures of the carbonyl clusters of these *d* elements have been discussed in detail[66] on the basis of the results of calculations for one-electron molecular orbitals of the trinuclear $Re_3Cl_{12}^{3-}$ and $Os_3(CO)_{12}$ groups.

Thus the absence of M–M π-bonds and, what is most important, the angular distribution of the valence $2\pi^*$ MO of the CO groups forming the dative M–CO π-bonds explain the conformational transformations of the carbonyl clusters of 3*d* elements, their existence in the form of molecular structures with bridging ligands, and the absence of similar phenomena in the chemistry of the cluster carbonyls of 5*d* elements.[21,62]

4. Oxygen-containing Cluster Compounds of 4*d* and 5*d* Elements and Their Characteristic Features; Intercluster Interactions

The influence of the ligand environment on the structure of the clusters and on the electronic structure of their M–M bonds is manifested particularly strikingly in the case of the cluster oxides. Distinctive clusters with oxygen atoms as ligands have been discovered so far for a comparatively small number of transition metal oxides: $La_4Re_6O_{19}$ (Re_2 groups), $Au_2^{II}Mo_3O_8$, and $A_2^{II}W_3O_8$ (where A^{II} = Mg, Mn, Fe, Co, Ni, Zn, or Cd) (Mo_3 and W_3 groups), $Ba_3Ru_3O_9$ (Ru_3 group), and certain others.[25,40,67–81] The oxygen clusters are formed only by 4*d* and 5*d* elements (clearly identified oxygen clusters of 3*d* elements have not so far been discovered) and in addition by elements in the middle of the transition series only.

We may note that in the crystal structures of the dioxides strong M–M bonds exist only for the 4*d* and 5*d* elements precisely in Groups VI and VII of the Periodic System (MoO_2, WO_2, TcO_2, and ReO_2, where the M–M bonds are probably double). On the other hand, in the dioxides NbO_2 and TaO_2 these bonds are greatly weakened and in the platinum group metal dioxides (RuO_2, OsO_2, etc.) the M–M bonds are most probably absent; the M–M bonds are known *a priori* to be absent from ZrO_2 and HfO_2, because of the highest oxidation state of the metal. The transition to 3*d* elements is accompanied by a sharp decrease of the strength of the M–M bonds and their disappearance (VO_2, CrO_2, MnO_2, CoO_2, etc.).

In the oxygen clusters (as well as chloride clusters) the M–M bonds arise with the preferential involvement of the valence *d* electrons of the M atoms and can be both single and multiple (in particular, double). However, in contrast to the chloride clusters, in the chloride clusters the M–L bonds have a multiplicity greater than unity (with a considerable π-contribution) and the M–M and M–L interactions are not isolated; on the other hand, the inter-relation between the M–M and M–L interactions (the mixing of the molecular orbitals of these bonds with respect to energies and the

contribution of the M and L atomic orbitals) constitute a permanent element in the structure of any oxygen cluster. The M–M bonds in such clusters (particularly the π-components) are formed with participation of the bridging oxygen atom; the decisive role of the bridging oxygen atoms in the formation of a system of delocalised π-bonds between the metal atoms is apparently the cause of the absence of non-bridged oxygen clusters. In an oxygen cluster the bridging ligands promote the delocalisation of the valence electrons of the M atoms over the M–M bonds of the π-type; the mixing of the molecular orbitals of the M–M and M–O bonds takes place owing to the transfer of electron density from the bridging oxygen atoms, which behave as π-donors (this effect is characteristic of polynuclear oxygen complexes, without it, such complexes apparently could not exist).

All these distinctive features of the electronic structures of oxygen clusters can be traced quite reliably (both experimentally and theoretically), in particular in the trinuclear $Mo_3O_{13}^{14-}$ and $Ru_3O_{12}^{12-}$ groups.[67,79,80] A specific feature of the M–M and M–O π-interactions in the oxygen clusters, noted above, explains an unexpected characteristic of the electronic structure of the $Ru_3O_{12}^{12-}$ (Fig.5), namely that the M–M π-bonds in the linear Ru_3 group (with Ru–Ru double bonds) are formed not only between neighbouring metal atoms [Ru(1)–Ru(2), (Ru(2)–Ru(3)] but also directly between the terminal metal atoms [Ru(1)–Ru(3)], separated from one another by "bridging" M atoms [Ru(2)]. On the other hand, both M–M σ-bonds are to a marked extent localised in the two-centre Ru(1)–Ru(2) and Ru(2)–Ru(3) fragments.

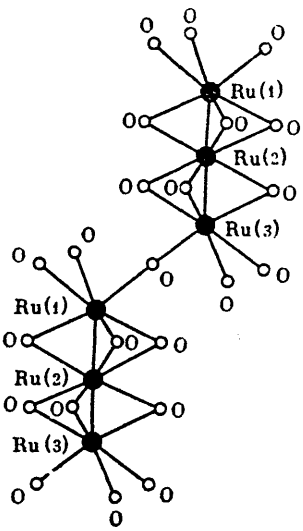


Figure 5. The $Ru_3O_{12}^{12-}$ (or $Ru_3O_6O_{6/2}^{6-}$) fragments of the crystal structure of barium ruthenite $Ba_3Ru_3O_9$.[78]

The results of the analysis of the magnetic properties of the $Ba_3Ru_3O_9$ crystal and of the characteristic features of the exchange interaction in the isolated $Ru_3O_{12}^{12-}$ cluster, carried out[79] within the framework of the Heisenberg–Dirac–Van Vleck model (which makes it possible to investigate the magnetism of cluster paramagnetic compounds), are fully consistent with the presence of two unpaired electrons in the MO of $Ru_3O_{12}^{2-}$ and with the strong electronic interaction of the terminal metal atoms in the linear Ru_3 cluster. The terminal atoms in the Ru_3 trimer are only formally geometrically isolated from one another. Apparently the M atoms in the cluster tend to equalise their states, not only by forming groups in which the M atoms are known to be equivalent (for example triangular Mo_3 clusters, as in $Mo_3O_{13}^{14-}$) but also by forming bonds between M atoms "not in contact" and which are in addition separated by the "third" M atom. In the linear Ru_3 cluster all three M atoms are probably in similar electronic states, which in no way follows *a priori* from its steterochemistry. [On the contrary, the non-equivalence of the electronic states of the middle Ru(2) atom, on the one hand, and the terminal Ru(1) and Ru(3) atoms, on the other, should seemingly follow from the geometry of the linear Ru_3 cluster.]

In cluster oxides the ligand environment not only determines in many respects the electronic structure of the M–M bonds but (and this is particularly important) is responsible for the strong intercluster interaction in the crystal structure. The bridging oxygen atoms, each linking two M atoms in different "neighbouring" clusters, ensure (also as a result of the formation of π-donor bonds with each M atom of this kind) the appearance of a single system of delocalised M–M and M–O π-bonds with the simultaneous participation of all the clusters (i.e. ensures the delocalisation of the valence π-electron density of the M atoms over all the clusters at once). Such strong intercluster interaction (Fig.5) is distinctly reflected in almost all the properties of the corresponding crystal and in the first place is manifested by a high conductivity ($Ba_3Ru_3O_9$, for example, exhibits metallic conductivity[78]). In contrast to this, in the cluster chlorides (which are dielectrics) such delocalisation of the valence electron density of the M atoms is negligible and in this sense one may speak of the absence of an appreciable intercluster interaction in their crystal structures.

V. THE EFFECTS OF CLUSTER FORMATION

The formation of cluster groups in crystalline structures of transition metal compounds naturally makes its own impression to a greater or lesser extent on all the physical characteristics of these compounds and this distinguishes them from the corresponding mononuclear complexes. Evidently the first in these series of properties should be the specific characteristics of the crystal structures of the cluster compounds which are revealed in X-ray diffraction studies, showing that groups of several (two or more) M atoms in direct contact, which are more or less isolated from one another, exist in the crystal;[31–40] the M–M internuclear distances within the limits of such groups are close to the values for the corresponding metallic crystal or even much smaller. The distances between the M atoms in different (neighbouring) clusters are as a rule much greater.

This factor by itself indicates the formation of M–M bonds in the cluster crystal together with the usual M–L bonds. The formation of M–M bonds has been confirmed by the magnetic properties of cluster compounds (or at least the latter do not conflict with their formation):[31–40] in the vast majority of cases the effective magnetic moments of cluster compounds are greatly reduced (down to the diamagnetic level) compared with the values expected on the basis of the formal valence of the M atom. Here we have in mind the following situation. In a cluster compound the M atoms always have a low formal valence (this is a permanent condition for cluster formation) and therefore several valence electrons (d^m), not involved in bonding to the ligands and responsible for the very high paramagnetism, should therefore remain in

each M atom. However, owing to the pairing of the spins of the valence electrons of the M atoms in the M–M bonds, the experimental effective magnetic moment of cluster compounds is always much less than the value expected for the d^m configuration and not only in terms of the approximation of the spin only values but also when account is taken of effects such as spin–orbital coupling, antiferromagnetism, etc.[27,34]

The formation of clusters with strong M–M bonds makes an important additional contribution, additional to that of the M–L bonds, to the total energy of the crystal structure. The energy effects of cluster formation (the M–M bond energies) in the chlorides and oxides of heavy *d* elements and in the carbonyls and certain other compounds of transition metals have been estimated from the enthalpies of formation of these compounds,[4,23,24,34,79,82–84] by semi-empirical calculation of the molecular orbitals of the corresponding isolated clusters,[2–4,12,21,23,51,79,84] and even by direct mass-spectrometric measurement of the energies of dissociation of clusters into mononuclear fragments.[85]

Both experimental and theoretical results have shown that the M–M interaction energies in the cluster chlorides and oxides with heavy *d* elements (calculated per electron involved in such interactions) are usually in the range 25–35 kcal, i.e. the structure is fairly stable despite the fact that these compounds include clusters of different *d* elements, with different formal valences of the M atoms, and with extremely different stereochemistries. This range is in fact most characteristic of the M–M interaction energies in the metallic crystals of 4*d* and 5*d* elements; the latter factor indicates that the formation of an M–M bond in clusters is one of the principal energy factors ensuring the compensation of the endothermic effect of the breakdown of the structure (i.e. the compensation of the enthalpy of atomisation) of the crystal of the transition metal on formation of its formally low-valence chlorides and oxides. At the same time, the stability indicated by the E_{M-M} values does not rule out the formation (particularly in chloride clusters—Table 3) of two-centre M–M bonds with different energies up to very high values, depending on the number of electrons in these bonds and hence on the M–M distances.

Table 3. Parameters of the two-centre M–M bonds in the chloride and carbonyl clusters.

Cluster	R_{M-M}, Å	n_{M-M}	E_{M-M}, kcal	k_{M-M}, mdyn Å^{-1}	Refs.
$Re_2Cl_8^{2-}$	2.24	8	270	4.2	[6]
$Mo_2Cl_8^{4-}$	2.14	8	297	3.4	[6, 53]
$W_2Cl_9^{3-}$	2.41	6	155	1.2	[26]
$W_6Cl_8^{4+}$	2.61	2	59	0.3	[26]
$Mo_6Cl_8^{4+}$	2.61	2	44	0.3	[26]
$Nb_6Cl_{12}^{2+}$	2.92	1.3	34	0.3	[2]
$Ta_6Cl_{12}^{3+}$	2.93	1.2	33	0.3	[2]
$Mn_2(CO)_{10}$	2.92	2	17	0.6	[22]
$Tc_2(CO)_{10}$	3.04	2	31	0.7	[22]
$Re_2(CO)_{10}$	3.02	2	38	0.8	[22]
$Os_3(CO)_{12}$	2.88	2	28	0.9	[66]
$Ir_4(CO)_{12}$	2.68	2	31	1.2	[64]

Notation: R_{M-M} is the M–M distance, n_{M-M} the number of valence electrons per two-centre M–M bond, E_{M-M} the energy of this bond, and k_{M-M} the force constant of the M–M stretching vibrations.

In the carbonyl clusters of 4*d* and 5*d* elements the M–M interaction energies (also calculated per electron) are lower by a factor of approximately 1.5–2.[4,20,85] The cause of this is that in the electronic structure of a carbonyl cluster the bonding σ MO responsible for the M–M bonds have an enhanced energy, because these MO are at the same time antibonding in relation to the M–*trans*-CO σ-interactions and in addition a large contribution to such orbitals comes not only from the $(n-1)d$ MO but also from the valence *np* orbitals, having an increased electron energy, of the M atoms. Furthermore, one should bear in mind that single (two-electron) two-centre M–M bonds of the σ-type are usually formed in carbonyl clusters (without an appreciable π-contribution), the bonds having comparatively large internuclear distances.

Thus the large contribution of the M–M bonds to the total energy of the cluster confirms the dominant role of the M–M interactions in the phenomenon of cluster formation (particularly in compounds of the formally low-valence chlorides and oxides of 4*d* and 5*d* elements) and the principal cause of the existence of clusters may be seen in the high M–M bond strength.

VI. SPECTROSCOPY OF CLUSTER COMPLEXES

The formationof clusters is manifested in EPR, NQR, Mössbauer, and magnetic circular dichroism spectra.[11,86–90] However, cluster formation is revealed most directly in optical, vibrational, X-ray emission, and X-ray electronic spectra; the last spectra yield the most direct information about the states of the valence electrons of the M atoms and ligands, about the valence of the M atoms, about the nature of the M–M bonds in the clusters, and about the electronic structure as a whole and also reveal the qualitative and quantitative characteristics of cluster compounds which are absent from mononuclear complexes; these appreciable differences between the properties of cluster and mononuclear compounds reflect the phenomenon of cluster formation.

1. Optical Electronic Spectra

The experimentally observed absorption maxima in the optical electronic spectra of cluster compounds mainly reflect the electronic transition from the occupied bonding MO of the M–M bonds to the corresponding unoccupied non-bonding or antibonding MO. These are "metal–metal" transitions, which are apparently characteristic of clusters in general, but have been most thoroughly investigated in the cluster chlorides of 4*d* and 5*d* elements.[11,26,27,51,92–103]

The generally accepted interpretation of the optical electronic spectra is based in this instance on the hypothesis that one-electron transitions involving the M–M MO, delocalised in the clusters between the M atoms and having a predominantly *d*-electron character, are mainly responsible for the absorption in the visible region of the spectra. Despite this assumption, the long-wavelength electronic transitions in the spectra of the compounds investigated reflect fairly accurately the electronic structure of the M–M bonds in the clusters: the number of bands, their positions in the spectrum, and their relative intensities agree with the number of MO of the M–M bonds, their energy sequence, their electron populations, and finally their symmetry, which makes it possible to distinguish (within the framework of the selection rules for the optical spectrum) the allowed and forbidden transitions.[26,51]

In contrast to the cluster compounds, the optical electronic absorption spectra of complexes without an M–M bond can be simply described in terms of *d*–*d* transitions significantly localised at each M atom; for this reason, the form of the spectrum constitutes an indication of the cluster or mononuclear nature of the complex.

2. Vibrational Spectra

In the study of cluster compounds by vibrational spectroscopic methods attention is naturally concentrated on the vibrations of the M–M bond, which can be regarded as characteristic for such bonds (apart from a small contribution by M–L bonds only). This characteristic nature of the vibrations consists in the fact that the optical absorption spectra of cluster compounds in the infrared range contain bands at frequencies in the range 100–400 cm^{-1}, frequencies closer to the lower limit being characteristic of clusters with comparatively weak (single) M–M bonds, while frequencies characteristic of clusters with very strong (quadruple) M–M bonds lie near the upper limit of the above range.

The results of studies on cluster transition metal chlorides, oxides, and carbonyls by infrared and Raman spectroscopic methods,[11,79,103–121] namely the ν(M–M) frequencies and k_{M-M} force constants for the two-centre M–M bonds, yield information about the strength of these bonds. The available data (presented in part in Table 3) make it possible to compare the force constants (or frequencies) of the stretching vibrations, the effective numbers of electrons, the energies, and the internuclear distances for the two-centre M–M bonds in clusters. The correlations between these characteristics are unambiguous and usually reveal a parallel variation of $k_{M-M}[\nu(M-M)]$, n_{M-M}, and E_{M-M}, in particular their increase as the M–M distances are shortened.

The situation is more complex in cluster oxides in the presence of strong intercluster interactions. Whereas in the infrared spectra of $Mg_2Mo_3O_8$ and $Zn_2Mo_3O_8$, where the internuclear interaction is comparatively weak, the stretching vibration frequencies of the Mo–Mo bonds in the trinuclear Mo_3 clusters are manifested (at approximately 200 cm^{-1}),[79] in the infrared spectra of $Ba_3Ru_3O_9$, MoO_2, WO_2 and RuO_2 with strong (double) M–M bonds, there is virtually no absorption in the frequency range 100–1700 cm^{-1}, i.e. the M–M stretching vibrations are not shown.[79] This can be accounted for by the specific features of the $Ba_3Ru_3O_9$, MoO_3, WO_2, and RuO_2 structures expressed by the fact that these compounds have, instead of an island structure, a coordination structure, which ensures their metallic conductivity[121] and precludes the manifestation in the spectrum of vibrations localised in the quasi-molecular fragments.

3. X-Ray Emission Spectra

The cluster chlorides and oxides with certain 4*d* elements, mainly Nb, Mo, and Ru,[4,79] have been most fully investigated by this method. The L_{β_2} and L_{γ_1} lines of the M atoms, which reflect the distribution of the valence 4*d* electrons of the M atoms, responsible for the formation of the M–M bonds, among the occupied MO of the clusters, have been used for the X-ray spectroscopic study of the valence electron structures of these M atoms. Fig.6 presents as an example the L_{β_2} spectrum of molybdenum in $Cs_3Mo_2Cl_8$. The X-ray spectra of cluster chlorides, which yield information about the energy sequence of the occupied MO of the cluster, the electron populations, the contributions to the MO by the valence 4*d* orbitals of the M atoms, etc., permit the following conclusions:

(1) The 4*d* orbitals of the M atoms make the main contribution to the M–M MO, which have the highest energies and lie above the MO of the M–Cl bonds, formed predominantly with the participation of the 5*p* orbitals of the M atoms, this implies that the M–M and M–L electronic interactions are in this instance truly isolated from one another to a large extent with respect to both the energies of the MO responsible for such interactions and the contributions of the valence atomic orbitals (AO).

(2) The 4*d* electrons of the M atoms participate mainly in the M–M bonds and to a much lesser extent in the M–Cl bonds; the M–M interactions, which are predominantly of the *d*-electron type, are largely localised within the limits of the M_n group of the "metallic nucleus" of the cluster.

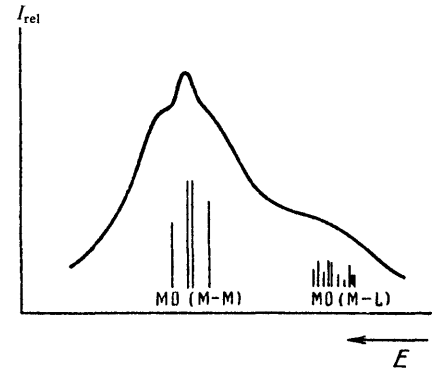


Figure 6. The X-ray emission L_{β_2} spectrum of molybdenum for $Cs_3Mo_2Cl_8$.[4]

At the same time the parameters $K_{\beta_{1,3}}$ of the line due to chlorine in the X-ray spectra of the same cluster chlorides show[4] that not all the valence 3*p* electrons of the Cl atoms are involved in the M–Cl bonds without conflicting with the idea that mainly M–Cl σ-bonds are formed with a low π-contribution to the metal–ligand interaction and that a large proportion of the $3p\pi$ electrons of the Cl atoms remain in a pseudoatomic state.

The X-ray spectra of cluster oxides have a somewhat different appearance. In the oxygen cluster the occupied MO are of a "mixed" character (they are simultaneously responsible for the M–M and M–O bonds) and the valence 4*d* orbitals of the M atoms make a considerable contribution to all these MO, including the MO of the M–L bonds. In the oxygen cluster the MO with a large contribution by the *d* AO of the metal therefore have a much greater energy range than in the chloride cluster, where the large (sometimes predominant) contribution of the *d* AO of the metal is present only in the highest-energy occupied MO, responsible almost exclusively for the M–M interactions, and not in the MO of the M–Cl bonds. The energy range including the MO of the chloride cluster with a large contribution by the valence *d* orbitals of the M atoms is much narrower.

All this ultimately explains why the X-ray spectra of the metal, reflecting the distribution of the valence *d* electrons of the M atoms among the molecular orbitals of the clusters (this applies particularly to the L_{β_2} spectrum of molybdenum), contain a wider band in the case of the cluster oxide (with a large involvement of the *d* electrons of the M atoms in the M–L bonds) than in the cluster chloride (with a small involvement of the *d* electrons of the M atoms in the M–L bonds) of the same transition metal.[79]

The study of the chemical shifts of the emission lines (*K*, *L*, etc.) of heavy *d* elements in the X-ray spectra of their various compounds yields important information. The results of

measurements of the chemical shifts of the K and L lines of Nb, Mo, and W in the X-ray emission spectra of numerous cluster and mononuclear compounds are available.[4,122-124] The chemical shifts ΔE have been measured for cluster compound–corresponding metal pair combinations. It has been found that the ΔE peaks for the metal increase linearly with increase of the formal valence of the M atoms for the chlorides in the structures of which there are no clusters and M–M bonds are known to be absent; Fig.7 presents as an example the values of ΔE(Nb) in the system of niobium chlorides. The linearity in the variation of the ΔE can be explained by the successive changes in the effective number of valence electrons of the M atoms not involved in bonding to ligands and localised in the pseudoatomic 4*d* or 5*d* states based on the M atom. The number of such electrons n is equal to the difference between the total number of valence electrons of the M atoms and their formal valence V_M, i.e. the number of their valence electrons in the M–Cl bonds. The observed linearity of the variation, implying proportionality of the changes in ΔE when the number of the unbound 4*d* or 5*d* electrons of the M atom is altered, corresponds to the overall physical nature of the effect of the chemical shifts of the X-ray lines.[125]

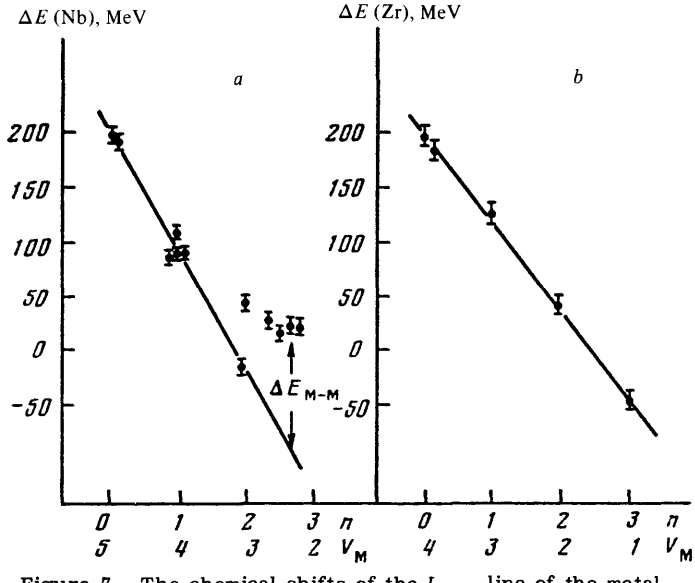


Figure 7. The chemical shifts of the $L_{\alpha_{1,2}}$ line of the metal (ΔE) in the X-ray spectra of niobium (*a*) and zirconium (*b*) chlorides as a function of the formal valence of the metal V_M and the number n of the valence electrons of the M atom not involved in the M–Cl bonds:[4,124] *a*: 1) $NbCl_5$; 2) $KNbCl_6$; 3) $NbCl_4$; 4) K_2NbCl_6; 5) Rb_2NbCl_6; 6) Cs_2NbCl_6; 7) $Cs_3Nb_2Cl_9$; 8) K_3NbCl_6; 9) Nb_3Cl_8; 10) $CsNb_4Cl_{11}$; 11) Nb_6Cl_{14}; 12) $K_4Nb_6Cl_{18}$; *b*: 1) $ZrCl_4$; 2) Na_2ZrCl_6; 3) $ZrCl_3$; 4) $ZrCl_2$; 5) ZrCl.

The chemical shifts of the lines in the X-ray spectrum of the metal for cluster compounds always deviate sharply from the linear relation characteristic of mononuclear compounds (Fig.7). These deviations reflect appreciable delocalisation of the valence 4*d* or 5*d* electrons of the M atoms not involved in bonds with the ligands, i.e. they reflect the effective electronic interactions between the metal atoms in the cluster chlorides. The "anomalous" values of ΔE thereby indicate directly the formation of M–M bonds in the chloride clusters. These deviations (ΔE_{M-M}) from the linear relations increase in proportion to the increase of the number of the valence electrons of the M atom which are not involved in the M–Cl bonds and are therefore fully available for involvement in the M–M interactions.

In the series of chlorides of the same heavy *d* element incorporating M atoms with the same formal valence, the deviations of ΔE from linearity, due to the M–M interactions in the clusters, increase in succession with increase in the number of electrons in the M–M bonds and also with decrease of the M–M distances and the accompanying decrease of the effective magnetic moments, i.e. as the M–M bonds become stronger. This can be traced particularly clearly in relation to the chlorides of the formally tervalent molybdenum (Fig.8), where the limiting M–M distance (approximately 3 Å), which is the beginning of the range of distances in the chlorides of 4*d* and 5*d* elements for which clusters with M–M bonds are virtually not formed, is very clearly shown.

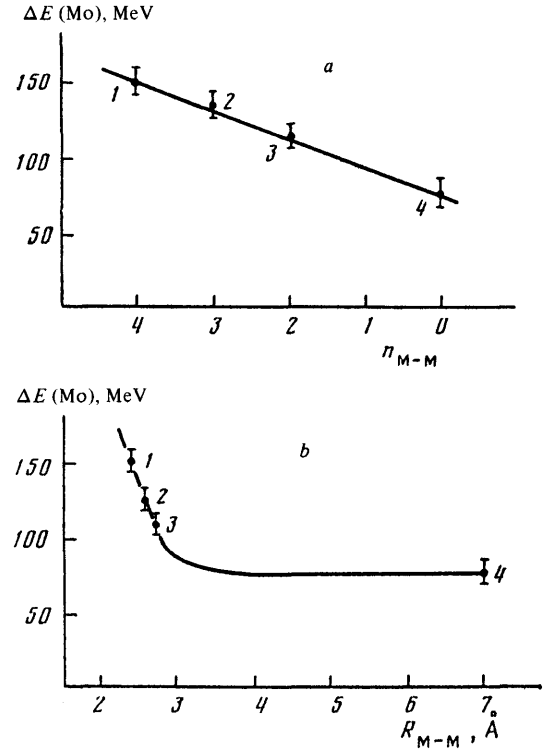


Figure 8. The chemical shifts of the $L_{\alpha_{1,2}}$ line of molybdenum ΔE in the X-ray spectra of the chlorides of the formally tervalent molybdenum as a function of the number n_{M-M} of the valence electrons of the M–M bonds (*a*) and the M–M distance R_{M-M} (*b*):[4,123] 1) $K_3Mo_2Cl_9$; 2) $Cs_3Mo_2Cl_9$; 3) $MoCl_3$; 4) K_3MoCl_6.

Study of the chemical shifts of the X-ray $L_{\alpha_{1,2}}$ line of molybdenum in the series of its formally low-valence chlorides with two-centre M–M interactions, i.e.

$$\underset{d^1}{Mo_2Cl_{10}}\,(MoCl_5) - \underset{d^2}{MoCl_4} - \underset{d^3}{MoCl_3} - \underset{d^3}{Cs_3Mo_2Cl_9} - \underset{d^3}{K_3Mo_2Cl_9} - \underset{d^3-d^4}{Cs_3Mo_2Cl_8} - \underset{d^4}{K_4Mo_2Cl_8}\ ,$$

has shown that, with increase of the number of 4*d* valence electrons of the Mo atom (d^m), not involved in bonds with the ligands, i.e. with decrease of the formal valence of the metal, the tendency towards M–M bond formation increases sharply: whereas in the Mo_2Cl_{10} (d^1) dimer direct M–M electronic interactions are completely absent, the Mo–Mo distances are 3.85 Å, and the chemical shift due to the involvement of the valence 4*d* electrons of the Mo atoms in the Mo–Mo bonds is zero, in the dinuclear $Mo_2Cl_8^{4-}$ (d^4) cluster there exists a quadrupole ($\sigma + 2\pi + \delta$) Mo–Mo bond, the Mo–Mo distances are 2.14 Å, and the chemical shift due to the involvement of the eight 4*d* electrons of both Mo atoms in the Mo–Mo interactions has proved to be the highest among those known.[123]

In addition, yet another important example clearly indicates the major role of the valence d^m electronic configuration of the metal atom in the formation of M–M bonds. In the series of compounds of the formally tervalent (d^3) molybdenum ($MoCl_3$, $Cs_3Mo_2Cl_9$, $K_3Mo_2Cl_9$), the ΔE differ markedly, which implies that the Mo atoms with the d^3 configuration form strong M–M bonds with increased multiplicity only under sterically favourable conditions and that the M–M distance is most likely to be the decisive factor in this instance. On the other hand, in the series of chlorides of formally bivalent (d^4) molybdenum the ΔE are almost identical despite the markedly different M–M distances and there is a sharp variation in sterochemistry from the dinuclear $Mo_2Cl_8^{4-}$ (D_{4h}) cluster to the hexanuclear $Mo_6Cl_8^{4+}$ (O_h) cluster; in this case the decisive factor is the effective number of electrons capable of forming direct M–M bonds.[4,123]

Thus the chemical shifts in the X-ray emission spectra of the cluster chlorides of heavy *d* elements reveal a delocalisation of the valence electrons of the M atoms in excess of that determined by the metal–ligand bonds, i.e. they do not correspond to the distance of M–Cl bonds alone in such compounds but can be accounted for by simultaneous M–M bond formation in the clusters. The ΔE constitute a direct conformation of the existence of effective M–M electronic interactions in the chlorides of heavy d elements.

4. X-Ray Electronic Spectra

The cluster chlorides, oxides, carbonyl, and carboxylates of certain heavy *d* elements have been investigated by X-ray electronic spectroscopy (ESCA),[126] which makes it possible to measure the energy distribution (orbital energies) of the valence electrons and also of the internal levels of the atoms in molecular complexes in crystals.

The X-ray electronic spectra of the valence region of the cluster compounds mentioned above[4,11,59–61,79,80,127–129] make it possible to determine the ionisation potentials (absolute energies) of the occupied MO, their electon populations, the contribution of the basis AO to the valence MO, and certain other characteristics of the electronic structure of the clusters. The parameters of these spectra refine and supplement the results of quantum-chemical calculations of the electronic structure of clusters. In particular, the photoelectron spectra (He-I–He-II) of trinuclear, tetranuclear, and hexanuclear carbonyl clusters confirm the calculated characteristics of the molecular orbitals of the M–M and M–CO bonds.[11,128] The photoelectron and X-ray electronic spectra of the dinuclear chloride and carboxylate d^4 complexes, M_2L_8, indicate directly the formation of the quadruple M–M bond.[59–61,127]

The parameters of the X-ray electronic spectra of the valence region of the chloride complexes indicate clearly the separation of the M–M MO from all the remaining MO and their position in the highest energy region: this is manifested particularly strikingly when the electronic structure of the same chloride cluster is described in terms of X-ray electronic and X-ray emission spectroscopic data.[129] In a concerted study of the electronic structure of the $Mo_2Cl_8^{4-}$ cluster[129] the energies of the internal Mo ($3d_{5/2}$) and Cl ($2p_{3/2}$) levels were measured in the X-ray electronic spectrum, while the energies of the L_{α_1}-Mo, L_{β_2}-Mo, K_{α_1}-Cl, and $K_{\beta_{1,3}}$-Cl X-ray lines were measured in the X-ray emission spectrum. Next the K_{α_1}-Cl and $K_{\beta_{1,3}}$-Cl spectra were superimposed on the valence ESCA spectrum on the same energy scale (Fig.9). It was then shown that the highest occupied MOs of the $Mo_2Cl_8^{4-}$ cluster do indeed represent the virtually pure 4*d* electronic states of the Mo atoms (multiple Mo–Mo bonds), while the energies of the MO involving the valence electrons of the ligands (Cl atoms) are much lower and reflect the existence of the M–L bonds and the $3p_\pi$ AO of the ligands.

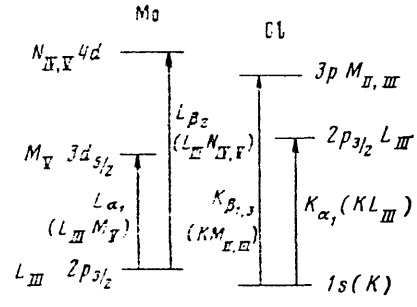


Figure 9. Schematic illustration of the method used in the superposition and the superimposed (with respect to energy) X-ray emission $K_{\beta_{1,3}}$.Cl (curve *1*), L_{β_2}.Mo (curve *3*) spectra and the X-ray electronic spectrum of the valence region of the $Mo_2Cl_8^{4-}$ cluster (curve 2).[129]

The X-ray electronic spectra of the valence region for cluster chlorides, oxides, and dimeric carboxylates with strong metal–metal bonds ($K_4Mo_2Cl_8$, $K_3Re_3Cl_{12}$, $K_3W_2Cl_9$, $Zn_2Mo_3O_8$, $Ba_3Ru_3O_9$, $Mo_2(O_2CCH_3)_4$, etc. differ appreciably from those for the corresponding mononuclear compounds of the same heavy *d* elements (K_3MoCl_6, K_2ReCl_6, K_2WCl_6, etc.). The formation of the cluster group (via the M–M bonds) in the structure of the chloride of a 4*d* or 5*d* element induces specific changes in the ESCA spectrum of such a cluster chloride (Fig.10). The formation of a cluster chloride with M–M bonds, whose electron density is concentrated in the "metallic nucleus" of the cluster, gives rise to significant changes in the interelectronic interaction in the polynuclear complex as a whole and "groups" the MO of this complex in terms of their energies in a specific manner.[4,59,60,79] It may be that the influence of the M–M bonds in the chloride cluster shortens the energy range within the limits of which the molecular orbitals of the M–L bonds, the pseudoatomic orbitals of the ligands, etc. are located compared with the greater possibilities for the energy distribution of the MO in a mononuclear complex. In this case it is understandable why the valence X-ray electronic spectra of the cluster chlorides consist of comparatively narrow bands grouped in terms of types of electronic interactions (M–M, M–L, AO–L, etc.).

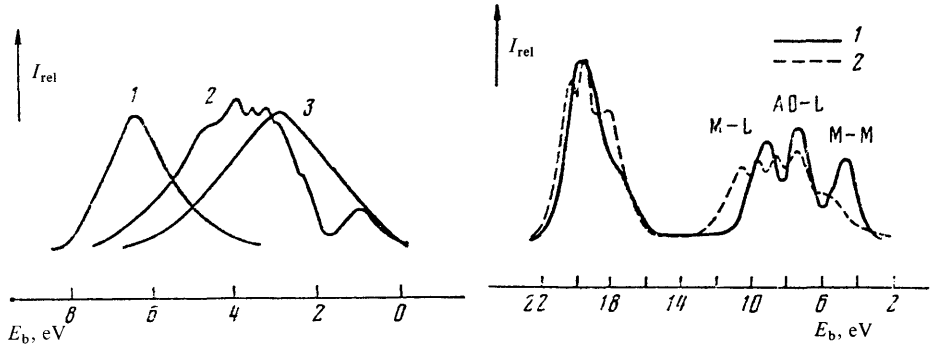


Figure 10. The X-ray electronic spectra of the valence regions in $K_3Re_3Cl_{12}$ (curve *1*) and K_2ReCl_6 (curve *2*).[6]

The experimental energies of the internal levels of the M atoms in the chlorides, dimeric carboxylates, and oxides of 4*d* elements (Mo, Ru) have led to the following finding (Fig.11). In the series of mononuclear molybdenum chlorides these energies increase successively with increase of the formal valence of molybdenum on passing from the metal to the higher chlorides, which can be explained by the increase of the number of valence electrons of the Mo atom in the Mo–Cl bonds and the corresponding increase of the effective positive charge on the Mo atom. For the cluster molybdenum chlorides (particularly those with strong M–M bonds), the chemical shifts greatly exceed the corresponding values of ΔE(Mo) for mononuclear chlorides with the same formal valence of the metal; this effect is caused by the additional delocalisation (additional to that due to the M–Cl bonds) of the valence 4*d* electrons of the M atoms in the M–M bonds in the chloride clusters.[24] The effects of the chemical shift of the internal levels of the transition metal atoms in the X-ray electronic spectra as well as the chemical shifts in the X-ray emission spectra[122,123] indicate an increase of ΔE for the cluster chlorides compared with the mononuclear chlorides having the same formal valence of the M atoms.

The pattern of the chemical shifts of the $3d_{5/2}$ level for the M atoms is somehow more complex for mononuclear and cluster molybdenum and ruthenium oxides.[79,80] The cause lies in the special character of the metal–oxygen bonds, which apparently possess a donor–acceptor π-component (M⇇O or M⇇C⇉M), which promotes the "leakage" of the valence electronic charge to the M atoms, particularly on formation of clusters with M–M bonds, and also in the cooperative interactions in these crystals manifested by their electrical conductivity. However, here too the effects of cluster formation are fairly distinctive, although in a somewhat different form. Thus X-ray electronic studies of a series of formally heterovalent compounds of a heavy *d* element make it possible to observe the formation of clusters (particularly those with strong M–M bonds) and yield varied information about their electronic structure.

VII. THE NATURE OF THE M–M BONDS IN THE CHLORIDE CLUSTERS OF 4*d* AND 5*d* ELEMENTS

The X-ray spectroscopic chacteristics of the cluster chlorides of 4*d* and 5*d* elements provide a preliminary answer to the following question: what is the physical nature of the M–M bonds present in the chloride cluster? Do they resemble the bonds between the M atoms in the corresponding metals or do they represent a different type of interaction?

In any system of chlorides of the heavy *d* elements the appearance of valence *d* electrons of the M atoms in the M–M bonds (the formation of the cluster) and the further increase of their number immediately entail a deviation of the chemical shift of the X-ray *K* or *L* line of the metal (relative to the ΔE for the corresponding mononuclear chlorides without M–M bonds but with the same formal valence of the M atoms) in the direction of the highest chloride, where all the valence electrons of the M atoms are involved in the M–Cl bonds and where the maximum valence of the metal obtains. In other words, the formation of M–M bonds in a cluster chloride always shifts ΔE in the same direction as that which occurs with increase of the number of valence electrons of the M atom in covalent bonding to the ligands (M–Cl). The contributions to the overall chemical shifts of the *K* or *L* line of the metal in the X-ray spectrum of a cluster chloride due to the formation of M–Cl and M–M bonds always have the same sign.

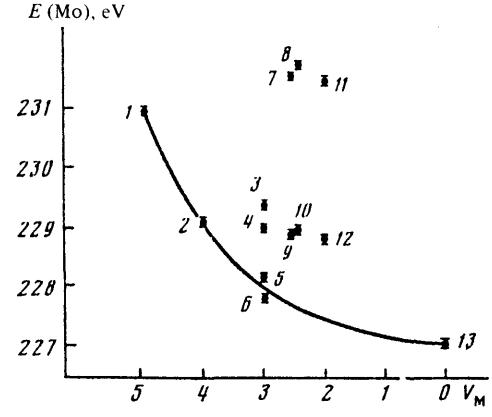


Figure 11. The energy of the $3d_{5/2}$ level in molybdenum atoms (E_b) in the X-ray electronic spectra of molybdenum chlorides as a function of the formal valence of molybdenum V_M.[4,124]

All this implies that the M–M bonds in the cluster chloride of a 4*d* or 5*d* element are formed in a manner similar to that of the M–Cl bonds. Precisely in this sense does the valence of the atoms of 4*d* or 5*d* elements in their cluster chlorides

greatly exceed (sometimes by a factor of 2–3) the formal value[3,30] determined by the involvement of a specific number of valence electrons of each M atom in the formation of M–Cl bonds alone.

Thus the M–M bonds in the cluster chlorides of heavy transition metals are close in their nature to the homoatomic covalent bonds. According to the results of molecular-orbital calculations,[4,11] the M–M bonds are localised (despite the fact that, with the exception of dinuclear clusters, they are many-centre bonds within the limits of the "island" cluster group) and different from the usual metallic bonds with their cooperative character.

If the M–M bonds in the chloride clusters resembled the usual metallic bonds in terms of the distribution of charge density of the valence electrons of the M atoms involved in them then measurement of the chemical shift relative to the lines due to the metal would have shown that the contribution to the overall chemical shift due to the formation of M–M bonds is zero. Consequently there would have been no deviations of ΔE (for cluster chlorides) from the linear relations observed for the mononuclear derivatives.

The latter is fully confirmed by the X-ray spectroscopic characteristics of zirconium chlorides.[124] The crystals of formally low-valence zirconium chlorides contain no clusters and have a chain or layer structure,[131] but the bonds between their M atoms are close to the usual metallic bonds in crystalline zirconium. Accordingly, the dependence of the chemical shift of the $L_{\alpha_{1/2}}$ line of zirconium on its formal valence and on the number of valence electrons of each zirconium atom not involved in bonds with the ligands is distinctly linear, which confirms the usual metallic nature of the M–M bonds with their cooperative character and the delocalisation of the valence electrons of the M atoms throughout the lattice of the non-cluster zirconium chlorides (ZrCl, $ZrCl_2$, or $ZrCl_3$; Fig. 7).

Thus the study of the chemical shifts of the emission *K* and *L* lines of heavy transition metals in the X-ray spectra of the mononuclear and cluster chlorides makes it possible to demonstrate the formation of M–M bonds in the clusters, to investigate the electronic structure of these bonds, and, what is most important, makes it possible to elucidate the nature of the M–M interaction in the cluster chlorides of 4*d* and 5*d* elements.

The cluster carbonyls, which frequently exist in the form of molecular crystals incorporating weakly interacting $M_n(CO)_m$ fragments, are apparently very closely related to the cluster chlorides, the main structural characteristic of which consists of the presence of a quasi-isolated "island" M_nX_n group. Cluster oxides constitute an example of crystal structures of a different nature—with a strong intercluster interaction and a high level of delocalisation of the valence electrons of the M atoms in the M–M bonds not only within the limits of the cluster but also between clusters in contact.

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Quantum-chemical and spectroscopic studies of chloride, oxide, carboxylate, and carbonyl clusters of 4*d* and 5*d* elements have revealed the fundamental principles of their electronic structure and showed, in particular, that direct (without a decisive influence of the bridging ligands) and effective (with a high energy) M–M bonds exist in the clusters. The corresponding MO indicate a high degree of delocalisation of the valence electrons of the M atoms in the M–M bonds, in excess of that which can be account for by M–L bonds, and the valence of the M atoms in the clusters is therefore always much higher than its formal value.

One of the main distinctive features of the electronic structure of the clusters is the spatial distribution of the electron density of the M–M bonds. Experimental and theoretical results[3,132] have shown that the electron density of the M–M bonds is localised mainly at the "metallic nucleus" of the cluster (at its M_n group), although in the oxygen (especially), carboxylate, and partly carbonyl clusters the nature of the M–M bond is much more complex owing to the inter-relation of the M–M and M–L interactions and also the intercluster interaction and the "spreading" of the valence electrons of the M–M bonds throughout the crystal. The characteristics of the distribution of the valence electrons of the M–M bonds in clusters (particularly in the chloride clusters but also apparently in many respects also in clusters with other ligands) impart to them properties significantly different from those of mononuclear complexes and probably playing a primary role in the catalytic activity of many cluster compounds.[133–137] The high catalytic activity of cluster complexes (particularly of their stereochemically open forms) in the catalysis of the redox reactions of small molecules, including photochemical reactions with participation of clusters in electronically excited states,[136,137] has been recently explained using the LCAO–MO and vibronic theories.[137]

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Leningrad State University