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Principles of Bonding and Reactivity in Transition Metal Cluster Compounds

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Abstract

The bonding in transition metal cluster compounds is examined by partitioning the system into the component parts suggested by expressions for the total energy. The nature of M–M (metal–metal) interactions, M–L (metal–ligand) interactions and L–L (ligand–ligand) interactions are examined, and their effect on the stability and hence structure of the system considered. The processes by which one structure can rearrange into another are discussed. Some consideration is given to the partitioning of a cluster into ML_j fragments, and the interactions between these fragments. Isolobal analogies are discussed in this context. The emphasis of this work is on the general principles behind the structure and reactivity of transition metal cluster compounds, rather than focusing on specific systems.

Introduction

The geometry which a transition metal cluster adopts is seldom obvious from inspection of its molecular formula. Symmetry arguments and semi-empirical molecular orbital approaches have proved useful tools in understanding and determining the geometries adopted by such compounds. Most success has been had in determining the polyhedron types into which the metal atoms of a cluster form when surrounded by a given number of ligands [1]; less success has been had in understanding the details of the arrangement of ligands around a metal core, though some progress has been made [2]. Even the success obtained in dealing with the metal core does not necessarily have a sound basis, since treating the metal atoms in isolation from considerations of metal–ligand bonding requires either the assumption that the metal–ligand bond energy is small compared with the metal–metal interactions, or the assumption that the metal–ligand bond energy is largely independent of the polyhedron adoped by the metal atoms.

Treating a system by considering it to be made up of component parts (*e.g.* a group of metal atoms plus a set of ligands) is frequently a profitable approach to take, both phenomenologically and quantitatively, since the properties required can often be determined in terms of properties of the component parts which are more easily determined than those for the whole system. In addition different systems involve some of the same component parts so results from one system can be transferred to another, thus reducing the amount of new analysis required. However, unless the partioning chosen relates to the physical nature of the system, the results will not have physical reality. Therefore the most important part of such an analysis is the first step of developing the partioning. In this work we shall be endeavouring to establish a physically realistic partioning of carbonyl metal clusters which enables feasible qualitative and quantitative analyses of their structure, bonding and rearrangements reactions. We shall make no attempt to include complete references to data to be found in the literature (for this see for example ref. 3), rather we shall use examples only to illustrate the principles and ideas we shall develop or consolidate from elsewhere.

The most important factor to be considered in the study of structure, bonding and reactivity is the energy of the system. Ways of partitioning the energy of the system should therefore suggest appropriate partitionings of the component nuclei and electron density in the system. The energy of a transition metal cluster $M_\mu L_\lambda$ can be symbolically written in one of two ways: the first as the sum of metal–metal (M–M) interactions plus metal–ligand (M–L) interactions plus ligand–ligand (L–L) interactions, *viz.*

$$E_{tot} = \Sigma M{-}M + \Sigma M{-}L + \Sigma L{-}L \tag{1}$$

and the second as the sum of interactions of μ ML_j fragments, *viz.*

$$E_{tot} = \Sigma(ML_j){-}(ML_k) \tag{2}$$

The structures which are observed are those which minimize E_{tot}. In order to understand why similar systems can adopt very different structures it is important to analyse E_{tot} and the conditions for its minimization. The different partitionings embodied in eqns. (1) and (2) lead to different types of analyses, which form the content of the remainder of this

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paper. We shall begin by examining the components of eqn. (1) and their interrelationships, and then consider the energy subdivision of eqn. (2).

Alternative approaches from those embodied in eqns. (1) and (2) are available in the form various of empirical rules for structure determination, including the various forms of polyhedral skeletal electron pair theory [1]. Justifications for such empirical rules have often resulted from the molecular orbital treatments of cluster bonding in particular systems [4]. However, even the more general molecular orbital approaches [5] focus on the details of one electron orbital and their energies, tending to obscure general behaviour trends and principles.

$$E_{tot} = \Sigma \text{M–M} + \Sigma \text{M–L} + \Sigma \text{L–L}$$

For the partitioning of the total energy into M–M, M–L and L–L contributions (eqn. (1)) to be useful we must be able to consider each type of bonding in isolation from the others. It is by no means obvious that such an approach bears any relationship to physical reality, until the results have been compared with experiment. To a large extent this comparison can be performed by collating the results of work already in the literature.

Many of the ideas and conclusions of this work are as applicable to non-transition metal clusters as to transition metal clusters, however we shall limit specific consideration to transition metals clusters. Transition metals have s, p and d electrons available for bonding; some of these will be involved with bonding to ligands and some to other metal atoms. If we remove the electrons (more strictly the electron density) required for M–L bonding from our initial consideration, the remaining s, p and d electrons bind the metal atoms together. It is in this way that the nature of the ligands affects the M–M bonding. Not all of the d electrons are involved in M–L bonding, so the M–M bonding might be expected to reflect the bonding characteristics of a small fragment of bulk transition metal and energy of M_μ be written as [6]

$$E_{\text{M–M}} = E_{\text{rep}}(\text{s,p}) + E_{\text{attr}}(\text{d}) \tag{3}$$

E_{rep} (s,p) is positive and due to the repulsion of valence s and p electrons by cores of adjacent transition metal atoms, it is thus short range [6]. E_{attr}(d) is negative and due to the attraction of the metallic-type bonding of the d electrons. The form for the cohesive energy of bulk metal where each atom has less than ten d electrons has been shown by Woolley to be an adequate description of E_{attr}(d) when account is taken of the reduced d electron density in a cluster due to M–L bonding. Thus we can write [7]

$$E_{\text{M–M}} \approx (R_{\text{M–M}})^{-5}\,(Z_{\text{M}})A \tag{4}$$

where $R_{\text{M–M}}$ is the nearest neighbour distance between metal atoms, Z_{M} is the number of M's nearest neighbours, and A is a constant determined by the number of d electrons and the details of the atomic potential at each site. Summation over metal atoms is implied in eqn. (4) which ignores the interaction between metal atoms which are not nearest neighbours. Broadly speaking the (Z_{M}) is a function of the polyhedron structure which M_μ adopts; $R_{\text{M–M}}$ reflects the size of the system; and A varies both as a function of the metal involved, and also of the ligand system, to the extent that the ligand system determines the number of electrons available for M–M bonding. A is generally taken to be approximately the same in the cluster as in an analogous bulk metal, it varies parabolically with band filling and accounts for the observed variation of cohesive energy across the non-magnetic 4d and 5d series [6]. The A factor also determines such features as the relative energies of a metal polyhedron composed of μ identical atoms and one composed of μ non-identical atoms. If the metallic type bonding in the mixed structure is less than in the pure metals (which will usually be the case due to the different energies of d orbitals in different metals which will result in less effective band formation [6]), then A will be smaller in magnitude for the mixed system, and the cohesive energy will be less stabilizing than in the pure system. The justification of eqn. (4) lies in the methods of solid state physics, for example chemical pseudo potential and Xα methods [8]. It should be noted that, contrary to the suggestions of extended Hückel and other semi-empirical molecular orbital theories, where the resonance integrals of molecular orbital theory are taken to be proportional to overlap integrals, the M–M bonding is largely due to the d electrons [9].

For a given $M_\mu L_\lambda$ system consideration of only the M_μ cohesive energy of eqn. 4 would suggest that M_μ will have the structure which maximizes the magnitude of the cohesive energy, *viz.* tetrahedral for $\mu = 4$, trigonal bipyramidal for $\mu = 5$, bicapped tetrahedron or octahedron for $\mu = 6$, tricapped tetrahedron or pentagonal bipyramidal for $\mu = 7$ etc. [10], since A will be approximately constant for the different possible structures. For the larger systems, $\mu > 7$, perhaps one might expect to see variations in structure since cohesive energies vary so little (0.2% difference in cohesive energy between the pentagonal bipyramid and the capped octahedron). In practice, a variety of M_μ structures are observed for all μ. This reflects the large (possibly dominant) contribution to the total energy of the M–L interactions. A metal polyhedron which does not maximize the cohesive energy may be observed because this M_μ structure gives rise to more favourable M–L interactions than the most stable metal polyhedron that is possible. The relative magnitude of the M–M interactions compared with the M–L interactions is also determined by the number and type of ligands since the ligands determine the number of electrons available for M–M bonding [11]. For example, a good π-acceptor ligand such as CO decreases the d electrons available for M–M bonding compared with say H.

The second two contributions to the total energy of a metal cluster are those due to M–L bonding and L–L interactions, both of which are present in metal complexes. The situation in a cluster is more involved than in a metal complex due to the M–M bonding and due to the possibility of bridging ligands. None-the-less a complete understanding of M–L and L–L interactions in a metal complex, were one available, would require little modification to be applied in principle to a metal cluster. Metal atoms in a cluster bond to ligands in much the same way as in a complex; it is just that the identity of the metal atom is perturbed due to the involvement of some of the electrons in M–M bonding. This affects the details rather than the principles of the bonding. (Note that in the previous section we talked about the identity of the metal atoms being perturbed from that in a bulk metal fragment by their bonding to ligands.) As in complexes, we might expect a range of M–L coordination numbers to be observed in clusters, depending on the identities of the metal atoms and the ligands. In addition to changing the type of metal or its formal oxidation state, in metal clusters the identity of the metal can be changed by changing the number of metal atoms or the metal polyhedron structure. Any of these factors can alter the relative magnitudes of the contribution of ΣM–M and ΣM–L to the total energy, and so may cause completely different structures to be found.

There is currently no satisfactory account of metal–ligand bonding in metal complexes available, so we cannot proceed further than the general comments made in the previous paragraph. For both metal complexes and metal clusters the simplest attempts to rationalize the observed number of ligands around a metal atom have been in terms of electron counting schemes. The eighteen electron rule for metal complexes, whereby a stable structure is taken to be one where the metal atom has a formal count of eighteen valence electrons, is one example of this. The eighteen electron rule and its cluster analogues, an eighteen electron rule based on localized two-centre electron pair [12] and Wade's skeletal electron pair rules for carbonyl clusters [1], are sufficiently successful to suggest that some sort of electron count is one criterion in the optimization of M–L bonding. The many failures indicate that other considerations are also important. The success of Wade's empirical rules resulted in a variety of attempts to rationalize them. Most of these were molecular orbital in nature and as a result take the form of consideration of specific examples [1]. The result is that Wade's rules have been validated for many systems and shown not to hold for others. However, little insight is given by this work into why Wade's rules have any success. In fact, depending on the molecular orbital formalism chosen, different theoretical bases for the rules seemed to be appropriate, which suggests that they are valid largely for symmetry determined reasons. In fact the broad features of bonding and anti-bonding molecular orbitals follow from symmetry considerations, as shown by Stone [13] who treated a cluster as a perturbed spherical shell or assembly of spherical shells. Stone's analysis suggests that the detailed geometry of the ligands relative to the metal is not usually due to M–L bonding effects (exceptions being when there is not a ligand s orbital of the same symmetry as a vacant and accessible metal orbital, to act as a donor orbital). In the context of this work, we would say that once the metal electrons involved in M–M and M–L bonding have been ascertained, the details of the ligands' orientation about the metal polyhedron structure are largely determined by ΣL–L.

The L–L interactions will be explored in some detail in a later work since it is not a trivial problem. For carbonyl ligands suffice it to say that the ligands in metal clusters are oriented about the metal(s) to which they are attached so as to maximize the L–L dispersive interaction subject to a short range repulsive interaction which can be approximated by a hard sphere radius. The L–L interaction is small compared with M–M and M–L interactions unless too many ligands are forced to pack around a single metal atom, in which case it can cause M–L bonds to lengthen and weaken and so may result in a completely different structure being more energetically stable.

In conclusion to the consideration of structure according to eqn. (1) we can say that the bonding in metal clusters can be understood as an interplay between the desire to (i) maximize the magnitude of the cohesive energy of the metal polyhedron, (ii) maximize M–L bonding energy, and (iii) not cause steric crowding of the ligands. Any one of these three can have a significant effect on the others, so that changing one can result in an entirely different cluster structure. For example, adding a ligand to form $M_\mu L_{\lambda+1}$ adds stability to the system due to the extra M–L bond (or bonds if the new ligand is a bridging one), may destabilize the system by removal of d electron density from M–M bonding in order to make the M–L bond(s) and may cause a destabilizing L–L interaction to become operative. The destabilization of M–M bonding, in the language of eqn. (4), occurs both by changing A and perhaps by increasing R_{M-M} (a 15% change in R_{M-M} alters the cohesive energy by a factor of 2) and altering Z_M. Whether $M_\mu L_{\lambda+1}$ is more stable than $M_\mu L_\lambda$ is determined by the net effect of the energy changes. If it is less stable, then $M_\mu L_{\lambda+1}$ may decompose. Alternatively there may be another geometry for which the total energy is lower. In this case, if there exists an allowed reaction pathway between the two structures whose activation energy is not large compared with kT, then the system will spontaneously rearrange. If the activation energy is large compared with kT, then the rearrangement will not readily occur, but other methods of preparing $M_\mu L_{\lambda+1}$ will result in the more stable structure rather than the one which results from the addition of a ligand to $M_\mu L_\lambda$. There are numerous examples of this type of behaviour to be found in the literature. One example is provided by $Os_6(CO)_{18}{}^{2-}$ which forms an octahedron, $HOs_6(CO)_{18}{}^{-}$ which forms a distorted octahedron, and $H_2Os_6(CO)_{18}$ which forms either a square based pyramid or a distorted octahedron.

Even without the impetus of altering the contents of the ligand system of a cluster, some clusters readily rearrange between different structures of similar or identical total energy (identical total energies if the structures are isomeric). So it is important to understand the process by which a rearrangement takes place. A reaction can be viewed as a series of reaction steps, each step of which goes from a locally stable point via a saddle point transition state to another locally stable point on a potential energy surface. Each step of a reaction path proceeds along a single normal mode of the reacting system with metal atoms and ligands moving in concert in a special symmetry adapted manner [14]. (The only possible exceptions to this are reactions involving light atoms, e.g. H, as the reacting atoms when local modes and branching points may become relevant for such systems.) As a result, identifying the normal modes of a cluster gives all the potential rearrangement pathway beginnings. This provides a clear systematic beginning to the study of rearrangement reactions in metal clusters. Some of the modes will be largely ligand motion and some largely metal motion, but all will involve at least limited coupling. Two conclusions about rearrangements in clusters follow immediately from this. Firstly, ligand rearrangements in clusters are not random motions of ligands about a metallic core, but precisely defined motions which will involve a limited amount of M_μ motion of the same symmetry. Secondly, rearrangement reactions of the metal polyhedron can, to a first approximation, be studied without reference to ligands as was done in ref. 14b, however, metal motion will be coupled to ligand motion, and it may be the ligand motion which determines the relative energetics of two symmetry allowed metal polyhedron rearrangement pathways. For example changes from axial to bridged ligation will substantially affect the total energy of the system.

$$E_{\mathrm{tot}} = \Sigma(\mathrm{ML}_j) - (\mathrm{ML}_k)$$

We come now to consider the partitioning of the system suggested by eqn. (2). It involves determining the energy of separate ML_j fragments and then considering the energy of interaction. This type of approach has been extensively exploited in an approximate way by the isolobal approaches. An isolobal approach to the bonding in a system is basically, in the context of this work, a shortcut to application of eqn. (2). One finds fragment systems whose 'relevant' electronic structures are the same as in the ML_j fragments of interest, and whose interactions are known. One then assumes that the interactions between the unknown ML_j fragments of interest are the same as those between the known fragments. In practice an isolobal analogy has required that the (outer parts of) the frontier molecular orbitals of the fragments be similar in symmetry and energetics. The use of isolobal analogies with boron hydrides or organic subunits such as methyl or methylene groups has been the most successful approach for determining the geometry of the ligand systems of transition metal clusters. The isolobal analogy has been used with success in a number of instances, for example Shaik *et al.* were able to understand the bonding of bridging carbonyls by taking it to be isolobal with methylene [15]. Hoffmann considered that the bonding in clusters containing only terminal carbonyl ligands could be analysed in terms of the isolobal analogy between CH_{n-2} and $M(CO)_n$ fragments [16].

It is interesting that although based in a molecular orbital formalism, an isolobal argument deals with localized orbitals, rather than the completely delocalized ones of molecular orbital theory. This suggests that localized bonding approaches may, in the future, prove to be the most successful ways to theoretically treat the structure of the ligand system in transition metal clusters. At the present stage of application one might expect an isolobal analogy to give any symmetry determined features of the fragment interactions, and to reproduce other features to the extent which the interacting orbitals are in fact isolobal. Problems are therefore most likely to arise when the specific nature of d orbitals comes in to play in the transition metal clusters or the greater variety of possible bonding orbitals becomes relevant (*i.e.* non-frontier orbitals take part in the bonding). Woolley [17] has warned of the problems that may be encountered when the M–M bonding is investigated using isolobal analogies with main group units, due to the importance of d electrons in the M–M bonding and the fact that the main group fragments only involve s and p orbitals, so cannot exactly reflect the behaviour of d orbitals. A good illustration of this is provided by the work of Evans and Mingos [18] on $Os(CO)_4$ as a vertex fragment. CH_2 is often considered to be analogous to $Os(CO)_4$, however $Os(CO)_4$ has additional orbitals which may become involved in the bonding and enable it to bond to three osmiums, whereas CH_2 has no such flexibility. In this instance it proved necessary to consider the available orbitals on the $Os(CO)_4$ fragment and determine its interaction with the rest of the cluster properly, not via the shortcut of an isolobal analogy with a more familiar system.

Conclusions

Consideration of the cohesive energies of given polyhedral metal units provides a clue to the variety of shapes observed for transition metal cluster compounds with identical electron counts. Formation of metal–ligand bonds is at the expense of the metal–metal cohesive energy, and since cohesive energy depends on metal atom connectivity and nearest neighbour distance changes in either of both of these are expected when there are changes in the ligand system. Changes in connectivity correspond to changes in metal polyhedron structure and changes in the nearest neighbour distance due to cluster expansion (or contraction). The nature of a ligand, particularly its ability to function as a good π-acceptor, is also an important influence on the cohesive energy due to its affect on A. Finally, interligand interactions are significant in determining the arrangement of the ligands about the metal polyhedron.

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