TRANSITION-METAL COMPOUNDS CONTAINING CLUSTERS OF METAL ATOMS

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1. Introduction

It is an interesting fact, quite indicative and typical of the extraordinary tempo of basic research in these times, that only about ten years ago the very existence of any significant number of stable metal-to-metal bonds among the transition elements was generally considered unlikely, while today there are scores of compounds containing such linkages and investigations in this field are very much in vogue. The entire area of metal–metal bonds has recently been the subject of several reviews.[1,2] This Review discusses one particular class of compound containing metal–metal bonds, namely those of the transition elements which may be called "metal atom cluster compounds". These compounds, to be defined more precisely below, contain triangular or polyhedral groups of metal atoms, and it is perhaps noteworthy that interest in these compounds is only one phase of a current interest among chemists in compounds with polygonal and polyhedral groups of like or similar atoms, as represented by such organic compounds as cubane, adamantane, or congressane and by such other inorganic compounds as the boranes, carboranes, and phosphanes.

Metal atom cluster compounds can be formally defined as "those containing a finite group of metal atoms which are held together entirely, mainly, or at least to a significant extent, by bonds directly between the metal atoms even though some non-metal atoms may be associated intimately with the cluster". This is essentially the definition suggested earlier,[3] but broadened to include compounds in which the metal atoms are held together *entirely* by metal–metal bonds. It is broad enough also to include compounds containing only two metal atoms, although these are atypic in the same sense as methane is an atypic aliphatic hydrocarbon. It also includes clusters in which not all the metal atoms are identical, although at present scarcely any such clusters, except for binuclear ones, have been identified.

The phrase "metal atom cluster" or something similar is necessary and useful since the more familiar term "polynuclear complex" would imply no more than the usual sort of polymer, lacking metal–metal interaction. The term staphylonuclear has also been suggested[4] but little used. The term

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[1] J. Lewis and R. S. Nyholm, *Science Progress*, 1964, **52**, 557.

[2] J. Lewis, *Pure and Appl. Chem.*, 1965, **10**, 11.

[3] F. A. Cotton, *Inorg. Chem.*, 1964, 3, 1217.

[4] C. Brosset, *Arkiv. Kemi Min. Geol.*, 1946, *A*, **20**, No. 7; 1947, **22**, No. 11; *Arkiv. Kemi*, 1947, **25**, 1.

"cage", often used in connection with boranes, is undesirable for two reasons: (1) binuclear and ternuclear clusters can scarcely be called cages, yet their relation to the polyhedral ones is genuine and should be connoted rather than obscured by the nomenclature; (2) the polyhedral clusters are generally packed so closely that they will be unlikely commonly or characteristically to serve as cages. This Review concentrates on the better characterised polynuclear species containing identical metal atoms.

The metal atom cluster compounds now known fall principally into two broad classes: (1) lower halides and, to a less extent, oxides; (2) polynuclear metal carbonyls and related species involving NO, organic π systems, or other π-acid type ligands.

Those of the first type are principally formed by the elements Nb, Ta, Mo, W, and Re. Several attempts have been made to identify the factors responsible for the stability of homonuclear metal–metal bonds just in this region of the Periodic Table. Certainly a low formal oxidation state is one such factor (cf. the metals themselves); others which have been discussed are the magnitude of radial wave functions[1,5] and bond energies as indicated by heats of sublimation of the metals.[1,6] However, this tendency of certain heavy transition metals to form bonds to themselves, which may be called *homophilicity*,[7] has not yet been fully clarified theoretically. In contrast, among the metal carbonyl-type systems the lighter metals seem about as homophilic as the heavier ones.

2. Structural Data

The most important technique thus far in the study of metal atom clusters has been *X*-ray diffraction, because of the primary need to prove with certainty that clusters exist and to discover their structures.

(a) Halide and Oxide Systems.—Among these systems have been found many M_2, several types of M_3, and two basic varieties of octahedral M_6 clusters.

(i) *Binuclear clusters.* Apparently the only ones known in which there are no bridging atoms are the $Re_2X_8^{2-}$ (X = Cl, Br, SCN) and $Tc_2Cl_8^{3-}$ ions. The structure of the $Re_2Cl_8^{2-}$ ion, which has been determined in several compounds,[8] is shown in Fig. 1; that of $Tc_2Cl_8^{3-}$ is very similar[9] except that the metal–metal bond is even shorter (2·13 Å). The existence of similar structures in other $Re_2X_8^{2-}$ and $Re_2X_6L_2$ species seems likely from spectroscopic results.[10] The salient and surprising features of these

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[5] J. C. Sheldon, *Austral. J. Chem.*, 1964, **17**, 1191.

[6] H. Schafer and H. G. Schnering, *Angew. Chem.*, 1964, **76**, 833.

[7] F. A. Cotton, N. F. Curtis, C. B. Harris, B. F. G. Johnson, S. J. Lippard, J. T. Mague, W. R. Robinson, and J. S. Wood, *Science*, 1964, **145**, 1305.

[8] B. G. Kuznetzov and P. A. Koz'min, *Zhur. strukt. Khim.*, 1963, **4**, 55; F. A. Cotton and C. B. Harris, *Inorg. Chem.*, 1965, **4**, 330; F. A. Cotton and W. R. Robinson, unpublished studies.

[9] F. A. Cotton and W. K. Bratton, *J. Amer. Chem. Soc.*, 1965, **87**, 921.

[10] F. A. Cotton, N. F. Curtis, B. F. G. Johnson, and W. R. Robinson, *Inorg. Chem.*, 1965, **4**, 326.

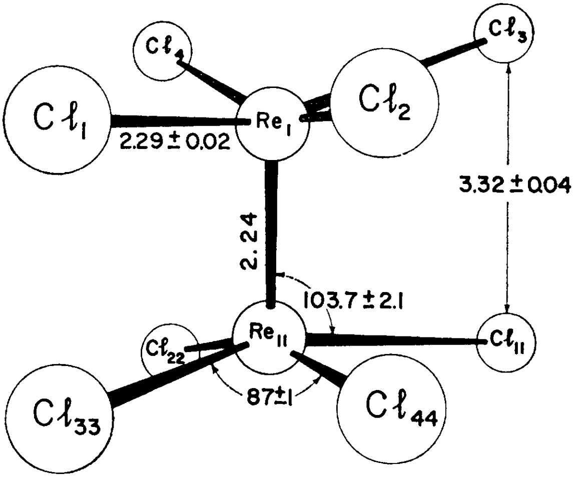

FIG. 1. *The structure of the* $Re_2Cl_8^{2-}$ *ion as it occurs in* $K_2Re_2Cl_8$, $2H_2O$. [Reproduced by permission from F. A. Cotton and C. B. Harris, *Inorg. Chem.*, 1965, **4**, 330.]

structures are (1) the exceedingly short M–M distances and (2) the *eclipsed* rotomeric configuration. The shortness of the metal–metal distances can be appreciated by comparing them with the M–M distances in the metals, *viz.*, 2·75 Å (Re) and 2·72 Å (Tc). The explanation of these features will be considered later.

The $Re_2X_8^{2-}$ compounds can be smoothly converted into or obtained from the $Re_2(O_2CR)_4X_2$ compounds[10] and it seems likely that the latter also contain very strong Re–Re bonds. The isoelectronic $Mo_2(O_2C{\cdot}CH_3)_4$ has been shown[11] to have an Mo–Mo distance (2·11 Å) similar to that in $Tc_2Cl_8^{3-}$.

There is an enormous number of compounds with pairs of metal atoms close enough that they must be considered bonded but with two or three bridging halide or chalcogenide atoms.[1,2,6,12] They will not be discussed here in detail, but it may be noted that very often when analogous compounds are formed by both the lightest and the heavier metals of a group, the heavier one shows much greater metal–metal interaction. For example,[12] in diamagnetic $W_2Cl_9^{3-}$ (W–W, 2·41 Å) there is a distinct metal–metal bond, while in $Cr_2Cl_9^{3-}$ the metal atoms remain in the centres of their respective octahedra and exhibit normal magnetic moments. A similar comparison[13] exists between CrO_2 and MoO_2. These facts demonstrate the greater homophilicity of the heavier metals.

(ii) *Triangular clusters.* Two distinct types are known. The earliest to

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[11] D. Lawton and R. Mason, *J. Amer. Chem. Soc.*, 1965, **87**, 921.

[12] A. F. Wells, "Structural Inorganic Chemistry", 3rd. edn., Clarendon Press, Oxford, 1962.

[13] J. B. Goodenough, *Compt. rend.*, 1965, 1200.

be discovered[14] occurs in $Zn_2Mo_3O_8$, in several isomorphous $M^{II}_2Mo_3O_8$ compounds and, probably, in $LiScMo_3O_8$. The ternuclear cluster with its associated oxide ions is shown in Fig. 2. The compounds can be described as close-packed arrays of oxide ions with the Mo atoms in adjacent octahedral interstices and thus the unit shown is not discrete, but the Mo_3 clusters are sufficiently separated from one another to be treated as individuals. More recently the compound Nb_3Cl_8 has been shown[6,15] to have essentially the same structure, with metal–metal distances relatively long but nonetheless indicative of appreciable metal–metal bonding.

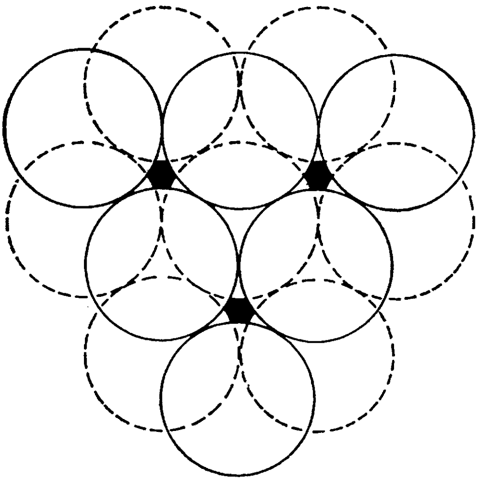

FIG. 2. *The type of ternuclear cluster (idealised) occurring in* $Zn_2Mo_3O_8$ (Mo-Mo, 2·53 Å) *and some closely related compounds and in* Nb_3Cl_8(Nb–Nb, 2·81 Å). [Reproduced by permission from F. A. Cotton, *Inorg. Chem.*, 1964, **3**, 1217.]

The second type of triangular M_3 cluster has been found in a number of compounds of tervalent rhenium. It was first discovered[16] in the compound $Cs_3Re_3Cl_{12}$, and has since been found[17] to be the basic structural unit of all compounds derived directly from Re^{III} chloride and bromide, such as the $Re_3X_{11}^{2-}$ and $Re_3X_{10}^{-}$ ions, and the numerous $Re_3X_9L_3$ (L = neutral ligand) compounds. The Re_3Br_9 group also occurs alone.[18] Finally, and most impressive, the chloride and bromide of Re^{III} both are built up of

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[14] W. H. McCarroll, L. Katz, and R. Ward, *J. Amer. Chem. Soc.*, 1957, **79**, 5410; P. C. Donohue and L. Katz, *Nature*, 1964, **201**, 180.

[15] H. G. Schnering, H. Worhle, and H. Schafer, *Naturwiss.*, 1961, **48**, 159.

[16] W. T. Robinson, J. E. Fergusson, and B. R. Penfold, *Proc. Chem. Soc.*, 1963, 116; J. A. Bertrand, F. A. Cotton, and W. A. Dollase, *J. Amer. Chem. Soc.*, 1963, **85**, 1963; *Inorg. Chem.*, 1963, **2**, 1106.

[17] F. A. Cotton, S. J. Lippard, and J. T. Mague, *Inorg. Chem.*, 1965, **4**, 508; F. A. Cotton and J. T. Mague, *ibid.*, 1964, **3**, 1094; J. E. Fergusson, B. R. Penfold, and B. R. Robinson, *Nature*, 1964, **201**, 181; B. H. Robinson and J. E. Fergusson, *J. Chem. Soc.*, 1964, 5683; M. Elder and B. R. Penfold, *Nature*, 1965, **205**, 276.

[18] F. A. Cotton and S. J. Lippard, *Inorg. Chem.*, 1965, **4**, 59.

Re_3X_9 units,[19] linked by bridging X atoms, and these units apparently constitute > 90% of the gaseous compounds[20] at temperatures of *ca.* 650°. The Re–Re distances are in all cases 2·43—2·50 Å, indicative of strong metal–metal bonding though not so strong as in the $Re_2X_8^{2-}$ ions. Fig. 3

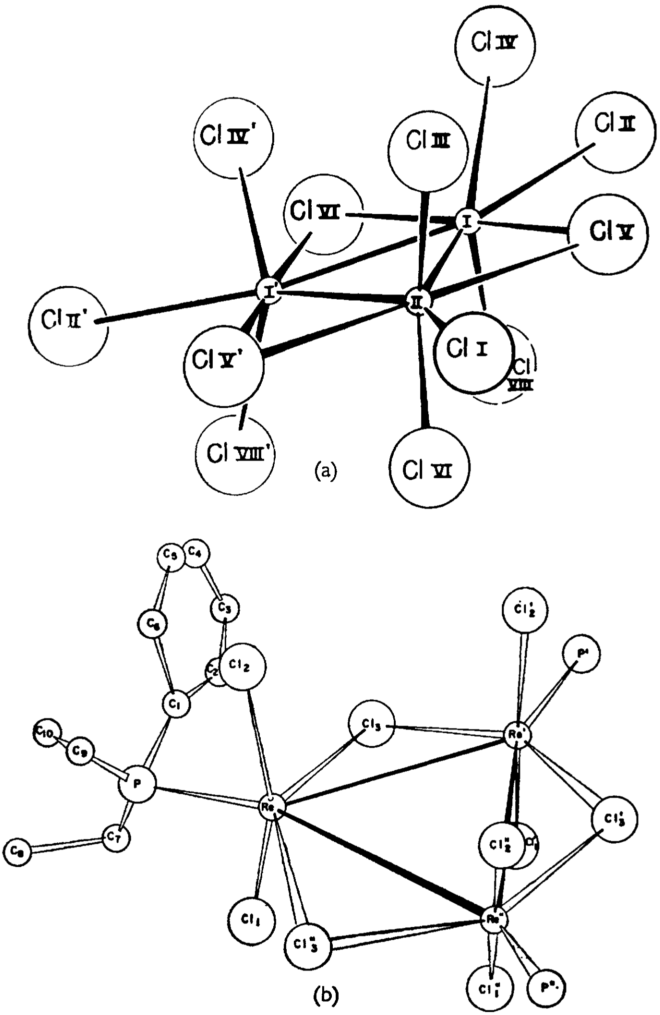

FIG. 3. (*a*) *The structure of the* Re_3Cl_{12} *ion as it occurs in* $Cs_3Re_3Cl_{12}$. [Reproduced with permission from J. A. Bertrand, F. A. Cotton, and W. A. Dollase, *Inorg. Chem.*, 1963, 2, 1166.] (*b*) *The structure of* $Re_3Cl_9(PEtPh_2)_3$. [Reproduced with permission from F. A. Cotton and J. T. Mague, *Inorg. Chem.*, 1964, 3, 1094.]

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[19] F. A. Cotton and J. T. Mague, *Inorg. Chem.*, 1964, 3, 1402.

[20] K. Rinke and H. Schaffer, *Angew. Chem. Internat. Edn.*, 1965, **4**, 148; A. Buchler, P. E. Blackburn, J. L. Stauffer, *J. Phys. Chem.*, 1966, **70**, 685.

shows two typical structures. It has also been suggested[21] on indirect evidence that $ReCl_4$ is built of Re_3Cl_{12} units isostructural with $Re_3Cl_{12}^{3-}$, although $TcCl_4$ has been definitely shown[22] not to contain clusters.

(iii) *Octahedral clusters.* These are the most widespread[6] and are of two types. First there is the M_6X_8 type (Fig. 4) established for the so-called "dihalides" of molybdenum and tungsten, in which there is a triply-bridging X atom on each face of the octahedron. Secondly, there is the M_6X_{12} type (Fig. 5) first found in the $Nb_6X_{14}, 7H_2O$ and $Ta_6X_{14}, 7H_2O$ compounds and now known[6,23] also in $NbCl_{2\cdot33}$ ($\equiv Nb_6Cl_{14}$), $TaI_{2\cdot33}$, $NbF_{2\cdot5}$ ($\equiv Nb_6F_{15}$), $TaCl_{2\cdot5}$, $TaBr_{2\cdot5}$, and $PtCl_2$.

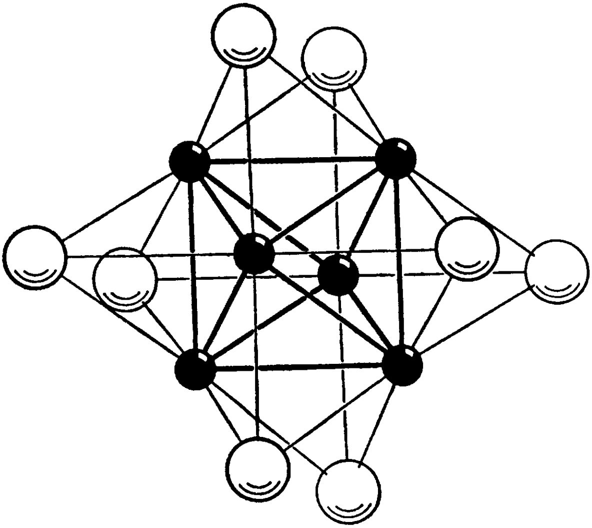

FIG. 4. *The* M_6X_8 *structure as exhibited by* $Mo_6Cl_8^{2+}$. [Reproduced by permission from L. Pauling, "The Nature of the Chemical Bond," 3rd edn., Cornell Univ. Press, Ithaca, New York, 1960.]

(b) Metal Carbonyls and Related Systems.—There is a very large number of metal carbonyls containing metal–metal bonds and only a few of the more symmetrical clusters will be mentioned.

(i) *Binuclear clusters.* Virtually all binuclear carbonyls fall into this category. Important representatives of the type lacking bridging groups are the isostructural[24] $M_2(CO)_{10}$ compounds of Mn, Tc, and Re.

(ii) *Triangular clusters.* Two good examples are provided by

[21] R. Colton and R. L. Martin, *Nature*, 1965, **205**, 239.

[22] M. Elder and B. R. Penfold, *Chem. Comm.*, 1965, 308.

[23] K. Brodersen, G. Thiele, and H. G. Schnering, *Z. anorg. Chem.*, 1965, **337**, 120; H. Schäfer and D. Bauer, *Z. anorg. Chem.*, 1965, **339**, 155.

[24] M. F. Bailey and L. F. Dahl, *Inorg. Chem.*, 1965, **4**, 1140.

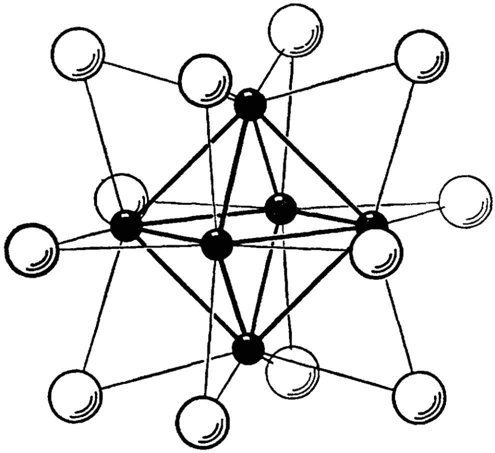

FIG. 5. *The* M_6X_{12} *structure as exhibited by* $Nb_6Cl_{12}^{2+}$. [Reproduced by permission from L. Pauling, "The Nature of the Chemical Bond," 3rd edn., Cornell Univ. Press, Ithaca, New York, 1960.]

$Os_3(CO)_{12}$[25] and $(\pi\text{-}C_5H_5)_3Ni_3(CO)_2$.[26] The former contains no bridging CO groups, while the latter has two triply-bridging CO groups; in each case the metal atoms form equilateral triangles.

(iii) *Tetrahedral clusters.* These have been found in $Co_4(CO)_{12}$, the structure of which (Fig. 6) has been established by a combination of *X*-ray[27] and infrared results,[28] and in the isoelectronic $FeCo_3(CO)_{12}$.

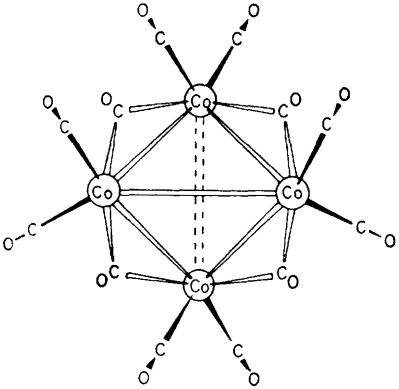

FIG. 6. *The structure of* $Co_4(CO)_{12}$ *deduced from a combination of* X-*ray and infrared data.* [Reproduced by permission from F. A. Cotton and G. Wilkinson, "Advanced Inorganic Chemistry," 2nd edn., John Wiley, Interscience, New York, 1966.]

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[25] E. R. Corey and L. F. Dahl, *Inorg. Chem.*, 1962, **1**, 521.

[26] A. A. Hock and O. Mills, "Advances in the Chemistry of the Co-ordination Compounds", ed. S. Kirschner, MacMillan, New York, 1961, p. 640.

[27] P. Corradini, *J. Chem. Phys.*, 1959, **31**, 1676.

[28] D. L. Smith, *J. Chem. Phys.*, 1965, **42**, 1460.

(iv) *Square pyramidal cluster.* The compound $Fe_5(CO)_{15}C$ contains such a cluster with a carbon atom imbedded in the base.[29]

(v) *Octahedral cluster.* The only one found[30] so far occurs in $Rh_6(CO)_{16}$ (Fig. 7).

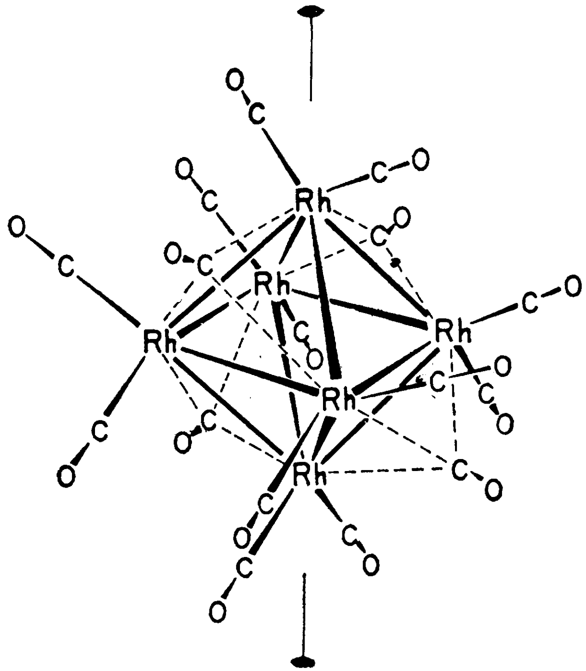

FIG. 7. *The structure of* $Rh_6(CO)_{16}$. [Reproduced by permission from E. R. Corey, L. F. Dahl, and W. Beck, *J. Amer. Chem. Soc.*, 1963, **85**, 1202.]

3. Chemical and Physical Properties

Much remains to be learned in this realm, especially concerning the chemistry. Aside from structure, the physical properties most studied, though still inadequately, are magnetism and electronic spectra. All of the clusters known have either zero or one unpaired electron. Those with no unpaired electrons often[6,31,32] show temperature-independent paramagnetism, however. Studies of electron spin resonance (e.s.r.) or magnetic anisotropy are almost totally lacking. The visible spectra of a number of lower halide-type clusters[5,10,17,18,33,34] have been reported (see section 4).

[29] E. H. Braye, W. Hubel, L. F. Dale, and D. L. Wampler, *J. Amer. Chem. Soc.*, 1962, **84**, 4633.

[30] E. R. Corey, L. F. Dahl, and W. Beck, *J. Amer. Chem. Soc.*, 1963, **85**, 1202.

[31] D. Brown and R. Colton, *Austral. J. Chem.*, 1965, **18**, 441.

[32] H. C. Longuet-Higgens and A. J. Stone, *Mol. Phys.*, 1962, **5**, 417.

[33] M. B. Robin and N. A. Kuebler, *Inorg. Chem.*, 1965, **4**, 798.

[34] R. J. Allen and J. C. Sheldon, *Austral. J. Chem.*, 1965, **18**, 277.

By chemical properties we mean (1) reactions of clusters once formed, and (2) preparation of clusters. Of the former we have some systematic knowledge; the latter is at present without rational principles.

(a) Reactions of Clusters.—Those known are of three general types: ligand exchange reactions, redox reactions, and degradation reactions.

(i) *Ligand exchange reactions.* It appears to be a general rule that the non-metal atoms which serve as bridges can be exchanged or replaced only slowly, if at all. Thus in the $Mo_6X_8^{2+}$ ions the eight X atoms are essentially non-reactive.[35] However, each Mo atom binds one additional ligand (six in all), and these can readily be varied giving for example $[(Mo_6X_8)Y_nL_{6-n}]^{(4-n)+}$ where Y is a −1 anion and L neutral.[35,36] Studies along this line have been fairly extensive.[35,36] The W_6X_8 species are much less stable and have been little studied. The $M_6X_{12}^{2+}$ (M = Nb, Ta) species appear to be relatively unstable and difficult to study[34] and little has been accomplished with them. In the Re_3X_9 species, there are again three positions for binding additional ligands in a relatively labile manner,[17] and in some cases all three positions need not be occupied. Moreover, of the nine X atoms, the three bridging ones are virtually unreactive, but the six others can be exchanged or replaced moderately easily, giving rise to $Re_3X_3Y_6$ species and their derivatives.[17] The $Re_2X_8^{2-}$ [and $Re_2(O_2CR)_2X_2$] species undergo rather easy ligand exchange reactions[10] with retention of the Re_2 group, however.

It seems likely that substitution of non-bridging CO groups by other ligands (*e.g.*, phosphines) in carbonyl-type clusters should be feasible but no such reactions have yet been reported.

(ii) *Redox reactions.* Apparently the only redox reactions so far carried out in solution are those[37] of the type

$$[M_6X_{12}]^{2+} = [M_6X_{12}]^{4+} + 2e \quad (M = Nb, Ta).$$

Despite the fact that $[M_6X_{12}]^{3+}$ species exist[6] in solid compounds ("$MX_{2\cdot5}$"), no evidence for this ion in solution has been obtained. It seems likely that other redox reactions of clusters remain to be discovered and studied.

(iii) *Degradation reactions.* Clusters can in general be degraded by severe oxidation, by base hydrolysis, and (for carbonyl types) by pyrolysis. There is essentially no detailed information available on these processes except those concerning[35] $Mo_6X_8^{2+}$.

(b) Preparation of Clusters.—There does not yet appear to be any instance in which a synthetic reaction (or series of reactions) was deliberately designed to produce a particular cluster compound from mononuclear starting materials. On the contrary, all known clusters were discovered

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[35] J. C. Sheldon, *J. Chem. Soc.*, 1960, 1007, 3106; 1963, 4183; 1964, 1287.
[36] F. A. Cotton and N. F. Curtis, *Inorg. Chem.*, 1965, **4**, 241.
[37] R. E. McCarley, B. G. Hughes, F. A. Cotton, and R. Zimmerman, *Inorg. Chem.*, 1965, **4**, 1491.

by chance or prepared unwittingly. Thus the student of cluster chemistry is in somewhat the position of the collector of lepidoptera or meteorites, skipping observantly over the countryside and exclaiming with delight when fortunate enough to encounter a new specimen. Naturally, one wishes to change this situation by devising rational syntheses for metal atom clusters and this is perhaps the greatest challenge the field now offers.

4. Bonding and Electronic Structure

Attempts to account for the electronic structures of metal atom clusters can at present be checked against three types of experimental result: (1) magnetic properties, (2) bond lengths, and (3) electronic spectra. Bonding has been discussed using (*a*) the valence-bond (VB, *i.e.*, localised two-centre bonds formed by directed hybrid orbitals) approach, (*b*) the molecular orbital (MO) approach (delocalised bonding), or (*c*), in certain instances, intermediate degrees of delocalisation. Most attention has been paid to the metal halide- and oxide-type clusters which will therefore be discussed here first and at greater length.

A pure valence-bond approach to these systems is not encouraged by their structures, since very bent bonds must be postulated. When two directed orbitals overlap to form an appreciably bent bond, the basic notion of the VB approach, namely that the orbitals should be directed to give maximum overlap between the bonded atoms, is vitiated. Moreover, in cases such as the $Nb_6X_{12}^{2+}$ or $Nb_6Cl_{12}^{4+}$ species there is not an integral number of electron pairs per metal–metal bond; thus a VB approach would have to be extended to encompass resonance among canonical forms. Finally, the general unsuitability of simple VB theory to deal with electronic spectra is relevant here as elsewhere. For these reasons it is the several recent MO treatments of clusters which merit attention.

A very crude but general form of MO treatment has been applied[4,38,39] to all of the structural types of clusters, with the aim of providing an approximate ordering of the MO's for the metal atom cluster alone, without detailed consideration of metal–halogen (or –oxygen) interaction or of absolute orbital energies. The best that can be expected from such an approach is that it may account for gross magnetic properties, correlate bond lengths, and be consistent with the molecular structures. While it seems to do these things adequately, it is not to be expected that such a treatment can cope directly with the electronic spectra and such success as may be observed[34] could well be fortuitous.

The simple MO treatment reserves certain metal orbitals for metal–ligand σ bonding (π-bonding being neglected); those so reserved have been the ones most appropriate for either square or octahedral co-ordination. The remaining orbitals are then combined according to the dictates of group theory to form MO's for the cluster and the energies of these MO's

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[38] F. A. Cotton and T. E. Haas, *Inorg. Chem.*, **1964, 3, 10.**

[39] F. A. Cotton, *Inorg. Chem.*, 1965, **4**, 334.

are crudely estimated as proportional to overlap. Instead of absolute energy units (which are impossible to assess when virtually no atomic spectral data are available, as for several of the heavy metals) the energy of the metal *d* orbitals is itself taken as a unit of energy. Moreover, the calculations are made over a reasonable range of values of the radial wave function of the *d* orbitals to assure that the results are not a sensitive function of this poorly known variable. Fig. 8 shows the result of such a calculation for the M_6X_{12} system.

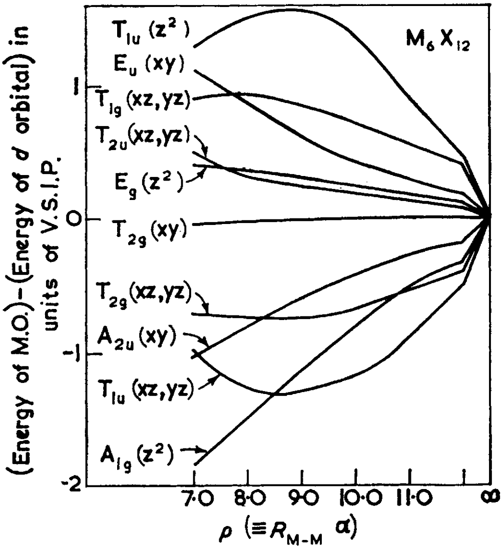

FIG. 8. *An energy level diagram for the* M_6X_{12} *species over the probable range of the* d *orbital exponent for* Nb *and* Ta. *The unit of energy is taken as the valence state ionisation potential* (*V.S.I.P.*), *approximately the* d *orbital energy of the metal atoms. The parameter* p *is the product of the metal–metal distance,* $R_{M\text{-}M}$, *in atomic units* (0·529 Å) *and the orbital exponent of the slater orbitals used,* α, *which seems very unlikely to be outside the range* 1·5—2·2 (see ref. 35). [Reproduced by permission from F. A. Cotton and T. E. Haas, *Inorg. Chem.*, 1964, 3, 10.]

This diagram accounts for the closed-shell structure of the $M_6X_{12}{}^{2+}$ (M = Nb, Ta) ions as well as for the presence[6] of one unpaired electron in the $M_6X_{12}{}^{3+}$ species. In the former compounds there are 16 electrons to be accommodated in the MO's of the cluster and thus the electron configuration is $A_{1g}{}^2\ T_{1u}{}^6\ T_{2g}{}^6\ A_{2u}{}^2$ (in the range of *p* from *ca.* 8 to *ca.* 11). In the 3+ ions there will be only one electron in the A_{2u} orbital. Assuming this same order of orbitals, we predict that the $M_6X_{12}{}^{4+}$ species should have no unpaired electrons, but experimental results on this are still lacking. In a similar manner the diagrams for the M_6X_8,[38] Re_3X_9,[38] and M_3X_8 (or M_3O_8)[3] systems indicate electron configurations in accord with their magnetic properties. Moreover, metal–metal bond orders can be estimated (as the number of electron pairs in bonding MO's divided by the number of pairs of adjacent metal atoms). These bond orders range from 8/12 = 2/3 for the $M_6X_{12}^{2+}$ species, through 12/12 = 1 for $Mo_6X_8^{4+}$ to 6/3 = 2 for the Re_3X_9 species.

The $Re_2X_8^{2-}$ ions are particularly interesting since here the Re–Re bonding[39] should consist of a σ bond, two π bonds, and a δ bond. Thus, the net bond order is four (a *quadruple* bond!), which explains the exceptionally short Re–Re distance. It also explains the eclipsed structure, because the δ bond creates a barrier against rotation with minima in the eclipsed configuration.

When the bond orders estimated in the MO treatments are plotted against the observed bond lengths (Fig. 9), a curve of physically reasonable shape is defined,[39] suggesting that the gross features of the electron configurations given are essentially correct.

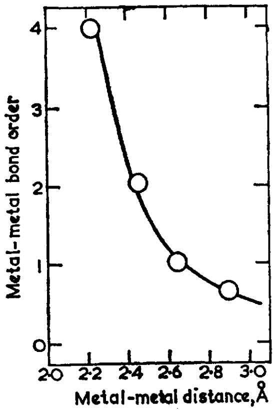

FIG. 9. *A plot of metal–metal distances* vs. *bond orders estimated by simple MO calculations in several metal halide-type metal atom cluster species. From upper left to lower right, circles represent* $Re_2Cl_8^{2-}$, Re_3X_9 (*several compounds*), $Mo_6Cl_8^{4+}$, *and the* $M_6X_{12}^{2+}$ (M = Nb, Ta) *systems* (*averaged*). [Reproduced by permission from F. A. Cotton, *Inorg. Chem.*, 1965, 4, 334.]

One drawback of an MO treatment with no arbitrary restrictions on delocalisation for systems as complex as these is that some qualitative features of the bonding are not made clear. In several cases, reformulation in terms of only moderately delocalised orbitals is helpful. For example, though it is not at all apparent from the MO diagrams,[38] it can be shown[40] by use of equivalent sets of three- and four-centre orbitals that the M_6X_8 and M_6X_{12} systems are related in an interesting way. Also, it is possible to describe the bond order of two in the Re_3X_9 species in terms of σ and π bonds.[41]

Quite recently, an attempt has been made to interpret in detail the

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[40] S. F. A. Kettle, *Theoret. Chim. Acta*, 1965, 3, 211.

[41] J. E. Fergusson, B. R. Penfold, M. Elder, and B. H. Robinson, *J. Chem. Soc.*, 1965, 5500.

electronic spectra of $Nb_6X_{12}^{2+}$ and $Ta_6X_{12}^{2+}$ systems.[33] By combining the spectral data with a crude MO approach and also allowing in an *ad hoc* way for the influence of metal–ligand interactions, an ordering of the MO's of the cluster somewhat different from that in Fig. 8 has been suggested. To some extent the discrepancy is susceptible to being resolved by magnetic data for the $M_6X_{12}^{4+}$ species.

The $Re_2X_8^{2-}$ species are particularly appropriate for spectroscopic study owing to their relative simplicity, and here the simple MO treatment has given a plausible account[39] of their spectra. Much more refined calculations[42] have confirmed these preliminary results.

The bond orders and extent of delocalisation in the clusters occurring in metal carbonyl-type compounds are generally less than in many of the lower halides as indicated by the relatively longer metal–metal bonds. However, even here an MO treatment allowing for delocalisation is to be preferred. Thus, in $Os_3(CO)_{12}$ the simple view that three $Os(CO)_4$ units based on octahedrally hybridised Os are fitted together to give three significantly bent Os–Os single bonds raises the obvious question of why then is $Os_4(CO)_{16}$, without bent bonds, not preferred. On an MO basis it can be shown[42] that the trimer is favoured because it permits a higher Os–Os interaction per $Os(CO)_4$ unit. Also, a formulation of $Rh_6(CO)_{16}$ in simple VB terms fails to account for its diamagnetism.[30] The chief difficulty which makes the carbonyl systems less susceptible to simple MO treatment is the existence of appreciable interaction of metal d_π orbitals with CO π orbitals. The nature and strength of the metal–metal bonding must be strongly influenced by these interactions in all cases, as has been demonstrated in the relatively simple $M_2(CO)_{10}$ (M = Mn, Re) system.[43]

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[42] F. A. Cotton and C. B. Harris, unpublished work.

[43] F. A. Cotton and R. M. Wing, *Inorg. Chem.*, 1965, **4**, 1328.