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BONDING IN COORDINATION COMPOUNDS CONTAINING METAL–METAL BONDS

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CONTENTS

A. INTRODUCTION

The metal–metal bond in coordination chemistry is one of those phenomena which quickly moved from the realm of being thought "scarce, if any" to the present idea of "rather commonplace". The literature dealing with these bonds continues to appear at such a rapid rate, that it is difficult to detect any sort of unity between the various physical methods being used, the synthetic work, and theoretical approaches. Several reviews have appeared[1–4], but these have mainly discussed compounds by classes, in general emphasizing descriptive chemistry of the metal–metal bonded or metal cluster compounds. An exception is the paper by Lewis[5] which discussed many of the X-ray crystallographic determinations through 1964.

In this Review, we wish to bring together the most recent results of spectro-

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scopy, crystallography, and theory, to show somewhat more clearly what is our current understanding of metal–metal bonds, and where the main gaps still lie. An attempt has been made to survey the pertinent literature as thoroughly as possible through early 1967; however the earlier collection of references to crystal structure data given by Lewis[5] will not be repeated here.

It now seems clear that the great interest manifested in metal–metal bonds in coordination compounds is justified by the key role which these bonds play in determining the chemistry of large classes of compounds, in particular compounds with heavy metals in low valent states, *e.g.* the metal carbonyls. It has been already pointed out[3] that the chemistry of these compounds is largely a matter of accident, when compared, for example, with the rules which can be set down for synthesis of other classes of chemical compounds. The most recent work of a physical nature has therefore been somewhat directed towards an application of the results as quickly as possible to chemical problems.

B. EXPERIMENTAL APPROACHES

(i) *Electrochemistry*

In view of the above, it is appropriate to begin a discussion of metal–metal bonding with brief mention of a series of papers by Dessy *et al.*[6] in which the electrochemical scission of 55 compounds containing metal–metal bonds was studied. It was felt that the electrochemical reduction potentials would give at least the relative strengths of metal–metal bonds, in both homonuclear and heteronuclear bonds. This expectation was apparently fulfilled.

Two general routes for the reductions were found:

1) $\mathrm{m{-}m' + 2e^- \rightarrow m\!:^- + m'\!:^-}$

2) $\mathrm{m{-}m' + 1e^- \rightarrow m\!:^- + m'}$.

All homonuclear compounds followed route 1, while heteronuclear compounds could follow either route 1 or 2. The ordering of cathodic potentials with variation of metal atoms was in agreement with our general ideas about the relative strengths of metal–metal bonds, *e.g.* Mn–Mn weaker than Re–Re, but S–S more stable than Se–Se, etc. Mn–Re appears intermediate to the two homonuclear compounds. Unfortunately, as the reactions are electrochemically irreversible, it is not possible to make direct correlations of reduction potentials with thermodynamic functions. Nonetheless, the extensive table of relative bond strengths and reactivities given by Dessy and co-workers will prove of direct aid to those exploring the chemistry of metal clusters. It will be interesting to see if these correlations survive the test of experiment better than previous attempts[7].

(ii) *X-Ray crystallographic investigations*

Beginning with the determination of the structure of iron enneacarbonyl by Powell and Ewens[8] in 1939, the use of X-ray crystallographic structure determination has been most active in the pursuit of the metal–metal bond. To date about 100 coordination compounds containing or suspected of containing metal–metal bonds have been investigated by this method. Two fundamental pieces of data are obtained: First, a rather accurate measure of the metal–metal distance and second, the molecular structure in the crystalline state is unambiguously determined.

While in the hands of several investigators much information about metal–metal bonding has been derived from these data, one must point out at the start certain traps into which the uninitiated have often fallen. First there is the problem of interpreting the metal–metal bond distance. Powell and Ewens[8] suggested that there was probably little or no metal–metal bonding in $Fe_2(CO)_9$ despite the fact that they measured an iron–iron distance of 2.46 Å, and the compound was known to be diamagnetic. On the other hand, Dahl and Rundle[9] found a Mn–Mn distance of 2.923 Å in $Mn_2(CO)_{10}$, about 0.5 Å larger than the sum of the covalent radii, yet in this compound the metal–metal bond is the only bridge between the two halves of the molecule. It is important to realize that sometimes a short metal–metal distance may result from the geometry of the molecule, *i.e.* bridging groups force two non-bonded metals into close proximity, while at other times a considerable amount of orbital overlap can occur even at quite long distances. Brown and Dunitz[10] considered the former situation to obtain in $Cu_2((C_6H_5)_2N_3)_2$ despite a Cu–Cu distance of 2.45 Å while on the other hand there is evidence for at least weak metal–metal bonding between layers of Au(dimethylglyoxime)$_2{}^+$AuCl$_2{}^-$ and in nickel, platinum and palladium DMG as well, though the intermetallic distances are on the order of 3.25 Å[11–13]. Mills[14,15] has shown a large variation in iron–iron bond lengths. Bryan[16] has recently pointed out this problem in the case of some compounds containing mixed metal bonds, showing that at the present time no suitable formula exists by which one can use additivity of atomic radii to calculate the length of a metal–metal bond. Furthermore, the concept of the so called "bent metal–metal bond" introduced by Dahl[17], as well as other recent orbital treatments of these compounds discussed below, cast doubt on the value of the bond length as a useful number in treating metal–metal bonding.

The second problem occurs when one tries to reconcile data obtained from other sources with crystallographic data, the problem here being the "valence tautomerism" of many compounds which can exist in bridged or unbridged structures. It appears that many conflicts will be resolved only when it is recognized that the compound in question exists in one or more tautomeric forms, and that only measurements made under the same conditions of sample (phase, temperature, etc.) may be expected to give the same result. This tautomerism has now been substantiated in several cases of compounds involving metal–metal bonds[18–24].

In Table 1 the results of recent crystallographic determinations of compounds containing metal–metal bonds are collected. Several interesting cases warrant further discussion.

The chalcogen $Se_2Fe_3(CO)_9$ was shown[44] to have a framework in which there was a square pyramid with an iron at the apex and alternate selenium and iron atoms in the basal plane. As the carbonyls are trigonally bound to the apical iron atom, and the iron was viewed as being coordinated to all of the basal atoms, the result is a seven coordinated iron atom. As the authors pointed out this is not surprising as $Fe_2(CO)_9$ also has 7 coordination at the iron if we consider that there is a metal–metal bond in that compound. The Fe_{basal}–Se–Fe_{apex} angle of only 68° is quite acute. The related sulfur compound $[C_2H_5SFe(CO)_3]_2$ has an Fe–S–Fe angle of 68.3° in an idealized C_{2v} structure which may be thought of as the junction of the basal planes of tetragonal pyramids along the chalcogen line[17]. In both of these compounds, it was proposed that bent bonds (bonds formed by the overlap of orbitals not along the same line) existed between the iron atoms, as well as between the iron and selenium or sulfur atoms. For octahedral iron orbitals the angle between overlapping orbitals in the sulfur compound is 113°. The sharp bridging angle is viewed as necessary to give better overlap. In considering the structure of Roussin's Black salt, $CsFe_4S_3(NO)_7 \cdot H_2O$ Lipscomb[45] pointed out that there is a four-center molecular orbital among iron atoms, which is weakly bonding. This was perhaps a foreshadowing of what was to be expected in the structures of the chalcogenides. More recently Dahl[31] has examined $(C_5H_5FeS)_4$ with similar results, and Bryan[30] has likewise found a C_{2v} nucleus in $([C_6H_5)C$–S-$Fe(CO)_3]_2$ where the Fe–S–Fe angle is only 67.4°.

The polynuclear iron carbonyls and carbonylferrates have been the subject of several investigations. The structure of $Fe_4(CO)_{13}$ was found[29] to consist of four iron atoms at the corners of a tetrahedron, to each of which is bonded three CO groups. The thirteenth lies beneath one of the planes of the tetrahedron and is symmetrically bridged to three irons. On the basis of this structure the authors have asserted that it is not possible to add a fourteenth CO group to the molecule in place of the two electrons, as consideration of models showed that there was no stereochemically reasonable way to arrange fourteen CO's about the iron framework. Cotton[7] has however pointed out the danger of drawing conclusions about the feasibility of synthesizing polynuclear organometallics on the basis of stereochemical considerations. Thus, though the argument relating to the hitherto unknown $Fe_4(CO)_{14}$ is convincing, it should provide a challenge to skeptical synthetic chemists.

$Fe_3(CO)_{12}$ has long been the subject of controversy, as it has been thought to be impossible to reconcile the infrared spectrum[46] in the CO stretching region with a triangular array of metal atoms. That this is indeed the structure of the solid, however, seems unquestionable, as a result not only of investigations of

TABLE 1

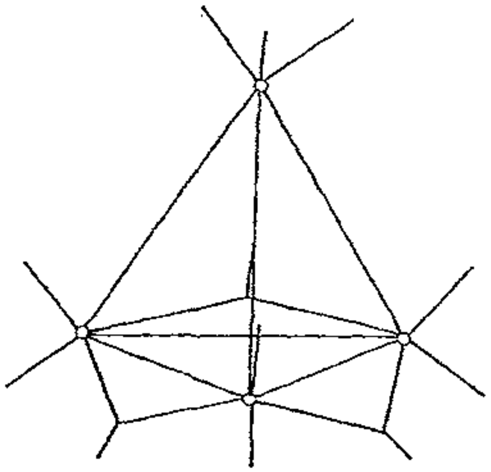
STRUCTURAL DETERMINATIONS INVOLVING METAL–METAL BONDS

Metals	*Compound*	*Metal–metal bond lengths (A)*	*Ref.*
Co–Co	$((CH_3NC)_5Co)_2$	2.74	25
Fe–Fe	$Fe_2(CO)_6(C_6H_5)_2C{=}C$	2.64	14
Fe–Fe	$Fe_2(CO)_6(CH_3C_6H_4{-}NCH_2(C_6H_5))$	2.43	15a
Fe–Fe	$Fe_2(CO)_6[C_6H_5{-}N{-}C_6H_4NH]$	2.37	15a
Fe–Fe	$(Azulene)Fe_2(CO)_5$	2.782	15b
Fe–Fe	$(C_6H_5)_3PFe_3(CO)_{11}$	—	26
Fe–Fe	$Fe_3(CO)_8(C_6H_5{-}C{=}C{-}C_6H_5)_2$	2.428	
	Black isomer	2.435	27
	Violet isomer	$\left\{\begin{matrix}2.469\\2.457\end{matrix}\right\}$	
Fe–Fe	$(C_2H_5)_3N^+HFe_3(CO)_{11}^-$	$\left\{\begin{matrix}2.685\\2.696\\2.577\end{matrix}\right\}$	28
Fe–Fe	$Fe_3(CO)_{12}$	2.73 2.64 2.25	28
Fe–Fe	$Fe(C_5H_5N)_6^{2+}Fe_4(CO)_{13}^{2-}$	2.58 2.50	29
Fe–Fe	$\{C_6H_5{-}C{-}S{-}Fe(CO)_3\}_2$	2.507	30
Fe–Fe	$\{C_5H_5FeS\}_4$	2.65	31
Mo–Mo	$[\{MoO(C_2O_4)H_2O\}_2O_2]^{2-}$	2.541	32
Re–Re	Re_3Cl_9	2.5	33
Tc–Tc	$Tc_2(CO)_{10}$	3.036	34
Sn–Fe	$Sn[Fe(CO)_4]_4$	—	35
Sn–Fe	$CpFe(CO)_2(C_6H_5)_2Sn$	2.536	16
Sn–Fe	$(CH_3)_4Sn_3[Fe(CO)_4]_4$	$\left\{\begin{matrix}2.747\\2.625\end{matrix}\right\}$	36
Sn–Fe	$Sn(Fe(CO)_4)_2$		37
Sn–Mn	$(C_6H_5)_2Sn(Mn(CO)_5)_2$	2.70	38
Sn–Mn	$(C_6H_5)_3SnMn(CO)_4P(C_6H_5)_3$	2.627	39, 40
Sn–Mn	$(C_6H_5)_3Sn{-}Mn(CO)_5$	2.67	39, 40
Hg–Fe	$(BrHg)_2Fe(CO)_4$	2.44 2.59	41
Ti–Al Ti–Ti	$[(C_5H_5)_2TiAl(C_2H_5)_2]_2$		
	Ti–Al	2.792	42
	Ti–Ti	3.110	
Cu–Mn	$\{[(CH_3)_2As(C_6H_4)]_2As(CH_3)\}Cu{-}Mn(CO)_5$	2.56	43
Ge–Mn	$(C_6H_5)_3Ge{-}Mn(CO)_5$	2.54 2.53	43
Au–Co	$(C_6H_5)_3PAuCo(CO)_4$	2.50	43

$Fe_3(CO)_{12}$ itself[28,47] (complicated by a disorder in the crystal), but also of related compounds such as $HFe_3(CO)_{11}^-$ [28] and $Ph_3PFe_3(CO)_{11}$[26]. In all cases the structure may be viewed as one in which one of the bridging CO groups of $Fe_2(CO)_9$ has been replaced by a *cis* di-substituted octahedral $Fe(CO)_4$ unit. The position of the hydrogen atom in $HFe_3(CO)_{11}^-$, which is not observed, is inferred as being a symmetrical bridge between the two iron atoms which are joined by the bridging

CO's. This is then regarded by the authors as a protonated metal–metal bond. Although it may yet be possible to resolve the conflict between infrared and crystallographic data through a valence tautomerism argument (*i.e.* two or more structures for $Fe_3(CO)_{12}$ in solution) preliminary attempts at experimental verification of this argument[26] have been negative.

A similar controversy between crystallographic data and infrared solution spectra in the 5 micron (CO stretching) region[48] occurs in the case of $Co_4(CO)_{12}$, for which Corradini[49] proposed the structure shown in Figure 1, despite a crystal disorder preventing the removal of all uncertainty. Dahl[24] has however recently verified this structure and found the same structure for $Rh_4(CO)_{12}$, though a simple tetrahedral structure, with three CO's bonded terminally to each metal atom was found for $Ir_4(CO)_{12}$. Smith[50] proposed the structure illustrated in Figure 2 to explain the infrared solution data for the cobalt compound, and recently Cotton[24] attempted a rationalization of these problems based upon the interconversion of Corradini's structure to Smith's structure through an unbridged structure of the iridium type.



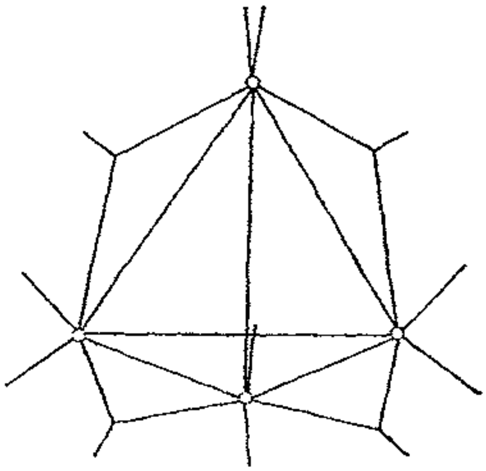


Fig. 1. Structure of crystalline $Co_4(CO)_{12}$ (from ref. 48).

Fig. 2. Proposed structure for $Co_4(CO)_{12}$ in solution (from ref. 50).

The structural work on manganese carbonyl showed some time ago[9] that the Mn–Mn distance was long, 2.923 Å. The isomorphous rhenium compound also showed a long metal–metal bond distance of 3.02 Å, and recently it was reported[34] that the compound $Tc_2(CO)_{10}$ was also isomorphous with manganese carbonyl and has a Tc–Tc distance of 3.036 Å. It seems that the characteristically large metal–metal distance is inherent in the bonding scheme of the unbridged, octahedral complexes of this sort, however no detailed work has been carried out to elucidate the reasons for this as yet. Cotton and Dunne[25] reported that the compounds

$Fe_2(CO)_8I_2$ and $\{(CH_3NC)_5Co\}_2^{2+}$ are also isostructural with $Mn_2(CO)_{10}$, the Co–Co distance being 2.74 Å. Further study of the implications of the structural work on all of these compounds should be exceedingly useful, for it bears heavily on the question of the forces involved in metal–metal bonding, pointing up the differences in such a dramatic way between the bridged and the unbridged complexes. It is, in a sense, the clearest inorganic example of the competing effects of steric and electrical forces in determining structure and bonding. The work on valence tautomerism in the metal–metal bonded compounds is, of course, along these same lines.

Several papers have appeared in the recent literature[14, 15], which have used crystallography as a tool to analyze and identify the products of a reaction. It seems strange at first that one should have to resort to such an elaborate analytical tool, but this merely points up the fact recently mentioned by Cotton[3] that the chemistry behind the production of compounds containing clusters of metal atoms is very much accidental, and we have as yet no clear-cut synthetic methods to produce particular compounds. It would seem that these methods will be the result not only of more synthetic work, but also of increased perseverance on the theoretical front, leading to a better understanding of the nature of the bonding.

In summary, it is apparent that crystallographic structure data is an absolute necessity before we may begin to compare any theoretical work with experiment. The structure, bond lengths and angles are essential pieces of information. However, it must be kept in mind that they give us only limited information about the forces between the atoms, the shape of the potential when we stretch a metal–metal bond, what energy is needed to dissociate it, and what conditions are needed to form it. For these data we must appeal to other methods.

(iii) *Infrared and Raman spectroscopy*

Commercial far infrared instrumentation has been available for almost 5 years, and inexpensive, laser-excited commercial Raman instrumentation for about 3 years; nevertheless, to date very few vibrations involving metal–metal bonds have been reported. For molecules possessing only one metal–metal bond about a center of symmetry, the metal–metal stretching frequency will only be Raman active; however, in cases of more than one metal–metal bond, or lower symmetry, it will frequently be possible to observe these stretches in the far infrared region. The expected low frequencies (250–100 cm^{-1}) are a result of both the heavy atomic weights of the atoms involved in the vibration, and the generally low force constants expected for these bonds in many molecules. In the absence of any significant amount of data on the force constants, we can in any case assume that the vibrations fall in the above region mainly as a consequence of the weight. The proof of a vibrational assignment of an infrared or Raman band to a metal–metal stretch is not usually trivial. In general, pure stable isotopic compounds are not available, so what one tends to do is to compare ligand vibrations with those of the uncoordinated ligand, more or less subtract away this spectrum, and hope that the remaining bands belong to the metal–metal skeleton. These bands are furthermore expected to show little variation in frequency as ligands are varied within a given class (*e.g.* Cl, Br, I).

A few frequencies have been reported. Woodward[51], many years ago, measured the Raman spectrum of the Hg_2^{2+} ion in aqueous solution as the nitrate salt, finding a band at 169 cm^{-1}. More recently, Corbett[52] examined the Cd_2^{2+} ion ($AlCl_4^-$ salt) and found a band at 183 cm^{-1} for the molten salt, which shifted to 177 cm^{-1} in the solid. Although comparison of the two frequencies is difficult, it appears that the force constant of the Cd–Cd bond is considerably less that of the Hg–Hg.

Stammreich and co-workers[53] examined the Raman spectrum of $Cd(Co(CO)_4)_2$ and $Hg(Co(CO)_4)_2$ in methanol, benzene, and cyclohexane solutions, and determined that the symmetric Co–M–Co stretching frequency occured at 152 cm^{-1} in the Cd compound and 161 cm^{-1} in the Hg. Recently Edgell *et al.*[54] have reported the asymmetric stretching frequency for the Hg compound at 192 cm^{-1} in tetrahydrofuran solution. Although results have not yet been reported, it seems reasonable that one can make some assumptions about the localization of motion of the $Co(CO)_4$ units in these molecules and derive force constants which should reproduce the symmetric and asymmetric frequencies. This will give a good measure of one aspect of the bonding in these compounds.

All other results extant in the literature are of a more speculative nature. Cross and Glockling [55] have assigned a band at 228 cm^{-1} to a Ge–Ge stretching mode in Ph_3Ge_3GeH and $Ph_3Ge_3GeCH_3$, however more detailed information was not given.

Cotton and Wing[56] tentatively assigned a band at 120 cm^{-1} in the Raman spectrum of $Re_2(CO)_{10}$ to the Re–Re stretching mode. This would result in a force constant of about 0.8 mdynes/Å. It will be quite interesting to see what force constants result from the Mn, Re, and Tc decacarbonyls to compare with other metal–metal bonds and discover if any connection can be found between the long bond length and the force constant.

Adams *et al.*[57] briefly noted that an infrared band at 219 cm^{-1} may be an iron–mercury stretch in $Fe(CO)_4(HgCl)_2$. As the bromo and iodo compounds are well known it should be possible to determine both the symmetric and asymmetric stretching frequencies, as well as to get some idea of the magnitude of the variation in interaction of the different halogens in the metal–metal bond. The mixed halo compounds would, of course, also be quite interesting to look at.

In the far infrared spectrum of the ions $Rh_2X_2(SnX_3)_4^{4-}$ one band was found[58] which remained nearly constant for X=Cl and Br. This was found at 209 cm^{-1} in the chloro compound and 217 cm^{-1} in the bromo compound. It was assigned to an Rh–Sn stretching mode. In the same paper, the authors reported one band in the very symmetric $Pt(SnX_3)_5^{3-}$ ion which could not be assigned to an SnX_3 vibration (X=Cl, Br). This band was found at "*ca.* 200 cm^{-1}" and was split into two bands in the bromo compound. Further details are not given, however this is probably a Pt–Sn stretching mode.

For seven compounds containing octahedral clusters of molybdenum and tungsten atoms Cotton *et al.*[59] recently reported metal–metal stretching vibrations in the region of 210–240 cm^{-1} for six Mo clusters, and 150 cm^{-1} for the single W cluster examined.

It is quite likely that there remains a good deal of unpublished data which will appear in the literature in the next year in this area. These data will be of great value for comparison with the calculations of molecular orbital theory on the compounds in question. We have seen in the past[60] how valuable accurate force constants can be in interpreting bonding in coordination compounds, especially if we at the same time keep in mind the approximations we have made to obtain these force constants, the importance of interaction constants which are difficult to determine[61], and the bridge we have used between the molecular orbital picture and the force constants. Although the experimental data can be obtained, the last point, interpretation of these data, is the area where effort must be concentrated. Little or no concrete work on metal–metal bonds yet exists in this area.

(iv) *Mass spectrometry*

Complementary information to that obtained from infrared and Raman investigations of metal–metal bonds comes from the recent work on the mass spectra of these compounds. This work provides information about the stability of the metal–metal framework relative to the attached ligands, and may also give information about the energy needed to break metal–metal bonds. Thus infrared spectroscopy supplies us with data about the lower part of the potential curve, while mass spectra attempt to examine the upper, dissociation section.

Experimentally, mass spectroscopists have been hesitant about allowing inorganic chemists to put their samples into the mass spectrometer, as the metals may short circuit the ion source, as well as deposit in various places, a particularly troublesome spot being the detector. The use of photoionization has partly eliminated these problems, and the metal deposits have apparently not been as severe a bother as was once supposed. It is of course important, that the compound have some realistic vapor pressure so that a mass spectrum can be obtained without unreasonable amounts of heating of the sample. As will be seen below, heating, even to moderate temperatures, can result in substantially different mass spectra.

Winters and Kiser[62] were the first to investigate the mass spectra of compounds containing metal–metal bonds, though Hurd *et al.*[63] reported some mass spectral data as proof of the composition of manganese carbonyl some time ago. In a detailed investigation of the mass spectra of $Mn_2(CO)_{10}$ and $Co_2(CO)_8$ it was found that ions of the type $M_2(CO)_x^+$(x=0–8 Co, 0–5, 10, Mn) occurred in relatively high abundance. Indications were that fragmentation occurs by successive removal of CO groups from the metal–metal framework. From appearance potential data it was concluded that $Co(CO)_4\cdot$ but not $Mn(CO)_5\cdot$ is formed in the dissociative process to a significant extent. An attempt was made to combine the appearance potential data with published data for the heat of formation of $Co_2(CO)_8$ to derive a value for the bond dissociation energy of the Co–Co bond in the reaction $Co_2(CO)_8 \rightarrow 2\ Co(CO)_4$, 76 kcal/mole being obtained. Since the appearance of this report, Bidinosti and McIntyre have also examined the mass spectra of these two compounds[64,65] using a pyrolysis cell described by Bidinosti and Porter[66]. By varying the temperature between 35 and 85° C, radicals could be produced which were then allowed to effuse into the mass spectrometer. By following the increase of the ratio $Co(CO)_4^+/Co_2(CO)_8^+$, for example, and noting the temperature at which $Co(CO)_4^+$ could be detected below its appearance potential, the ionization potential for the reaction $Co(CO)_4\cdot + e \rightarrow Co(CO)_4^+ + 2e$ could be determined, and the appearance potential for $Co(CO)_4^+$ in the assumed reaction $Co_2(CO)_8 + e \rightarrow Co(CO)_4^+ + Co(CO)_4\cdot + 2e$ was measured using the method of Warren[67]. The difference of the appearance potential and the ionization potential thus determined might be the radical dissociation energy for the metal–metal bond; in the case of $Co_2(CO)_8$ a value of 11.5 ± 4.6 kcal was obtained by this method. For $Mn_2(CO)_{10}$ a radical dissociation energy of 18.9 ± 1.4 kcal was obtained. Just what relation these values bear to the 76 kcal for $Co_2(CO)_8$ of Kiser[62] and the 34 ± 13 kcal for $Mn_2(CO)_{10}$ given by Cotton and Monchamp[68] is an intriguing question. It seems likely that one must consider more carefully the processes taking place in fragmentation, and that perhaps the view of Bidinosti *et al.* is oversimplified. On the other hand, all four values may be accurate determinations for different processes. More work is needed.

King[69] measured the mass spectra of several polynuclear metal carbonyls. For $Co_4(CO)_{12}$ all ions of the type $Co_4(CO)_n^+$ $n = 1$–12 were found; although relative abundances were not given. It was asserted that the Co_4^+ ion was perhaps a tetrahedral cluster of cobalt atoms. Similarly, successive removal of CO groups from $Ru_3(CO)_{12}$ to give the Ru_3^+ ion was observed, but for $Fe_3(CO)_{12}$ stepwise loss of CO was found only up to the $Fe_3(CO)_3^+$ ion after which rupture of the iron–iron bonds occurred. This implies that the iron–iron bonds are weaker than the ruthenium–ruthenium or cobalt–cobalt bonds in these compounds. This conclusion would be completely consistent with Dahl's[24,28] results on the structures of the polynuclear carbonyls. King has also reported in the same paper that the mass spectrum of $[C_5H_5Cr(CO)_3]_2$ shows no Cr_2^+ ion or any other ion containing two chromium atoms, whereas the corresponding molybdenum compound showed all ions of the formula $(C_5H_5)_2Mo_2(CO)_x$ $x = 0, 2, 3, 4, 5, 6$. It thus appears that unlike its molybdenum analog the chromium compound readily dissociates to the monomer in the gas phase.

Johnson *et al.*[70] have compared the mass spectra of $Mn_2(CO)_{10}$, $Re_2(CO)_{10}$ and $MnRe(CO)_{10}$. The doubly charged species $Re_2(CO)_n^{2+}$ were seen, but for the other two compounds they were not observable. It was felt that this provided some evidence for the fact that the Mn–Re bond was probably intermediate in strength between Mn–Mn and Re–Re. The fact that $MnRe(CO)_5^+$ appears in high abundance may be indicative of the fact that 5 CO groups are lost quite easily from this molecule, though this conclusion is perhaps a bit premature. Other polynuclear carbonyls were also examined in this work, including $Os_3(CO)_{12}$, which showed no fragmentation to mono- or binuclear species, and gave successive removal of CO groups to the Os_3^+ core. $Rh_4(CO)_{12}$ showed the Rh_4^+ core, plus fragmentation to binuclear species, and $Os_4O_4(CO)_{12}$ gave a mass spectrum which was believed to be consistent with the schematic formulation of this compound as an adduct of $Os_3(CO)_{12}$ and OsO_4.

In an examination of the mass spectra of halogen bridged metal nitrosyls[71], it was found that the breakdown pattern observed depended upon the stability not only of the metal–metal bond but of the four membered ring as well. The spectra indicated that CO groups were lost more readily than NO groups in metal–metal bonded compounds. Thus far there has been no quantitative work in this direction, however.

C. THEORETICAL APPROACHES

A few ventures have been made into the area of a description of the metal–metal bond from the point of view of bonding theory. Those due to Cotton have recently been summarized[3]. Essentially the approach used by Cotton and co-workers to treat $Re_2Cl_8^{2-}$[72,73] $Re_3Cl_{12}^{3-}$, $Mo_6Cl_8^{4+}$, and $Ta_6Cl_{12}^{2+}$[74] is an approximate molecular orbital treatment (more exact in the case of the $Re_2Cl_8^{2-}$ ion than for the others) which is in practice limited to consideration of the bonding within the metal polyhedra. Despite the approximations, the work of Cotton and Haas does account for the observed magnetic properties of the ions considered, and seems to predict well the relative orbital energies. More data, carefully analyzed, on the electronic spectra of the complex ions is needed before we can know just how well these calculations have succeeded in determining the molecular orbital picture of the molecule. (One attempt[75] made thus far for $Nb_6X_{12}^{2+}$ and $Ta_6X_{12}^{2+}$ disagrees partially with Cotton's results, but neither work is free from ambiguous interpretation.) The work of Cotton also points up the inadequacy of using standard electron pair bond concepts and methods in treating these ions. In view of this, it is somewhat surprising that the authors have attempted to establish the degree of multiple bonding in these and other compounds[72]. This is done by dividing the number of electron pairs in bonding molecular orbitals by the number of pairs of adjacent metal atoms. For $Re_2X_8^{2-}$ this procedure gives the interesting result that there is a Re–Re quadruple bond. Further, Cotton has shown that the degree of multiple bonding calculated in this way seems to decrease with the metal–metal bond length. It should be pointed out that such correlations must be used with extreme caution, because they essentially involve a translation of molecular orbital, delocalized, results, into electron pair bond language.

Kettle, in a series of papers[76–81], has discussed the use of equivalent orbitals for the treatment of compounds with metal–metal bonds. It is clear that though we gain tremendously in our ability to explain the properties of the metal cluster compounds when we leave the electron pair bond behind and go to molecular orbital descriptions, there is a certain loss of the concept of the bond itself. This can be recovered in certain cases (note particularly the requirement that $S=O$, no unpaired electrons) through the use of equivalent orbitals. These were first developed by Lennard-Jones and Pople[82], and Hall[83] for just this reason. From the SCF molecular orbitals linear combinations are constructed without regard to symmetry type, along the bonds. The details and several simple examples are to be found in an article by Pople[84]. Jørgenson[85] has pointed out the advantages and difficulties in working with equivalent orbitals. What has been done by Kettle in the case of metal–metal bonded compounds is to use this topologically equivalent orbital method to calculate relative orbital energies, making many of the approximations inherent in Cotton's treatment but including all contributions due to ligand sites, and see what picture of the metal atom cluster, with ligands results. In general, the same relative orbital energies are obtained as those of Cotton[72–74] but the larger basis set used results in a better picture of the bonding in the ions, together with a better "feeling" for the forces in the metal–metal bonds. The latter is of course the reason for this work. A large number of octahedral, tetrahedral and triangular complexes have been treated in this way. More recently, the method has been applied to the metal carbonyls[80,81]. The general considerations, preliminary to description of the electronic structure in detail, were reported for $Ir_4(CO)_{12}$, $Co_4(CO)_{12}$, $Os_3(CO)_{12}$, $Fe_3(CO)_{12}$, $Fe_2(CO)_9$, $Co_2(CO)_8$, $Mn_2(CO)_{10}$ in the first article, and in the second the very interesting compound $Rh_6(CO)_{16}$ was treated in more detail. This compound is one of the only known metal carbonyls which does not obey the so called rare gas rule, that is, it has two electrons more than the nearest closed shell. Kettle has shown, however, that if one constructs equivalent orbitals for this molecule and begins to allocate electrons to the bonding orbitals, one has two electrons less [60–62] than the number needed to fill the bonding orbitals. This is explained as being due to the destabilization of an A_2 orbital, causing it to be bonding but unoccupied. The problem comes in evaluating such a destabilization, or, in other words, evaluating the extent of Metal–π_{CO}^* orbital interaction. From an experimental point of view, it is clear that if the description of Kettle is reasonable, as it seems to be, then the infrared and electronic spectra of $Rh_6(CO)_{16}^-$ and $Rh_6(CO)_{16}^{2-}$ would provide a quantitative method of evaluating the interaction between the CO π antibonding orbitals as a function of negative charge on the ion. To date these ions have not been synthesized.

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REFERENCES

1 R. S. Nyholm, *Proc. Chem. Soc.*, (1961) 273.
2 M. Beck, ed., *Proc. Symp. Coord. Chem. Akademiai Kiado, Budapest*, 1965, p. 335.
3 F. A. Cotton, *Quart. Rev.*, 20 (1966) 389.
4 E. L. Muetterties and C. M. Wright, *Quart. Rev.*, 21 (1967) 109.
5 J. Lewis, *Pure Appl. Chem.*, 10 (1965) 11.
6 R. E. Dessy, P. M. Weissman and R. L. Pohl, *J. Am. Chem. Soc.*, 88 (1966) 5117. See also *ibid*, 5112, 5121, 5125, 5129.
7 F. A. Cotton and G. Wilkinson, *Advanced Organic Chemistry*, 2nd ed., Interscience, New York, 1966, pp. 652–59.
8 H. M. Powell and R. V. G. Ewens, *J. Chem. Soc.*, (1939) 286.
9 L. F. Dahl and R. E. Rundle, *Acta Cryst.*, 16 (1963) 419.
10 I. D. Brown and J. D. Dunitz, *Acta Cryst.*, 14 (1961) 480.
11 R. E. Rundle, *J. Am. Chem. Soc.*, 76 (1954) 3101.
12 F. Frasson, C. Panattoni and R. Zannetti, *Acta Cryst.*, 12 (1959) 1027.
13 L. E. Godycki and R. E. Rundle, *Acta Cryst.*, 6 (1953) 487.
14 O. S. Mills and A. D. Redhouse, *Chem. Comm.*, (1966) 444.
15 a. P. E. Baikie and O. S. Mills, *Chem. Comm.*, (1966) 707.
b. M. R. Churchill, *Inorg. Chem.*, 6 (1967) 190.
16 R. F. Bryan, *J. Chem. Soc. A*, (1967) 192.
17 L. F. Dahl and C. H. Wei, *Inorg. Chem.*, 2 (1963) 328.
18 K. Noack, *Spectrochim. Acta*, 19 (1963) 1925.
19 G. Bor, *Spectrochim. Acta*, 19 (1963) 2065.
20 C. E. Keller, G. K. Emerson and R. Pettit, *J. Am. Chem. Soc.*, 87 (1965) 1388.
21 R. D. Fischer, A. Vogler and K. Noack, *J. Organometal. Chem.*, 7 (1967) 135.
22 K. Noack, *J. Organometal. Chem.*, 7 (1967) 151.
23 F. A. Cotton and G. Yagupsky, *Inorg. Chem.*, 6 (1967) 15.
24 F. A. Cotton, *Inorg. Chem.*, 5 (1966) 1083.
25 F. A. Cotton and T. G. Dunne, *Proc. Chem. Soc.*, (1964) 175.
26 R. J. Angelici and E. E. Seifert, *Inorg. Chem.*, (1966) 1457.
27 R. Dodge and V. Shomaker, *J. Organometal. Chem.*, 3 (1965) 274.
28 L. F. Dahl and J. F. Blount, *Inorg. Chem.*, 4 (1965) 1373.
29 R. J. Doedens and L. F. Dahl, *J. Am. Chem. Soc.*, 88 (1966) 4847.
30 H. P. Weber and R. F. Bryan, *J. Chem. Soc. A*, (1967) 182.
31 C. H. Wei, G. R. Wilkes, P. M. Treichel and L. F. Dahl, *Inorg. Chem.*, 5 (1966) 900.
32 F. A. Cotton and S. M. Morehouse, *Inorg. Chem.*, 4 (1965) 1377.
33 F. A. Cotton and J. T. Mague, *Inorg. Chem.*, 3 (1964) 1402.

34 M. F. Bailey and L. F. Dahl, *Inorg. Chem.*, 4 (1965) 1140.

35 M. I. Bruce, J. Cotton, D. A. Harbourne, S. A. R. Knox, I. Paul, T. Rosevear and F. G. A. Stone, *Abstr. 9th Int. Conf. Coord. Chem.*, (1966) 173.

36 R. M. Sweet, C. J. Fritchie, Jr., and R. A. Schunn, *Inorg. Chem.* 6 (1967) 749.

37 J. D. Cotton, *Chem. Comm.*, (1966) 253.

38 B. T. Kilbourn and H. M. Powell, *Chem. Ind.*, (1964) 1578.

39 R. F. Bryan, *Proc. Chem. Soc.*, (1964) 232.

40 R. F. Bryan, *J. Chem. Soc. A* (1967) 172.

41 H. W. Baird and L. F. Dahl, *J. Organometal. Chem.*, 7 (1967) 503.

42 P. Corradini and A. Sirigu, *Abstr. 9th Int. Conf. Coord. Chem.*, (1966) 179.

43 B. T. Kilbourn, T. L. Blundell and H. M. Powell, *Chem. Comm.*, (1965) 444.

44 L. F. Dahl and P. W. Sutton, *Inorg. Chem.*, 2 (1963) 1067.

45 G. Johansson and W. N. Lipscomb, *Acta Cryst.*, 11 (1958) 594.

46 G. R. Dobson and R. K. Sheline, *Inorg. Chem.*, 2 (1963) 1313.

47 R. E. Rundle and L. F. Dahl, *J. Chem. Phys.*, 26 (1957) 1751.

48 H. Haas and R. K. Sheline, *J. Inorg. Nucl. Chem.*, 29 (1967) 693.

49 P. Corradini, *J. Chem. Phys.*, 31 (1959) 1676.

50 D. L. Smith, *J. Chem. Phys.*, 42 (1965) 1460.

51 L. A. Woodward, *Phil. Mag.*, 18 (1934) 823.

52 J. D. Corbett, *Inorg. Chem.*, 1 (1962) 700.

53 H. Stammreich, K. Kawai, O. Sala and P. Krumholz, *J. Chem. Phys.*, 35 (1961) 2175.

54 W. F. Edgell, A. T. Watts, J. Lyford, iv and W. M. Risen, Jr., *J. Am. Chem. Soc.*, 88 (1966) 1815.

55 R. T. Cross and F. Glockling, *J. Organometal. Chem.*, 3 (1965) 146.

56 F. A. Cotton and R. M. Wing, *Inorg. Chem.*, 4 (1965) 1328.

57 D. M. Adams, D. J. Cook and R. D. W. Kemmitt, *Nature*, 205 (1965) 589.

58 D. M. Adams and P. J. Chandler, *Chem. Ind.*, (1965) 269.

59 F. A. Cotton, R. M. Wing and R. A. Zimmerman, *Inorg. Chem.*, 6 (1967) 11.

60 See, for example, W. F. Edgell, W. E. Wilson and R. Summitt, *Spectrochim. Acta*, 19 (1963) 863.

61 L. H. Jones, *Coord. Chem. Rev.*, 1 (1966) 351.

62 R. E. Winters and R. W. Kiser, *J. Phys. Chem.*, 69 (1965) 1618.

63 D. T. Hurd, G. W. Sentell, Jr., and N. J. Norton, *J. Am. Chem. Soc.*, 71 (1949) 1899.

64 D. R. Bidinosti and N. S. McIntyre, *Chem. Comm.*, (1966) 555.

65 Ibid, (1967) 1.

66 D. R. Bidinosti and R. F. Porter, *J. Am. Chem. Soc.*, 83 (1961) 3737.

67 W. Warren, *Nature*, 165 (1950) 810.

68 F. A. Cotton and R. R. Monchamp, *J. Chem. Soc.*, (1960) 533.

69 R. B. King, *J. Am. Chem. Soc.*, 88 (1966) 2075.

70 B. F. G. Johnson, J. Lewis, I. G. Williams and J. M. Wilson, *J. Chem. Soc. A*, (1967) 341.

71 Ibid, 338.

72 F. A. Cotton, *Inorg. Chem.*, 4 (1965) 334.

73 F. A. Cotton and C. B. Harris, *Inorg. Chem.*, 6 (1967) 924.

74 F. A. Cotton and T. E. Haas, *Inorg. Chem.*, 3 (1964) 10.

75 M. B. Robin and N. A. Kuebler, *Inorg. Chem.*, 4 (1965) 798.

76 S. F. A. Kettle, *Theor. Chem. Acta*, 3 (1965) 282.

77 Ibid, 211.

77 Ibid, 4 (1966) 150.

79 S. F. A. Kettle, *J. Organometal. Chem.*, 5 (1966) 588.

80 S. F. A. Kettle, *J. Chem. Soc. A*, (1966) 1013.

81 Ibid, (1967) 314.

82 J. Lennard-Jones and J. A. Pople, *Proc. Roy. Soc. A*, 202 (1950) 166.

83 G. G. Hall, *Proc. Roy. Soc. A*, 202 (1950) 323.

84 J. Pople, *Quart. Rev.*, 11 (1957) 273.

85 C. K. Jørgenson, *Orbitals in Atoms and Molecules*, Academic Press, New York, 1962, p. 72.