METAL–METAL INTERACTION IN TRANSITION METAL COMPLEXES

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INTRODUCTION

Interest has recently centred around compounds containing metal–metal bonds, and the range of complexes has covered interaction between transition elements and a large number of the post-transition elements. In order to restrict the general discussion of these complexes, we would like to deal with compounds involving bonding between the elements of the transition series and to include interaction with the elements of the copper and zinc triads ($d^{10}s^1$ and $d^{10}s^2$ configurations). However, before discussing the complexes it is important to define the use that will be made of the terms oxidation state and configuration. The oxidation state may be defined as "the formal charge left on an atom when all the ligands are removed in their closed shell configuration and any element–element bonds are broken homolytically". The *formal* electron configuration of the metal atom may similarly be defined as the configuration of the metal atom *before* metal–metal bonding is considered to occur. Thus in $Mn_2(CO)_{10}$ and Hg_2Cl_2 the electron configuration of the manganese is d^7 whilst the mercury is $d^{10}s^1$, whereas the corresponding oxidation states are Mn(0) and Hg(I). It is convenient to divide the discussion of the subject of metal–metal interaction into three sections, namely:

(*a*) Metal–metal bonding between atoms of the same element.
(*b*) Metal–metal bonding between atoms of different metals.
(*c*) Methods employed to detect metal–metal interaction.

METAL–METAL BONDING BETWEEN ATOMS OF THE SAME ELEMENT

Table 1 summarizes the elements and oxidation states in which metal–metal bonding is found to occur. Metal–metal interaction has been postulated for every element in the transition block with the exception of the scandium triad. For the early transition elements this type of bonding appears to occur readily, even in the higher oxidation states, whereas for the later transition elements the bonding appears to be restricted to the lower oxidation states. Although the data are limited, the tendency for metal–metal bonding in the various oxidation states appears to reach a maximum in the middle of the transition series and be greater for second and third row elements than for the first row elements. Thus for molybdenum interaction has been postulated for the following oxidation states: (V) $[Mo(OC_6H_5)_3Cl_2]_2$, (IV) $[MoO_2]_x$, (III) $[Mo_2Cl_9]^{3-}$, (II) $[MoCl_2]_x$, (I) $[Mo(\pi C_5H_5)(CO)_3]_2$, (−I) $[Mo_2(CO)_{10}]^{2-}$. This series also illustrates many of the classes of complexes and problems that can be encountered in

Table 1a

Electron configuration		Oxidation number		
	II	III	IV	V
d^1–d^1	— —	$TiCl_3$ $ZrCl_3$ $HfCl_3(?)$	VO_2 NbI_4 TaO_2	$[Mo(OC_6H_5)_3Cl_2]_2$ — —
d^2–d^2	— —	$NbCl_3$ —	CrO_2 MoO_2 WO_2	— —
d^3–d^3	—	$[Mo_2Cl_9]^{3-}$ $[W_2Cl_9]^{3-}$	TcO_2 ReO_2	— —
d^4–d^4	$[Cr(CH_3COO)_2]_2 \cdot 2H_2O$ $MoCl_2$ WCl_2	— $[Re_3Cl_{12}]^{3-}$	— —	— —

Table 1b

Electron configuration	$-I$	0	I	II
d^5–d^5	— — —	$V(CO_4)[P(C_6H_{11})_3]_2$ — —	$[\pi C_5H_5)Cr(CO)_3]_2$ $[\pi C_5H_5)Mo(CO)_3]_2$ $[\pi C_5H_5)W(CO)_3]_2$	— — —
d^7–d^7	$[Cr_2(CO)_{10}]^{2-}$ $[Mo_2(CO)_{10}]^{2-}$ $[W_2(CO)_{10}]^{2-}$	$Mn_2(CO)_{10}$ $Tc_2(CO)_{10}$ $Re_2(CO)_{10}$	$[(CO)_4FeI]_2$ — —	$[Co(CNCH_3)_5]_2(ClO_4)_4$ $[Rh(CH_3COO)_2.H_2O]_2$ —
d^8–d^8	— — —	$Fe_2(CO)_9$ $Ru_3(CO)_{12}$ $Os_3(CO)_{12}$	$[Rh(CO)_2Cl]_2$ — —	$Ni(DMG)_2$† $[Pd(NH_4)_4][PdCl_4]$ $[Pt(NH_4)_2][PtCl_4]$
d^9–d^9	$[Fe_2(CO)_8]^{2-}$ —	$Co_2(CO)_8$ $Rh_2(CO)_8$ $Ir_2(CO)_8$	$[Ni_2(CN)_6]^{4-}$ —	$[Cu(CH_3COO)_2H_2O]_2$ — —
s^1–s^1	$H_2[Ni_2(CO)_6]$ —	Cu_2 Ag_2 Au_2	$Cd_2(AlCl_4)_2$ Hg_2Cl_2	— —

Oxidation number

† DMG = dimethylglyoxime

the field of metal–metal bonding. Thus, one notable fact about the above series and also the data in *Table 1*, is the absence of any examples of bonding for the configuration $d_e{}^6$. This may be associated with the ready formation of octahedral spin-paired complexes for metals with this configuration, and the related high stability of the resulting $d_e{}^6$ configuration.

We may consider in more detail the specific examples in the above series of complexes.

(*a*) $[Mo(OC_6H_5)_3Cl_2]_2$: This molecule has been shown to be dimeric with chlorine-bridging groups[1], and a relatively short metal–metal distance (2·8 Å). In contrast to this, the "parent" molecule molybdenum pentachloride, although dimeric with chlorine bridges, has a much longer (3·84 Å) metal–metal distance[2]. The metal–metal distance in the phenoxide is of the order observed in molybdenum metal (2·73 Å), and is consistent with the formation of a metal–metal bond, whereas in the pentachloride the distance is too great to be considered as indicative of direct metal–metal bonding. The magnetic properties of the complexes are also consistent with such an interpretation, the phenoxide being virtually diamagnetic[1] whereas the pentachloride shows a magnetic moment of 1·65 β at room temperature which varies with temperature[3]. If we consider that the residual charge on the metal, in a complex, is important in determining the formation of metal–metal bonds (*vide infra*), then the replacement of chloride by phenoxide would be expected to reduce the resultant charge on the metal and hence favour metal–metal bonding.

(*b*) MoO_2: In molybdenum dioxide we have an example of a polymeric structure in which metal–metal bonding occurs. The solid has a modified rutile structure, and there are two molybdenum–molybdenum distances of 2·50 and 3·10 Å observed in the solid, the former distance corresponding to that between pairs of molybdenum ions with a molybdenum–molybdenum bond[4]. The compound is diamagnetic in agreement with this interpretation. A similar type of association between pairs of metal ions in a rutile structure is also found to occur in the dioxides of vanadium[5], tungsten[4], technetium[4], and rhenium[4]. Niobium tetrachloride and tetraiodide also have octahedral polymeric structures[6], in which the pairing of the ions with metal–metal bonding is postulated.

(*c*) $[Mo_2Cl_9]^{3-}$: This ion is considered to have a similar structure to the $[W_2Cl_9]^{3-}$ ion, in which two chlorine octahedra around each tungsten are fused together by a common face of the octahedra. The tungsten–tungsten distance is 2·40 Å as compared with 2·74 Å in the metal[7]. In order to account for the diamagnetism and the very short metal–metal distance of the complex it is suggested that there is a triple bond between the metal ions. A more detailed examination of the structure shows that the octahedral of chlorine ions is distorted to allow the tungsten groups to move closer together. In the corresponding ion of chromium, $[Cr_2Cl_9]^{3-}$, the chromium ions appear to move apart to give a chromium–chromium distance of 3·12 Å, and this compound is paramagnetic[8]. The molybdenum complex is also found to be diamagnetic[8], and a structure similar to the tungsten compound is postulated for this ion.

(*d*) $MoCl_2$: The molybdenum (II) chloride structure is based on the unit $[Mo_6Cl_8]^{4+}$, the structure of which is given in *Figure 1*. The six molybdenum

ions are at the centres of the face of a cube while the eight chlorine atoms occupy the corners[9]. There is direct interaction between the molybdenum ions, to give a multicentred metal bonding system, each molybdenum ion bonding to four other metal ions at 2·64 Å. The bonding in this type of complex is treated most satisfactorily in terms of molecular orbital theory[10]. The whole system has been shown to behave as a pseudo-atom, coordinating
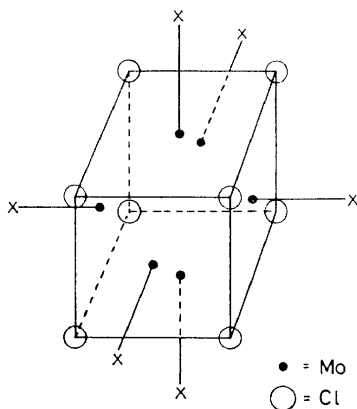

Figure 1. The structure of $[Mo_6Cl_8]^{4+}$

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six further groups, one to each molybdenum ion to give complexes of the type $[Mo_6Cl_8X_42L]$ where $X = Cl^-$ or OH^- and $L = C_5H_5N$, NEt_3, or ions of the type $[(Mo_6Cl_8)X_6]^{2-}$ (Sheldon[11]).

(*e*) $[Mo(\pi C_5H_5)(CO)_3]_2$: This complex was one of the first compounds in which the X-ray structure established that the two halves of a dimer unit were bonded only by the metal–metal bond, and involved no bridging group between the metal ions[12]. As with the previous structure of this type $Mn_2(CO)_{10}$[13], the metal–metal bond appears to be very long (3·22 Å) when compared with the valve observed in the metal (2·73 Å). As discussed below, the metal–metal distance in complexes may be critically dependent on a number of factors. For mercurous complexes large changes in bond length are observed with variation of the coordinating groups, and it would be of great interest to determine if any major variation in metal–metal distance occurs for similar complexes in this part of the periodic table.

(*f*) $[Mo_2(CO)_{10}]^{2-}$: This molecule is isoelectronic with technetium carbonyl, and is presumed to have a similar structure involving a metal–metal bond with no bridging carbonyl groups.

From this brief survey, it is apparent that metal–metal bonding may be widespaced in oxidation state, and involve a variety of structural types. Recent structural determinations for compounds of the earlier transition elements indicate that metal–metal bonding is relatively common and may play a dominant role in the chemistry of these elements. Many of the lower halide complexes of niobium and tantalum have been shown to involve

structures with metal–metal bonds, and the "mixed" valency compound $NbCl_{2.33}$ has been shown to involve clusters of Nb_3Cl_8 groups[14, 15].

Metal clusters containing three, four, five and six metal ions per unit have been established, and it appears that many of these structures may be maintained in solution[16]. Polynuclear aggregates of these types may certainly be of importance in the structure of many solvolysis intermediates of transition metal complexes.

The importance of metal–metal bonding and the inter-relationship between complexes may be illustrated by considering the recent work on the rhenium (III) halide systems. The ion $[ReCl_4]^-$ was considered to be tetrahedral, in order to account for the diamagnetism of the salts[17]. The actual structure of the complex involves the trinuclear rhenium ion[18, 19] $[Re_3Cl_{12}]^{3-}$. The structure of this ion is shown in *Figure 2*. The three

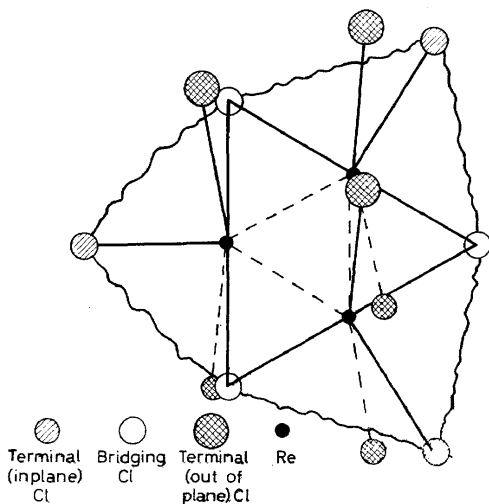
Terminal (inplane) Cl   Bridging Cl   Terminal (out of plane) Cl   Re

Figure 2. The structure of the triangular rhenium ion $[Re_3Cl_{12}]^{3-}$
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rhenium atoms are bonded to each other and lie at the corners of an equilateral triangle. There are three classes of chlorine atom in the structure, which, if we refer to the plane of the rhenium atoms, may be defined as bridging, terminal "in plane" and terminal "out of plane". Other rhenium compounds have been shown to have a related structure to this ion. Thus the structure of the $[Re_3Cl_{11}]^{3-}$ ion is obtained by removal of one of the terminal in plane chlorine atoms[20] and in the complex $(Et_2 \cdot PC_6H_5)_3Re_3Cl_9$, the phosphine groups replace the three terminal in plane chlorine atoms[21]. One of the remarkable things about the structure of these complexes is the small variation in the structural parameters within the systems on substitution and this has been taken as indicative of the high stability of the trinuclear rhenium array[20]. The data for these complexes are summarized in *Table 2*. It has also been shown that the structure of rhenium trichloride is related to these structures[22]. The molecule contains clusters of triangular rhenium units, with bridging between each cluster via one set of the terminal

out of plane chlorine atoms and the in plane terminal chlorine atoms of the $[Re_3Cl_{12}]^{3-}$ unit. This unit is considered to persist in solutions of rhenium trichloride and to be the basic starting structure for the formation of the other related compounds discussed above. A similar series of complexes appear to occur for the rhenium (III) bromide system[23].

Table 2

Complex	$[Re_3Cl_{12}]^{3-}$	$[Re_3Cl_{11}]^{2-}$	$Re_3Cl_9(Et_2PPh)_3$
Re–Re *distance* (Å)	2·47	2·46	2·49
Re–Cl (*bridge*) (Å)	2·39	2·41	2·39; 2·37
Re–Cl (*terminal* Re *plane*) (Å)	2·52	2·53	—
Re–Cl (*out of plane*) (Å)	2·36	2·30; 2·19	2·32
Cl (*term*)–Re–Cl (*term*) *out of plane* (degrees)	158	158	159

Reduction of perrhenate in aqueous hydrochloric acid solution with hypophosphite has been found to give a new type of rhenium binuclear chloro-complex $[Re_2Cl_8]^{2-}$. The structure of this binuclear ion has been recently determined[24] and the molecule has a very short rhenium–rhenium bond (2·27 Å) with no bridging halide groups. The chlorines are arranged in two square arrays around the rhenium ions, and are in an eclipsed configuration. In order to account for this and the short metal–metal distance it has been suggested that the molecule involves four sets of bonding orbitals between the rhenium atoms. If we define the rhenium–rhenium axis as the z axis, then a σ-bond is formed between the metals by overlap of the d_{z^2} orbitals, two π-bonds by interaction of the d_{xz} and d_{yz} orbitals and a δ-bond by overlap of the d_{xy} orbitals. The eight electrons of the rhenium system, four from each rhenium ion, would then occupy these four sets of orbitals to give a diamagnetic complex. For effective overlap of the d_{xy} orbitals on the two rhenium atoms, the chlorine atoms must be eclipsed; this arrangement would, however, lead to maximum steric interaction between the chlorines, and the δ-bond must be of reasonable stability to balance this effect. A similar orbital pattern has been suggested to account for the diamagnetism of the binuclear chromous acetate, in which the eight electrons of the two chromous ions, four from each chromium, would occupy the four bonding orbitals[25].

METAL–METAL BONDING BETWEEN DIFFERENT METALS

Table 3 summarizes the compounds that have been prepared containing metal–metal bonds between atoms of different metals. Although this list is not very long, this probably reflects that little directive preparative work has been carried out in this field, and is not associated with the intrinsic instability of metal–metal bonds of this type. One of the most productive areas to date has been the use of groups of the $d^{10}s^1$ configurations. A large number of adducts of phosphine gold complexes and mercury halides with transition metal complexes have been prepared recently, and these groups behave in many ways as pseudo-halogens.

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Table 3. Metal–metal bonds between different metals of the transition series

Configuration	Compound	Ref.
d^5–d^5	$[\pi C_5H_5(CO)_3W\text{—}Mo(CO)_3\pi C_5H_5]$	26
d^7–d^5	$[\pi C_5H_5(CO)_2Fe\text{—}Mo(CO)_3\pi C_5H_5]$	27
d^7–d^7	$[\pi C_5H_5(CO)_2Fe\text{—}Mn(CO)_5]$	27
	$[(CO)_5Mn\text{—}Re(CO)_5]$	28
d^8–d^8	$[Pd(NH_3)_4][PtCl_4]; [Pt(NH_3)_4][PdCl_4]$	29
d^9–d^7	$[(CO)_4Co\text{—}Mn(CO)_5]$	30
	$[(CO)_4Co\text{—}Fe(CO)_2\pi C_5H_5]$	30
	$[\pi C_5H_5(CO)_2Fe\text{—}Ni(CO)\pi C_5H_5]$	31
	$[(\pi C_5H_5Ni)_2C_6H_5C\equiv CC_6H_5.Fe(CO)_3]$	31
	$[(\pi C_5H_5Ni)_2C_6H_5C\equiv C_6H_5(Fe(CO)_3)_2]$	31
d^9–d^8	$[Cu(NH_3)_4][PtCl_4]$	32
d^9–d^9	$[FeCo_3(CO)_{12}]^-$	33
$d^{10}s^1$–d^5	$[Ph_3PAu\text{—}W\pi C_5H_5(CO)_3].Ph_3PAuV(CO)_6$	34; 35
$d^{10}s^1$–d^7	$[LAu\text{—}Mn(CO)_5]; \; L = Ph_3P, (PhO)_3P, (pMeOC_6H_4)_3P$ Ph_3As, Ph_3Sb	36
	$[Ph \, P\text{—}Au\text{—}Mn(CO)L']; \; L' = Ph \, P, (PhO) \, P,$ Ph_3As, C_5H_5N	36
	$CH_3\text{—}C\overset{\diagup CH_2AsMe_2AuMn(CO)_5}{\underset{\diagdown CH_2AsMe_2AuMn(CO)_5}{}}$	37
	$(TrA)\dagger Ag\text{—}Mn(CO)_5$	37
	$CH_3\text{—}C\overset{\diagup CH_2AsMe_2\diagdown}{\underset{\diagdown CH_2AsMe_2\diagup}{}}Cu\text{—}Mn(CO)_5$	37
$d^{10}s^1$–d^7	$[X\text{—}Hg\text{—}IrClX(CO)(Ph_3P)_2]; X=Cl, Br, I, CH_3COO$	38
	$[(Ph_2AsMe)_3Cl_2Rh\text{—}HgX]; X=F, Cl, Br, I, CH_3COO$	39
$d^{10}s^1$–d^8	$[(Ph_3PAu)_2Fe(CO)_4]; [(TrA)Cu]_2Fe(CO)_4$	34
	$[(Ph_3AsCu)_2Fe(CO)_4]; [(TrA)Ag]_2Fe(CO)_4$	35
$d^{10}s^1$–d^9	$[Ph_3PAu\text{—}Co(CO)_4]; (TrA)AgCo(CO)_4$	34
	$(TrA)CuCo(CO)_4$	35

†TrA = $(o\text{-}Me_2AsC_6H_4)_2AsMe$

The diatomic molecules involving atoms of the $d^{10}s^1$ configuration have appreciable bond strengths, that of the diatomic gold molecule only being exceeded in the halogens by chlorine. Table 4[40, 41] contains some bond energy data, obtained from mass spectroscopic studies, for these diatomic molecules. Spectroscopic studies also indicate a high bond energy and appreciable force constants for a variety of diatomic molecules involving gold and another element[42] and it is of interest to note that in addition to the relative high bond energy between like atoms, relative stable molecules can be formed between different metals. The instability of the diatomic

molecules in this region of the periodic table is not to be associated with an intrinsic low bond energy of the bond in the molecule, but with the higher bond energy obtained by "polymerization" to the metallic state. It should therefore, in principle, be possible to modify the chemistry of these metals, by coordination of other groups, to form stable metal–metal bonds.

Table 4[40, 41]

Configuration	Mol.	Bond energy (Kcal/mole)	Mol.	Bond energy (Kcal/mole)
s^1–s^1	Li–Li	26		
	Na–Na	17·8		
	K–K	11·8	Na–K	14·3
	Rb–Rb	11·1		
	Cs–Cs	10·4	Na–Rb	13·1
$d^{10}s^1$–$d^{10}s^1$	Cu–Cu	45·7	Cu–Ag	40·7
	Ag–Ag	37·6	Cu–Au	54·5
	Au–Au	51·5	Ag–Au	47·6
$d^{10}s^1$–d^5s^1			Au–Cr	50·4
$d^{10}s^1$–d^{10}			Au–Pd	33·3
$d^{10}s^1$–s^2p^2			Cu–Sn	41·4
			Ag–Sn	31·6
			Au–Sn	57·5

Using metathetical reactions, or simple addition of metal halides to planar complexes, it has been possible to prepare a variety of complexes containing gold, copper, silver and mercury to transition metal bonds as will be seen from Table 3. From the data in Table 4, it seems that stable metal–metal bonds with a variety of other metals are possible, e.g. Au–Sn. Many complexes containing metal–metal bonds of this class have been prepared previously but not recognized. The complexes $(XHg)_2Fe(CO)_4$, where X = Cl, Br, I, CN, CNS, were initially prepared in 1928 by Hock and Stuhlman[43]. We have reinvestigated these and they appear to contain mercury–iron bonds with cis distribution of the groups.

Using these complexes we have attempted to assess the order of electro-negativity relative to iodine of the gold and mercury halide adducts by comparing the infra-red spectra of the iron carbonyl complexes[44]. Table 5 summarizes the data on the infra-red spectra of a series of complexes with these metals. As the groups $Ph_3PAu–$ and $X–Hg^+$ both have the $d^{10}s^1$ configuration the electronegativity of the $X–Hg^+$ group would be expected to

Table 5. Infra-red spectra of $L_2Fe(CO)_4$

Ligand	Position of absorption bands, $\bar{\nu}$ (cm^{-1})		
$Ph_3P–Au$	2004 (m)	1934 (s)	1894 (s)
X–Hg	2090–2095 (m)	2040–2025 (s)	2020 (s)
I	2135 (m)	2089 (s)	2068 (s)

m = medium; s = strong

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be greater than that of the phosphine–gold group because of the charge on the mercury. From the pattern of the CO-frequencies in the infra-red, the structure of the three sets of complexes is similar and from the variation in the CO-frequencies, the electronegativity of the mercury–halide moiety is intermediate between that of triphenyl–phosphine–gold and iodine.

As with the phosphine and arsine substituted gold–manganese penta-carbonyl[36] derivatives, a surprising feature of the infra-red spectra is the small change in the carbonyl region on varying the group $[Hg-X]^+$ where $X = Cl, Br, I, CN$. Similarly, Nyholm and Vrieze[38] found only small changes in the carbonyl frequency for the rhodium–mercury complexes of the $[X-Hg-IrClX(CO)(Ph_3P)_2]$ group (see *Table 3*) on changing the group X. In the case of the latter complexes and the iron–mercury compounds we have measured the infra-red spectra in the low frequency region and identified mercury–metal vibrations in the region $250-140$ cm^{-1}. There appears in this instance to be a variation in this frequency with substituent on the mercury, but as metal–halogen vibrations also occur in this region it is difficult at this stage to assess the degree of coupling between the metal–metal and metal–ligand vibrations.

It is of obvious importance to discuss the factors which influence the stability of metal–metal bonding in these systems. At the moment the data on which such an assessment can be made are limited, but as stated above, from a consideration of *Table 1*, the tendency to form metal–metal bonds appears to be greater for second and third row elements than for first row metals. Metal–metal bonding is also more common in high oxidation states for elements on the right hand side of the transition block. These variations may in part be correlated with the effective nuclear charge of the metal ion. In a given oxidation state, as we move across the periodic table the effective charge on the metal ion will increase and the bonding orbitals will become more contracted in size, thus effecting the overlap properties between the bonding atoms. This may therefore reduce the bonding between the different atoms considerably. If we assume stable bond formation for the early transition series then the stability would be expected to decrease as we move across the periodic table. The stability of metal–metal bonds in the lower oxidation states for the later transition metals may then be associated with the increase in orbital size on reduction of the charge on the ion. The effect of charge on metal–metal bonding may be seen by considering the d^9 series of complexes (*Table 1*). Stable metal–metal bonds occur with Fe(I), Co(O), Ni(+I), but with Cu (II) the stability of the metal–metal bond is dependent on the groups attached to the metal. This point will be considered later with reference to the magnetic properties of the systems.

In addition to σ-bonding we must also consider the influence of π-bonding and non-bonding interactions in the systems. Three classes of π-bonding may be considered in metal-complexes of this type:

(*i*) direct π-bonding between the metals in the metal–metal bond,

(*ii*) back donations of electrons from the metal to the ligand and

(*iii*) the alternative possibility of donation of electrons from the ligand to the metal.

It is difficult to estimate the amount of multiple bond character between

the metal ions in the metal–metal bond in many of these systems, or the factors which influence them. However, it is apparent that a considerable degree of multiple bond character is possible and is postulated for many compounds, *e.g.* $[Re_2Cl_8]^{2-}$. Back-donation from the metal to the ligand is likely to occur most readily with metals in a low oxidation state and co-ordinated to electron acceptor molecules. This type of bonding is typified by the carbonyl and substituted carbonyl complexes. Any bonding of this type will increase the effective nuclear charge on the metal and as such will influence the σ-bonding as discussed above. In addition it will reduce the possibility of any non-bonding interaction between the orbitals of the metal (*vide infra*). The alternative form of π-bonding by back donation of electrons from the ligand group to the metal is most likely to occur with metals in the higher oxidation states. This will reduce the effective charge on the metal and once again may effect the σ-bonding in the system.

The remaining factor that may influence the bond strength of metal bonds may be termed "non-bonding interactions". If we relate the stability of metal–metal bonds in these systems to similar considerations for the element–element bond strengths for the carbon to fluorine elements in the periodic table, then the bond strength will also be reduced by (*i*) the presence of groups favouring electron delocalization of the electrons used in bonding; (*ii*) steric interaction between the two monomer units and (*iii*) repulsion of non-bonding electrons[34].
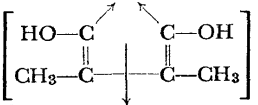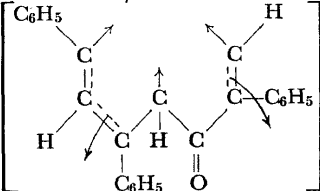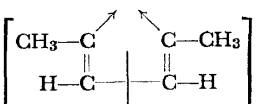
It has been suggested that the tendency to monomer–dimer formation observed in the manganese–carbonyl substituted phosphine derivatives is related to the π-bonding capacity of the phosphine[34]. The more effective the π-bonding capacity of the phosphine, the less probable are the *d*-electrons on the two manganese atoms, not used in the primary σ-bonding, to interact with each other and the more probable is dimer formation.

It is of interest to consider the above discussion with reference to the bond-length data available for mercurous complexes. From *Table 6* the mercury–mercury bond length appears to vary over a very large range in these complexes changing by 0·47 Å from the fluoride to the acetyl hydrazide
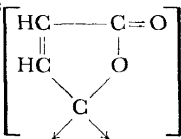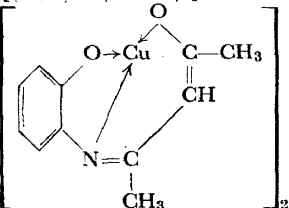
Table 6. Metal–metal bond distances

Compound	Metal–metal distance (Å)	Ref.
Ti		
β-TiCl₃	2·91	54
V		
VO₂	2·65	5
Nb		
NbI₄	3·2	6
NbCl₄	3·06	6
NbOCl₂	3·14	14
NbOI₂	3·16	14
Nb₃Cl₈	2·78	14
[Nb₆Cl₁₂]²⁺	2·85	55
Ta		
[Ta₆Cl₁₂]²⁺	2·90	55
[Ta₆Br₁₂]²⁺	2·90	55

Table 6—contd.

Compound	Metal–metal distance (Å)	Ref.
Cr		
[Cr$_2$Cl$_9$]$^{3-}$	3·12	56
[Cr(CH$_3$COO)$_2$]$_2$.2H$_2$O	2·64	57
Mo		
[MoCl$_5$]$_2$	3·84	2
[Mo(OC$_6$H$_5$)$_3$Cl$_2$]$_2$	2·8	1
Zn$_2$Mo$_3$O$_8$	2·53	58
MoO$_2$	2·50	4
MoOCl$_2$	2·96	14
MoCl$_3$	2·76	14
[Mo$_6$Cl$_8$]$^{4+}$	2·64	9
[πC$_5$H$_5$Mo(CO)$_3$]$_2$	3·22	12
W		
WO$_2$	2·49	4
[W$_2$Cl$_9$]$^{3-}$	2·41	7
Mn		
Mn$_2$(CO)$_{10}$	2·93	13
Tc		
TcO$_2$	2·48	4
Re		
ReO$_2$	2·49	4
[Re$_3$Cl$_{12}$]$^{3-}$	2·47	18, 19
[Re$_3$Cl$_{11}$]$^{2-}$	2·46	20
[Re$_2$Cl$_9$(PEt$_2$C$_6$H$_5$)$_3$]	2·49	21
[Re$_2$Cl$_8$]$^{2-}$	2·25	24
Re$_2$(CO)$_{10}$	3·02	13
Fe		
Sc$_2$Fe$_3$(CO)$_9$	2·65	59
[C$_2$H$_5$SFe(CO)$_3$]$_2$	2·54	60
Fe$_2$(CO)$_4$(πC$_5$H$_5$)$_2$	2·49	61
[Fe$_2$(CO)$_3$(πC$_5$H$_5$)$_2$(C$_6$H$_5$NC)]	2·53	62
Fe$_3$(CO)$_{15}$C	2·64	63
Fe$_2$(CO)$_6$ [HO—C ⋯ C—OH ; CH$_3$—C ⋯ C—CH$_3$]	2·49	64
Fe$_2$(CO)$_5$ [C$_6$H$_5$ ⋯ H ; C ⋯ C ; C—C—C—C$_6$H$_5$; H C H C ; C$_6$H$_5$ O]	2·50	65
Fe$_2$(CO)$_9$	2·46	66
Fe$_3$(CO)$_{12}$	2·75	67
[Fe$_2$(CO)$_8$]$^{2-}$	2·88	68
[C$_2$H$_5$SFe(NO)$_2$]$_2$	2·72	69
K[(NO)$_7$Fe$_4$S$_3$]	2·76; 3·57	70
Os		
Os$_2$(CO)$_6$ [CH$_3$—C ⋯ C—CH$_3$; H—C ⋯ C—H]	2·76	71
Os$_3$(CO)$_{12}$	2·88	72
Co		
[Co(CNCH$_3$)$_5$]$_2$$^{2+}$	2·74	73

Table 6—contd.

Compound	Metal–metal distance (Å)	Ref.
$Co_2(CO)_8$	2·52	74
$Co_4(CO)_{12}$	2·50	75
	2·45 (triclinic) 2·43 (orthorhombic)	76
$Co_2(CO)_6(C_6H_5C\!\!-\!\!-\!\!CC_6H_5)$	2·47	77
$Co_4(CO)_{10}(C_2H_5C\!=\!C.C_2H_5)$	2·43; 2·55; 3·55	78
$Co_2(CO)_4(C_2HBu^t)_3$	2·45	79
Rh		
$[Rh(CH_3COO)_2]_22H_2O$	2·45	80
$[Rh(CO)_2Cl]_2$	3·12; 3·31	81
$[Rh_2Cl_2(C_8H_{12})_2]$	3·50	82
$[Rh_2(\pi C_5H_5)_2(CO)_3]$	2·68	83
$Rh_6(CO)_{16}$	2·78	84
Ni		
$Ni(acetylacetonate)_2$	2·90	85
$Ni(dimethylglyoxime)_2$	3·25	86
$Ni_2(\pi C_5H_5)_2(C_6H_5C\!\!=\!\!CC_6H_5)$	2·33	87
$Ni_3(\pi C_5H_5)_3(CO)_2$	2·39	88
Pd		
$Pd(dimethylglyoxime)_2$	3·26	89
$[Pd(NH_3)_4][PdCl_4]$	3·25	90
$[Pd(NH_3)_4][PdBr_4]$	3·33	48
$[Pd(NH_3)_4][Pd(SCN)_4]$	3·35	48
Pt–Pd		
$[Pt(NH_3)_4][PdCl_4]$	3·25	48
$[Pd(NH_3)_4][PtCl_4]$	3·25	48
Pt		
$[Pt(dimethylglyoxime)_2]$	3·23	48
$K_2[Pt(C_2O_4)_2]$	2·75	90
$[Pt(NH_3)_4][PtCl_4]$	3·25	48
$[Pt(NH_2Me)_4][PtCl_4]$	3·25	48
$[Pt(NH_3)_4][PtBr_4]$	3·31	48
$[Pt(NH_2Me)_4][PtBr_4]$	3·30	48
$[Pt(NH_3)_4][Pt(SCN)_4]$	3·35	48
Cu		
$[Cu(N\text{-methylsalicylaldimino})_2]$	3·33	91
$[(py).Cu(acetate)_2]_2$	2·63 (monoclinic) 2·64 (orthorhombic)	92 93
$[(H_2O)Cu(acetate)_2]_2$	2·64	94
	3·00	95
$[Cu(C_6H_5N\!=\!N\!\!-\!\!NC_6H_5)]_2$	2·45	96
$[(CH_3)_3As\!\!-\!\!Cu\!\!-\!\!I]_4$	2·60	97
$[Me_3PCuC\!\!=\!\!CC_6H_5]_4$	2·45; 2·45; 2·69	98

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Compound	Metal–metal distance (Å)	Ref.
Cu–Pt		
$[Cu(NH_3)_4][PtCl_4]$	3·23	99
Ag		
$[Me_3PAgC \equiv CC_6H_5)_x$	3·03	98
Au		
$[i\text{-}C_3H_7NH_2AuC \equiv CC_6H_5]_x$	3·72; 3·28	98
$[(n\text{-}C_3H_7)_2NCS_2Au]_2$	2·76	100
$[Au(dimethylglyoxine)_2][AuCl_2]$	3·26	101
Hg		
Hg_2F_2	2·43	102
Hg_2Cl_2	2·53	103
Hg_2Br_2	2·58	103
Hg_2I_2	2·69	103
$[Hg_2N_2(COCH_3)_2]_x$	2·90	104
$Hg_2(NO_3)_2.2H_2O$	2·54	105

complex. These data are not readily explained on simple electronegativity arguments, as presumably the electronegativity of the group X in the complex Hg_2X_2 decreases the positive charge on the metal and this would lead to a shorter metal–metal bond as direct repulsion between the metal ions would be reduced. However, the fluoride, the most electro-negative group, has the smallest metal–metal distance. The large effective positive charge on the metal ions in the fluoride would also reduce the possibility of multiple bonding between the mercury ions as this would tend to contract the lower filled d-orbitals and increase the energy separation between the d-orbitals and the empty p-orbitals of the mercury which will presumably act as the acceptor orbitals in any π-bonding mechanism.

Alternatively, any back donation of electrons from the group X to the mercury would reduce the effective charge on the metal and presumably favour more stable and shorter mercury–mercury bonds. In order to explain the order of bond lengths observed, the fluoride would then have to be considered as a more effective group for back-donating than the chloride < bromide < iodide. This, of course, is the halogens order postu-lated for back donation in the case of the boron halides. However, it would also require that water was as effective as chlorine in electron donation so that although this may be part of the reason for the variation, it cannot be the complete explanation. The variation observed also seems very large to account for on this basis alone.

The bond length change may also be associated with hybridization changes in the system. If we consider the hybridization around the mercury to be sp or sd, then in the mercurous complexes Hg_2X_2, as the electronega-tivity of the group X increases the Hg–X bond will take on more d or p character, resulting in more s character for the Hg–Hg bond and a shorter bond. Calculations have shown that for systems involving d-orbitals variations of up to 0·1 Å may be accounted for in this way[45].

The effects of these variations on the "non-bonding" interactions would also favour a shorter bond for the fluoride complex as the higher positive

charge on the metal, in this instance, would reduce the size of the non-bonding *d*-orbitals and hence reduce any interaction between the two sets of mercury orbitals. It is obvious that it would be of interest to determine if similar variations in metal–metal distances occur in other complexes, and what factors appear to influence the metal–metal distance.

DETECTION OF METAL–METAL INTERACTION

The main techniques that have been used to detect the presence of metal–metal interaction are summarized in *Figure 3*. It is obviously not
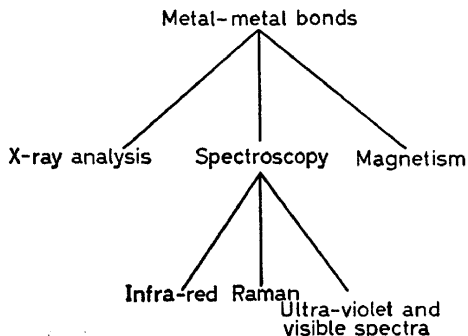

Figure 3. Techniques for detecting metal–metal interactions

going to be possible to review these fields in detail, and the main emphasis of the following section will be on the magnetic criterion for metal–metal interaction. However, a brief survey of the other techniques will be given.

X-ray structure

The X-ray determination of structures is normally considered the most direct way of indicating the presence of a metal–metal bond. However, difficulty is often experienced as to the maximum distance between two ions consistent with the presence of a metal–metal bond still being present. Very often reference is made to the interatomic distances in the pure metal and Pauling[46] has compiled radii based on this data. However, it has become apparent that in certain instances distances between metal ions may be considerably longer than given by this data and yet involve direct metal–metal bonding. Thus for the manganese carbonyl dimer[13] and cyclopentadiene molybdenum tricarbonyl dimer[12], the molecules involve "long" metal–metal bonds based on the Pauling radii, but in these molecules the metal–metal bond is the only bonding entity between the metal ions.

Table 6 summarizes the X-ray data available on the metal–metal bonds studied to date. The values of these bond lengths vary considerably and cover situations where weak bonding is envisaged, as in nickel dimethyl-glyoxime complexes and related compounds, to strong metal–metal bonded systems such as $[Re_2Cl_8]^{2-}$. Certain ambiguities exist, thus for the complexes of Cu(I), Ag(I) and Au(I), given in *Table 6*, the metal–metal distance is relatively small. Normally, it is not considered that metal–metal bonding

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would occur with ions of the configuration d^{10}. However, if the distance between the metal ions is taken as indicative of bonding, then metal–metal interaction must be present in these complexes. Since these complexes are diamagnetic, it is further necessary to assume multiple bonding between the metal ions. Consideration of systems of this type lead one to reassess the criterion of what constitutes a bond between two atoms.

Spectroscopy

The ultra-violet and visible spectroscopic properties of metal–metal systems has not been very extensively investigated. However, the polarized spectra of complexes has been used by Yamada[47] to suggest metal–metal interaction in the d^8 donor-system such as Magnus' salt, and the nickel dimethylglyoxime group of compounds. Recent work by Miller[48] has also interpreted the absorption spectra of similar systems in terms of metal–metal bonding. However, the detailed assignment of the absorption spectra of polynuclear complexes has not been undertaken in many cases.

The infra-red and Raman spectra of metal–metal bonded complexes have also not been used to any great extent to measure metal–metal vibrations directly, as these normally occur at low frequencies >200 cm^{-1}. However, the study of the Raman spectra of mercurous nitrate solutions was one of the first examples of the application of a spectroscopic technique to an inorganic problem. Woodward[49] was able to verify the presence of a mercury–mercury bond in these systems by the detection of a mercury–mercury vibration at 160 cm^{-1}. Recently the same technique has been used to establish the presence of a dimeric cadmium ion $Cd_2{}^{2+}$, by studying the spectra of the Cd_2 $(AlCl_4)_2$ system[50]. The general application of Raman studies to these systems is limited because of the nature of the sources available.

Indirect evidence for the nature of metal–metal bonding in species has been deduced by considering the variation in the metal–ligand and ligand vibrations in the infra-red. It has recently been shown that the spectra of dicobalt octacarbonyl is markedly dependent on the solvent used[51]. In the solid, the complex has been shown to involve a metal–metal bond between the two cobalt atoms and two bridging carbonyl groups[52]. The infra-red spectra in the carbonyl region of the spectrum in various solvents has been interpreted as indicating an equilibrium between a bridged and a non-bridged species[53]. It is obvious that the detection of structural changes of this nature is extremely important particularly in any discussion of the reactivity of these complexes.

Magnetic properties

The determination of the magnetic properties of complexes is one of the most common methods used to detect the presence of a metal–metal bond in the case of transition metal complexes. The diamagnetism of molecules such as iron enneacarbonyl, coupled with the short iron–iron distance[66], was used to indicate the presence of an iron–iron bond in this complex. There are, however, a number of difficulties that may arise when applying the magnetic criterion for metal–metal interaction as the diamagnetism or

reduction in paramagnetism in a system may arise from alternative inter-actions. These may be summarized as follows:

(*a*) For systems with an even number of electrons in the metal, electron pairing may result from some stereochemical requirement rather than metal–metal bonding. The interpretation of the structure of the $[ReCl_4]^-$ ion as tetrahedral rather than polymeric is an example of the reversal of this reasoning.

(*b*) For metals with orbitally degenerate ground states, the magnetic properties may be modified by spin-orbit coupling interaction. For d^1 octahedral complexes, the ground term is $^2T_{2g}$, spin-orbit coupling removes this degeneracy to give a ground level with a zero magnetic moment. The paramagnetism observed for metals with this configuration and having large values of the spin-orbit coupling arises from a temperature inde-pendent paramagnetic term[25]. The "effective diamagnetism" of zir-conium trichloride may therefore arise from metal–metal interaction, as postulated for the β-form of titanium trichloride[54], or alternatively from the large value of the spin-orbit coupling constant for zirconium (III) (λ ~500 cm^{-1}), which would give a temperature independent susceptibility of ~300 × 10^{-6} c.g.s. units. Since this susceptibility is small and independent of temperature, compounds such as this are often reported as "diamagnetic". It is obviously much easier in dealing with the magnetic properties of systems involving metal–metal interaction and in which there is residual paramagnetism to consider those which are orbitally non-degenerate.

(*c*) The magnetic interaction between metal ions may occur through the participation of bridging groups. An extreme example of this occurs in antiferromagnetism interactions in simple metal halide and oxide systems. For the simpler systems, the diamagnetism of the binuclear complex $K_4 [Ru_2OCl_{10}]H_2O$ is one of the classical examples of such an interaction. The diamagnetism of this complex was interpreted in molecular orbital terms by Dunitz and Orgel[107] and effectively arises from strong π-inter-action in the Ru–O–Ru system. As in antiferromagnetic interaction in oxide systems, the most effective magnetic coupling appears to be related to systems with linear metal–oxygen–metal groups. In many cases it is difficult to differentiate between direct interaction between two metal ions, and interaction via a bridging group, and there is little doubt that both occur in certain systems.

The most interesting systems magnetically, are those in which complete spin-pairing has not occurred. The mono-carboxylic acids of copper (II) provide one of the best examples of this class, and it is considered that for the dimeric molecules in this series, the main magnetic interaction occurs via a direct metal–metal bond.

Copper acetate monohydrate has been shown to be a binuclear complex with four acetate bridges between the two copper ions[94] (*see Figure 4*). The metal–metal distance is 2·64 Å, and a direct bond between the two copper ions is postulated. Recently there has been some discussion as to whether this bond involves overlap of the d_{z^2} orbitals of the copper ions[108] or formation of a δ-bond by overlap of the $d_{x^2-y^2}$ orbitals[109]. The water molecules are coordinated to the terminal position and if the metal is con-sidered to occupy a stereochemical position in the coordination sphere of the

other copper then each copper is octahedrally coordinated. Many metal-carboxylic acid complexes seem to involve polynuclear structures, and a similar structure to the copper acetate has been established for chromous[57] and rhodium acetate monohydrate[80], the metal–metal bonds being 2·64 and 2·45 Å respectively. The rhodium salt involves a remarkable short metal–metal distance. Both the chromium and the rhodium salts are effectively
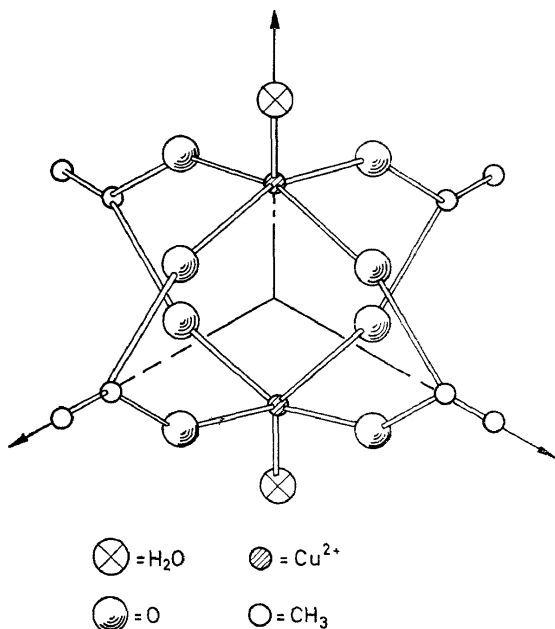

$\bigotimes = H_2O$ $\oslash = Cu^{2+}$

$\bigcirc = O$ $\bigcirc = CH_3$

Figure 4. Structure of copper acetate monohydrate

diamagnetic. A series of aliphatic chromous carboxylates has been investigated by Herzog[110] who reports a small paramagnetic susceptibility for the complexes at room temperature of $\sim 200 \times 10^{-6}$ c.g.s. units. Earnshaw, Larkworthy and Patel[111] suggest that chromous formate exists in two forms, one which is binuclear with considerable magnetic interaction and one which is mononuclear with a normal magnetic behaviour.

If we postulate an octahedral stereochemistry for copper in the acetate complexes then for octahedral complexes of copper (II), moments in the range 1·9–2·0 β would be expected. The magnetic moment is given by $\mu_{eff} = \mu_{s.o.} [1 - (2\lambda/\Delta)]$ where Δ is the ligand field splitting of the d-levels, λ is the spin-orbit coupling constant, and $\mu_{s.o.}$ is the spin-only moment[25]. The susceptibility would then be expected to follow a Curie–Weiss Law. In contrast to this, copper acetate and the monohydrate have moments of 1·39 and 1·43 β at room temperature and the susceptibility temperature curves show maxima at 270°K and 260°K[112].

Figgis and Martin[112], following the interpretation of Bleaney and Bowers[113] of the e.s.r. spectra, were able to explain the magnetic behaviour

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of copper acetate and copper acetate monohydrate on the assumption of a spin-singlet ground state and a thermally accessible spin-triplet state, the separation between the singlet and triplet states being 302 cm^{-1} for the anhydrous salt and 286 cm^{-1} for the hydrate salt. A series of aliphatic carboxylates of copper (II) was subsequently investigated by Martin[114] and the data were interpreted on a similar basis. Copper formate[114] was, however, shown to be magnetically different, three forms being isolated and none showing the copper acetate behaviour. The structures of these salts were considered to be polynuclear with no direct copper–copper bonding.

The difference between the formate and the other aliphatic complexes may be related to the change in polarizability of the carboxyl oxygens. As the pK_a of formic acid is less than the other aliphatic carboxylic acids, it was considered that the polarizability of the bonding oxygens would be smaller and that the effective charge on the copper ions would be larger. This would lead to a greater repulsion between copper ions in a binuclear complex.

If we consider the manner in which the carboxylic group may act as a bridging group there are three forms of bonding that may arise:

$$
\begin{array}{ccc}
\text{I} & \text{II} & \text{III}
\end{array}
$$
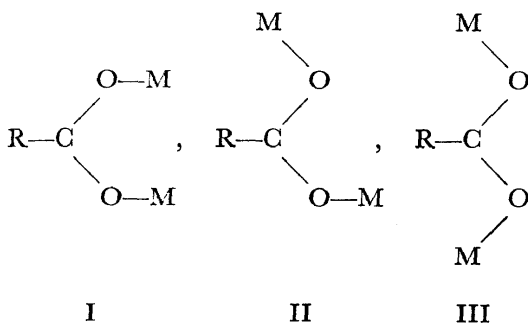
Structure I corresponds to the arrangement in copper acetate, while structure II has been established for one of the forms of anhydrous copper formate [115] and structure III the arrangement in copper formate tetra-hydrate[116]. Maximum metal interaction and metal–metal bonding would be expected for structures of type I, and it is suggested that the formate adopts structures of types II and III to reduce the metal repulsions due to the charge on the metal. In addition to considering the pure electrostatic interaction between the metal ions, it has also been suggested that the increase in effective charge on the metal will influence the overlap of the bonding orbitals[34]. There is no doubt that the tendency to form metal–metal bonds in the d^9 configuration Fe(−I), Co(0), Ni(I), Cu(II) is influenced by the effective charge of the metal ion.

In order to extend this data to systems where there is a much larger variation in the pK_a of the acids and possibly to detect any steric effects, we have investigated the magnetic behaviour of substituted benzoic acids. *Figure 5* shows the variation in the susceptibility with temperature for some of the salts. They appear to fall into two classes on the basis of the magnetic

behaviour and this in itself is suggestive of difference in structures between the series. The magnetic properties of a number of interacting magnetic centres is dependent upon the number of metal ions in the metal cluster. *Table 7* shows the variation with temperature of the magnetic moment in a system of copper ions $(s = \frac{1}{2})$, for different numbers of ions, n,

1. Copper (II) m-chlorobenzoate
2. Copper (II) p-chlorobenzoate
3. Copper (II) m-methylbenzoate (β)
4. Copper (II) o-chlorobenzoate
5. Copper (II) o-nitrobenzoate
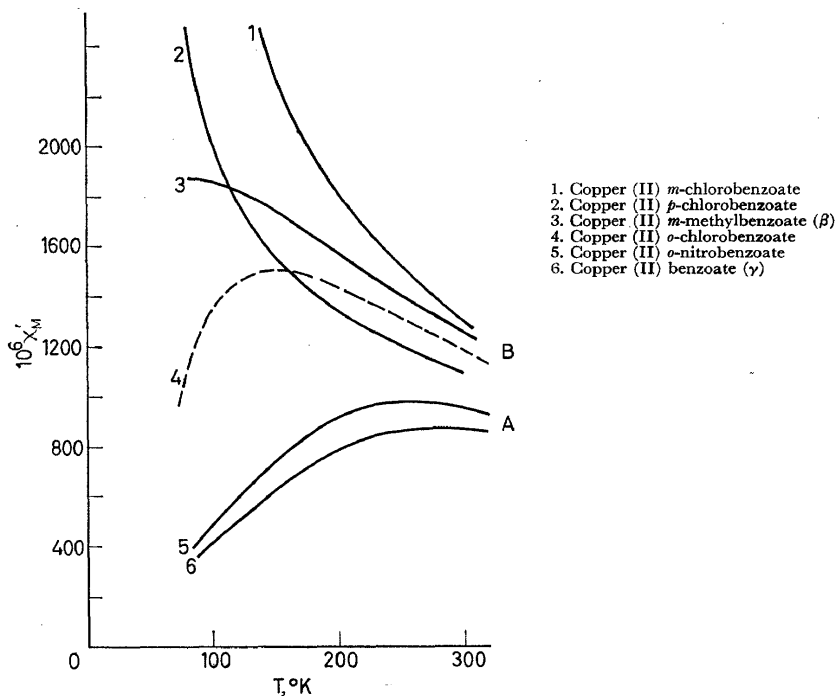6. Copper (II) benzoate (γ)

Figure 5. Variation of susceptibility with temperature for some of the salts of benzoic acid

with the exchange integral "J". If the exchange integral J is large, it is possible to differentiate, on the basis of magnetic behaviour over a temperature range, between dimeric and polymeric structures. The behaviour of the orthobenzoic acid derivative is of interest as this appears to be binuclear with a much lower singlet–triplet separation. The room temperature moment is therefore much higher than the other binuclear molecules and this emphasizes the danger of using a room temperature moment to indicate the class of compound, as has been suggested in the past.

Table 7. Moments of polynuclear copper (II) complexes

J/kT	Magnetic moment (β)			
	$n = 2$	$n = 3$	$n = 4$	$n = 9$
0·5	1·48	1·44	1·43	1·42
1	1·07	1·22	1·21	1·22
2	0·46	1·04	0·88	0·99
3	0·17	1·00	0·61	0·82

Table 8 shows the variation in magnetic behaviour for a series of substituted benzoates with change in pK_a of the acid. For the acids with high pK_a, the magnetic data can be readily analysed in terms of a binuclear complexes, whereas for acids with low pK_a values, the magnetic data on the complexes cannot be interpreted in this way. There are a number

Table 8a

Compound	pK_a	μ_{eff} (β)	$-2J$ (cm^{-1})	g
acetate	4·75	1·39	302	2·17
p-methylbenzoic	4·35	1·36	289	2·14
α-m-methylbenzoic	4·25	1·42	289	2·18
γ-benzoic	4·18	1·38	340	2·18
p-chlorobenzoic	4·05	1·57	——	——
o-methylbenzoic	3·92	1·41	278	2·13

Table 8b

Compound	pK_a	μ_{eff} (β)	$-2J$ (cm^{-1})	g
m-chlorobenzoic	3·80	1·72	—	—
formate	3·75	1·61	—	—
m-nitrobenzoate	3·47	1·67	—	—
p-nitrobenzoate	3·40	1·59	—	—
o-nitrobenzoate	3·21	1·45	278	2·19
o-chlorobenzoate	2·89	1·64	167	2·14

of exceptions to this rule. Certain ortho-substituted acids, *e.g.* ortho-nitrobenzoic acid, appear to be binuclear in structure although the corresponding meta and para acids are weaker acids and show a polymeric structure. We consider that this is due to steric interaction involving an ortho-substituted group which would be greater for structures II and III. This then forces the structure into the binuclear form (I)[117]. It appears significant that the value of the exchange integral "J" is very similar to that observed for the aliphatic carboxylates. This may imply that the interaction via the intermediate carboxylate ion is of some considerable importance in these complexes.

For some of the complexes it is possible to prepare more than one form. Copper benzoate has been prepared in three forms[118, 119], two of which appear to be polymeric and one dimeric (γ-form). The X-ray powder photographs indicate that there are three distinct phases[118, 119] and the reflection spectra of the solids are also different in agreement with the existence of three distinct forms[118]. For the meta methyl benzoate and ortho chlorobenzoate two products have been isolated, one being dimeric and the other polymeric[117]. The occurrence of more than one modification in this instance may be related to the pK_a of the acids as benzoic and methylbenzoate appear to be in the region of pK_a range where change over from binuclear to polynuclear forms occur. The two forms of the ortho-chloro

acids may, alternatively, be associated with the balance between any steric and charge effects.

The absorption spectra of these binuclear copper complexes have been studied in detail. For the aliphatic carboxylic acid derivatives a band at ∼375 mμ has been associated with dimeric molecules showing copper–copper interaction. The polarized absorption spectra indicates that the absorption at 375 mμ is much stronger along the copper–copper bond than in the plane of the complex. It appears that this band is most likely due to a transition within the molecule as a whole rather than any single d–d transitions[108]. Although it is not necessarily true that this band is indicative of the presence of a metal–metal bond, all complexes that have a binuclear structure and in which there is considerable interaction between the metal ions appear to show a band of this type.

For the benzoic acid derivatives given in *Table 8*, all complexes that appear dimeric have a weak band in the region 380–420 mμ. The variation in the band position is greater than that shown for the aliphatic acid series; with complexes where more than one modification occurs, the band appears in the form that magnetically conforms to dimeric behaviour and not in the polynuclear forms.

Molecular weight determinations in dioxan have also shown that all compounds that magnetically behave as dimeric molecules, have molecular weights corresponding to a dimeric structure. However this cannot be taken as indication of a dimeric structure for the solid as the absorption spectra of the solution normally differs from that of the solid implying the formation of a new species. Martin[114] observed that many of the anhydrous derivatives of the copper (II) aliphatic carboxylate formed addition compounds, and with copper formate it was possible to prepare a binuclear adduct of the type $[Cu(HCOO)_2.L]_2$ where L = pyridine and the α-, β-, γ-picolines. It is also possible to isolate similar binuclear adducts in the benzoate series. *Table 9* contains some adducts of copper o-chlorobenzoate.

It thus appears possible to relate the magnetic interaction in this series of complexes with the pK_a of the acid after allowance has been made for any steric effects in the system. In certain instances however it is extremely difficult to decide on the basis of magnetic evidence alone if exchange is directly between the metal ions or occurs through the agency of bridging groups. It appears that in many instances the nature of the bridging group is critical in determining any magnetic interaction that takes place in the system. A considerable amount of work has been carried out on oxygen bridging groups and it has been established that a linear metal–oxygen–metal bridge is a very effective means of causing magnetic exchange, presumably through a π-bonding mechanism. In addition to the ruthenium

Table 9. o-chlorobenzoate. Adducts

Compound	μ_{eff} (β)	$-2J$ (cm^{-1})	g	Nα
o-chloro	1·62	167	2·14	60
H$_2$O	1·51	245	2·17	60
py.	1·32	312	2·07	60

complex $K_4Ru_2OCl_{10}H_2O$ discussed above, Trzebiatowska[121] and co-workers have extensively studied rhenium (IV) complexes involving the system $[Re-O-Re]^{4+}$ and interpreted their magnetic results in terms of exchange through an oxygen bridged system[25].

The effect of the nature of the oxygen bridge can be readily illustrated by considering the binuclear chromium ammine complexes— $[(NH_3)_5CrOHCr(NH_3)_5]X_5$, the rhodo series, and $[(NH_3)_5CrOHCr(NH_3)_4(H_2O)]X_5$, the erythro series. In addition to the acid salts each forms a corresponding series of basic salts in which a proton is lost from the bridging hydroxy group for the rhodo series, and the coordinated water molecule in the erythro series[106]. The erythro salts and acid rhodo salts therefore contain a bridging hydroxy group, whereas the basic rhodo salt has an oxygen bridge. The two classes of complexes have very different magnetic properties; the hydroxy bridged complexes show a slight reduction in the moments from the behaviour expected for mononuclear complex ($\sim 3\cdot 83\ \beta$) (see Table 10), whereas the basic rhodo complex with the oxygen bridge

Table 10

Compound	μ_{eff} at 20°C (β)	J (cm^{-1})	g
Acid rhodo-bromide	3·44	−20·25	1·94
Acid erythro-bromide	3·52	−20·7	1·99
Acid erythro-chloride	3·62	−20·7	1·99
Basic erythro-bromide	3·50	−14	1·91

shows a large reduction in the moment to $1\cdot 29\ \beta$ at 300°K falling to $0\cdot 7\ \beta$ at 100°K[122]. The data for the basic rhodo complex cannot be analysed satisfactorily in terms of binuclear complex as it is difficult to ensure the absence of small traces of the basic erythro salt which has a very marked effect on the magnetic properties. The difference in behaviour of these two series may therefore be correlated with the metal–oxygen–metal bond angle, as this must be of the order of 120° in the hydroxy-bridge whereas it can be linear for the oxygen bridged basic rhodo salt. In the latter case there is the maximum possibility of overlap between the metal d-orbitals and the oxygen p-orbitals leading to maximum magnetic interaction.

A final example of an oxygen bridged structure in which there is magnetic exchange may be furnished by the basic acetates of iron (III) and chromium (III). The chromium (III) and iron (III) hydroxy-acetates which are normally formulated as $[M_3(OAc)_6(OH)_3]_xH_2O$, M = Fe, Cr have been considered to be trinuclear on the basis of electrometric titrations[123] and dialysis

Table 11a

Compound	μ_{eff} solid (β)	μ_{eff} aq. soln. (β)	$-J$ (cm^{-1})
$[Cr_3(CH_3COO)_6(OH)_2]Cl.8H_2O$	3·39	3·37	15·6
$[Cr_3(C_2H_5COO)_6(OH)_2]NO_3.3H_2O$	3·48	3·41	14
$[Cr_3(CH_3COO)_6(OH)_2]CNS.3H_2O$	3·42	3·37	15

33

Table 11b

Compound	μ_{eff} solid (β)	μ_{eff} aq. soln. (β)	$-J$ (cm^{-1})
$[Fe_3(CH_3COO)_6(OH)_2]Cl.4H_2O$	3·34	3·68	40·3
$[Fe_3(CH_2ClCOO)_6(OH)_2]ClO_4.4H_2O$	3·22	3·09	45·4
$[Fe_3(CCl_3COO)_6(OH)_3].7H_2O$	3·18	4·60	47·3
$[Fe_3(C_6H_5COO)_6(OH)_2]ClO_43H_2O$	3·28	—	42·0

measurements[124]. We have studied the magnetic properties of a number of these complexes and some of the data is given in *Table 11*[125]. The exchange integral J was evaluated from the magnetic data by curve fitting products using essentially the procedure of Kambe[126]. The X-ray structure of a complex chromic acetate complex has been carried out by Figgis and Robertson[127], and the structure is shown in *Figure 6*. An oxygen atom is surrounded by three chromium ions at the corners of an equilateral triangle.

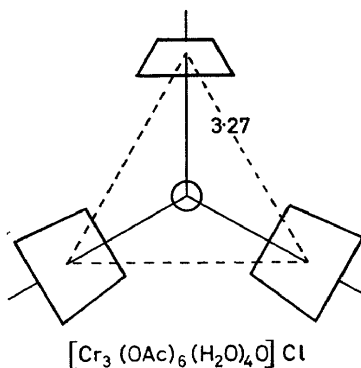

$[Cr_3 (OAc)_6 (H_2O)_4O] Cl$

Figure 6. The X-ray structure of complex chromium acetate complex

Each chromium ion is octahedrally coordinated with three pairs of acetate bridges bonding between the chromium ions and the sixth position of a chromium octahedron being occupied by a water molecule. This is essentially the structure postulated by Orgel for this series of compounds[128]. The three chromium ions and the centre oxygen atom lie in a plane and if we consider that the oxygen bonds to the metal ions through an sp^2 hybrid system, then the magnetic interaction occurs by overlap of the d-orbitals of the metal and the filled non-bonding p-orbital of the oxygen. However, from the magnetic behaviour of this series of complexes this form of interaction does not appear to be as effective as the linear metal–oxygen–metal system.

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