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Metal-Metal Bonds and Covalent Atomic Radii of Transition Metals in Their π-Complexes and Polynuclear Carbonyls

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The review presents a compilation of recent results in one of the most important fields of structural chemistry at the present time—compounds with metal-metal bonds.
The bibliography includes 56 references.

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I. INTRODUCTION

The rapid development of the chemistry of the π-complexes of transition metals has already led to the synthesis of numerous groups of compounds the molecules of which contain two or several metal atoms linked either directly or via additional bridging ligands. The considerable interest in this unusual class of compounds is due to the fact that metal–metal bonds in many respects determine the chemistry of transition metal compounds.

The problem of the interaction between metal atoms in complexes has attracted attention for a long time. The accumulation of extensive experimental data led to many attempts at reviews, primarily those listed in Refs. 1–12.

The present review deals with the metal–metal interaction in the π-complexes of transition metals and is based on the experimental interatomic distances and valence angles in their molecules.

The most successful classification of compounds on the basis of metal–metal bond types has been proposed by Nyholm[2,5] and is partially applicable also to π-complexes and polynuclear carbonyls. In the first place, it is necessary to distinguish a group of compounds with covalent bonds between metal atoms, including both molecules with covalent bonds between transition metal atoms—for example, $Mn_2(CO)_{10}$[$(\pi\text{-}C_5H_5)Mo(CO)_3$]$_2$, $(\pi\text{-}C_5H_5)Mo(CO)_3$-$Mn(CO)_5$—and molecules with covalent bonds between elements in Groups IB–IVB and transition metals—for example, $(C_6H_5)_3PAuMn(CO)_5$, Hg[$Co(CO)_4$]$_2$, and [$(C_6H_5)_3SnMn(CO)_5$]. The first group may be subdivided into homopolymetallic complexes with identical electronic configurations of the transition metal atoms—for example, $Mn_2(CO)_{10}$ and [$(\pi\text{-}C_5H_5)Mo(CO)_3$]$_2$—and heteropolymetallic complexes, i.e. with different electronic configurations of the transition metal atoms—for example, $(\pi\text{-}C_5H_5)Mo(CO)_3$-$Mn(CO)_5$.

It is possible to distinguish further a group of π-complexes with metal–donor bonds, the molecules of which are combined in the crystal into polymeric chains owing to metal–metal interaction.

II. π-COMPLEXES WITH COVALENT METAL–METAL BONDS

In their reviews Lewis and Nyholm[2-6] attempted to estimate the factors which determine the nature of the interaction between covalently linked metal atoms. Most important among these factors are the effective charge of the metal atom, its electronic configuration, and also the electronic properties of ligands and their steric characteristics. However, these factors probably do not exhaust the entire set of influences on the type of metal–metal bonds, since, as will be shown in the discussion of interatomic distances, these bonds are fairly variable in their strength, length, and number of electrons involved in them. The effect of bridging groups, which in many complexes to a considerable degree determine the nature of the metal–metal interaction, is also undoubtedly important.

A. COMPOUNDS WITH COVALENT BONDS BETWEEN TRANSITION METALS

1. Homopolymetallic Complexes

The lengths of the metal–metal bonds in homopolymetallic complexes (Table 1) vary within fairly wide limits (up to about 0.5 Å for Fe–Fe bonds). As pointed out by Poray-Koshits and Gilinskaya[11], this means that the curve relating the metal–metal interaction energy to the interatomic distance has a fairly gently sloping profile with a diffuse minimum or a series of several closely spaced minima.

Therefore the problem arises of the validity of the application of a widely used criterion—the sum of single bond covalent radii—to characterise the metal—metal interaction forces. The problem of the values of the single bond covalent radii of transition metal atoms in their π-complexes has been frequently discussed (see, for

Table 1. Lengths (Å) of metal–metal bonds in molecules of homopolymetallic π-complexes.

Bond	Range of variation of metal–metal bond lengths		Twice the single bond covalent radius	Bond	Range of variation of metal–metal bond lengths		Twice the single bond covalent radius	Bond	Range of variation of metal–metal bond lengths		Twice the single bond covalent radius
	with bridging ligands	without bridging ligands			with bridging ligands	without bridging ligands			with bridging ligands	without bridging ligands	
Ti—Ti	—	3.11	3.1_2	Zr—Zr	—	—	3.52	Hf—Hf	—	—	3.5_4
V—V	—	—	2.98	Nb—Nb	2.73—2.74	—	3.1_2	Ta—Ta	—	—	3.1_2
Cr—Cr	2.67—2.94	3.40 *	2.92	Mo—Mo	2.89—3.26	3.22—3.27	3.1_6	W—W	—	3.24	3.1_8
Mn—Mn	2.50—2.94	2.91—2.97	2.76	Tc—Tc	—	3.94	3.0_8	Re—Re	—	2.96—3.18; 3.39*	3.02
Fe—Fe	2.37—2.88	2.67—2.88	2.6_8	Ru—Ru	2.74; 2.95	2.85	2.9_6	Os—Os	2.74	2.88	3.00
Co—Co	2.37—2.64	2.66	2.58	Rh—Rh	2.62—2.73	2.66—2.73	2.92	Ir—Ir	2.73	2.68—2.73	2.9_4
Ni—Ni	2.33—2.80	—	2.7_0	Pd—Pd	2.58	—	2.9_8	Pt—Pt	2.75—2.79	—	2.8_6

*Three-centre metal–hydrogen–metal bond.

Table 2. Single bond covalent radii of transition metals in their π-complexes.

Ti 1.5_6* (1.36; 1.46)**	V 1.49 (1.22; 1.34)	Cr 1.46 (1.19; 1.28)	Mn 1.38 (1.18; 1.27)	Fe 1.3_4 (1.17; 1.26)	Co 1.29 (1.16; 1.25)	Ni 1.3_5 (1.15; 1.24)
Zr 1.76 (1.51; 1.60)	Nb 1.6_8 (1.34; 1.46)	Mo 1.5_8 (1.30; 1.39)	Tc 1.5_2 (1.27; 1.36)	Ru 1.4_9 (1.25; 1.34)	Rh 1.46 (1.25; 1.34)	Pd 1.4_9 (1.28; 1.37)
Hf 1.7_7 (1.50; 1.59)	Ta 1.6_8 (1.34; 1.46)	W 1.5_9 (1.30; 1.39)	Re 1.51 (1.28; 1.37)	Os 1.50 (1.26; 1.35)	Ir 1.4_7 (1.27; 1.36)	Pt 1.4_3 (1.30; 1.39)

*According to Andrianov et al.[13]

**Single bond covalent radii according to Pauling[14]: the first for a coordination number of 6 and the second for a coordination number of 12.

example, Andrianov et al.[13]), since theoretical and experimental results have shown that the single bond transition metal radii proposed by Pauling[14] cannot be used to analyse the interatomic distances in their π-complexes. Incidentally, we may note that the revision of the atomic radii of transition metals was in fact stimulated by the study of compounds with metal–metal bonds. Indeed the Mn–Mn bond length (2.926 Å) in the dimanganesetetracarbonyl molecule[15] $Mn_2(CO)_{10}$ is greater by about 0.4 Å than twice the value of Pauling's atomic radius of manganese (2.54 Å). However, Cotton[16] found a contradiction between the fairly high energy of this bond (34 kcal mole^{-1})† and its very marked extension, which clearly indicated that the value of 1.27 Å for the atomic radius of manganese is too low.

The single bond covalent radii of transition metals in their π-complexes[13], which will be employed‡ in the analysis of the metal–metal interatomic distances, are compared in Table 2 with the values proposed by Pauling[14]. In the analysis of the interatomic metal–metal distances in homopolymetallic π-complexes (Table 1) the fact that the shortest of them are observed in molecules with bridging ligands attracts attention. This suggests that such ligands draw the metal atoms together by virtue of the rigidity of their geometry.

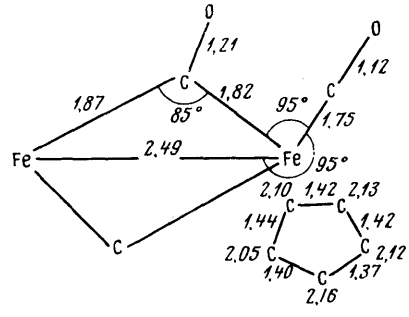


Figure 1. Geometry of the $[(\pi\text{-}C_5H_5)Fe(CO)_2]_2$ molecule.

The most widespread and the most readily available molecules for a simple geometrical examination are those in which the bridging ligands are linked to only two metal atoms (the so called "edge" bridges) and form MXM groups (X = C, N, S, etc.) via only one of their atoms, for example in bis(dicarbonyl-π-cyclopentadienyliron) $[(\pi\text{-}C_2H_5)Fe(CO)_2]_2$ (Fig. 1).[20] In the formation of the FeCFe group in this molecule the bridging carbon atom is in the sp^2-hybridised state and therefore the most favourable angle is probably 120°. However, examination of the geometry of the planar fragment Fe_2C_2 (Fig. 1) shows that in this case the distance between the bridging carbon atoms not linked by valence bonds is 1.9–2.0 Å (while twice the van der Waals radius is 3.6 Å), i.e. is unexpectedly small. This factor probably in fact forces the bridging carbon (nitrogen, sulphur) atoms to move apart to acceptable distances with a decrease of the real

† See the footnote on p. 791.

‡ It must be specially emphasised that, according to one view[17], the very concept of atomic radius is inapplicable to complex (three-dimensional) cluster systems (see p. 791) and this undoubtedly true owing to the many-centre nature of all the bonding orbitals responsible for the metal–metal interaction[8,18,19]. Therefore the system of radii proposed by Andrianov et al.[13] is applicable to complexes in which the bonds are largely localised and collective groups of atoms are absent.

MX_{bridge} M angles to 67–86°C (instead of the "ideal" value 120°C). Thus if the FeCFe angle in the molecule under discussion is assumed to be 90°C and the length of the Fe–C bond is taken to be 1.9 Å, the C...C distance between bridging carbon atoms not linked by valence bonds increases to the now admissible value of 2.7 Å. Then the Fe–Fe distance also becomes close to 2.7 Å, i.e. it is virtually equal to twice the single bond radius of the iron atom (2.68 Å). Thus it appears that the FeCFe angle close to 90°C corresponds to the optimum configuration of the Fe_2C_2 fragment.

However the problem then arises of the cause of the decrease of the Fe–Fe distance to 2.49 Å and the decrease of the FeCFe angle to 85°C in the $[(\pi\text{-}C_5H_5)Fe(CO)_2]_2$ molecule compared with the optimum values 2.7 Å and 90°C, and in the more general case of the cause of the considerable variability of the metal–metal distance and of the bridging angle in the range 67–86°C§. An attempt may be made to answer these questions in the following way. By virtue of the rigidity of their geometry, the bridging ligands exert a purely geometrical influence on the metal–metal distance; then the difference between the geometrical requirements of the bridging groups (and in particular the dimensions of the bridging atom) are responsible for certain differences in the metal–metal distances. This is combined also with effects which determine the nature of the direct interaction between the metal atoms, namely their electronic configuration, effective charge, the repulsion of the non-bonding electrons, and the steric effects of the ligands. All these factors give rise to variations in the metal–metal distances, which in turn lead to a change in the bridging angles. Thus it becomes quite evident that the variability of the metal–metal distances over a wide range in π-complexes in the presence of bridging ligands is reasonable.

All that has been said refers also to molecules containing bridging ligands linking three metal atoms (the so called "face" bridges); in this case the geometrical requirements of the ligands also give rise to an appreciable variation in the metal–metal distances but now in trigonal systems comprising metal atoms.

It is clear from these facts that, in the presence of bridging or pseudo-bridging groups, a widely used criterion of bond types, such as the sum of single bond covalent radii, cannot be applied because the metal–metal distance does not reflect the true nature of the interaction. Moreover, magnetic measurements have shown[10] in many cases that in some molecules the bridging groups may bring appreciably more closely together the non-bonded metal atoms, while in others the marked overlapping of the orbitals of the metal atoms can occur over a large distance. The problem arises of the characterisation of the force of the metal–metal interaction in molecules with bridging groups. In many cases the magnetic properties of the compound may serve as a criterion of this kind but, as pointed out by Lewis[4], it is often difficult to distinguish direct interaction between two metal atoms from interaction via a bridging group and there is no doubt that sometimes interactions of both types occur.

In a comparison of metal–metal bond lengths in molecules (not containing bridging ligands) with twice the values of single bond radii (Table 1) it is important to note that, for elements of the first series, the bond lengths are appreciably increased. This indicates some weakening of the bonds between the metal atoms of the first transition series compared with ordinary covalent bonds. However, with increasing atomic number of the metal within the limits of a given transition series, a tendency is observed for the experimental interatomic metal–metal distances to approach twice the values of the single bond covalent radii, i.e. in the first transition series the force of the metal–metal interaction increases from vanadium to nickel. This tendency is maintained also in the second and third series and the metal–metal bonds actually become shorter than twice the single bond radii (Table 1), which according to Lewis and Nyholm[2-6] is due to a change in the dimensions of the atomic orbitals participating in the formation of the metal–metal bond.

Thus metals in the second and third transition series form stronger bonds than their analogues in the first transition series, which is clearly illustrated by an examination of similar $M_2(CO)_{10}$ (M = Mn, Tc, or Re) molecules with the same structures (Fig. 2). Comparison of the Mn–Mn bond length (2.923 Å) in the dimanganesedecacarbonyl $Mn_2(CO)_{10}$ molecule[15], the Tc–Tc bond length (3.036 Å) in the ditechnetiumdecacarbonyl $Tc_2(CO)_{10}$ molecule[22], and the Re–Re bond length (3.02 Å) in the dirheniumdecacarbonyl $Re_2(CO)_{10}$ molecule[23] with twice the single bond covalent radii (2.76, 3.0_6, and 3.02 Å respectively) indicates a significant difference between the metal–metal bonds in these molecules with identical structures: the Mn–Mn length is increased by about 0.16 Å (i.e. is weakened compared with the ordinary covalent bond), while the Tc–Tc and Re–Re bond lengths are virtually equal to twice the radii (i.e. these bonds are essentially of the ordinary covalent type).

This conclusion is fully consistent with the relative anionic nucleophilicities $[Mn(CO)_5^- \ll Re(CO)_5^-]$,[24] the dissociation energies[25] of the Mn–Mn (0.96 eV or 22 kcal)¶ and Re–Re (2.22 eV or 51.1 kcal) bonds and force constants (Mn–Mn < Re–Re).[25] The strengthening (or more precisely the lack of weakening) of the Tc–Tc and Re–Re bonds compared with the Mn–Mn bond cannot be due to steric effects: the molecules have the same structures and the distances in them between valence non-bonded atoms are similar. Probably the causes of the difference in the behaviour of transition metals of the same Group should be sought also in the variation of the dimensions of their atomic orbitals.

In the case of homopolymetallic complexes where metals of the same Group but different series are combined, their "additive" interaction is observed. Thus in the $(CO)_5Mn$–$Re(CO)_5$ molecule the Mn–Re bond (length 2.96 Å)[26] is intermediate in strength between the Mn–Mn and Re–Re bonds in the decacarbonyls of the two metals: the Mn–Mn bond length increases by about 0.16 Å, Mn–Re by about 0.07 Å, and the Re–Re bond length is the same as the length of the ordinary covalent bond.

The work of Dahl and coworkers on structural studies of homopolymetallic complexes is outstanding; they investigated the dinuclear carbonyls of iron in which the sulphur

§ As pointed out by Wei and Dahl[21], who analysed structures with bonds between metal atoms of the first transition series and with symmetrical CO bridging groups, in these molecules, with the exception of $C_8H_8Fe_2(CO)_5$ and $[C_8H_4(CH_3)_4]Fe_2(CO)_5$, the metal–metal distances do not exceed 2.58 Å, the $M\text{–}C_{bridge}$ bond lengths are in the range 1.82–1.96 Å, and the MCM angles are in the range 78–86°C. A direct correlation between these quantities has not been observed.

¶ We may note that clearly contradictory data are quoted in the literature for the energy of the Mn–Mn bond: 34 ± 13 kcal mole^{-1} (kinetic data[16]) and 18.9 ± 1.4 and 22.1 kcal mole^{-1} (mass-spectrometric data[24]).

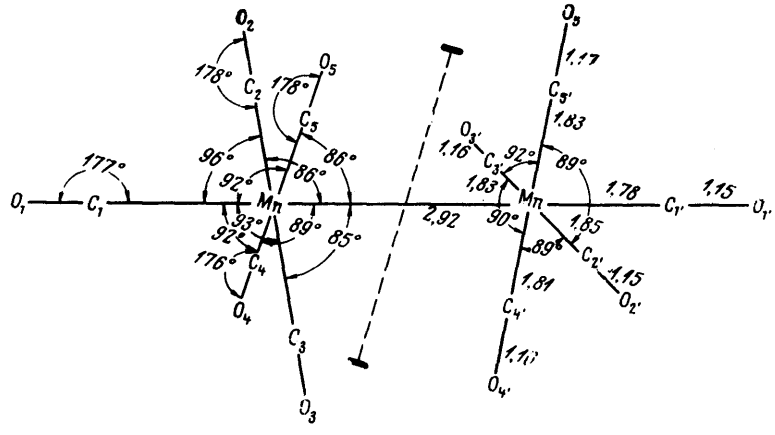


Figure 2. Molecules of the series $M_2(CO)_{10}$(M = Mn, Tc, or Re).

or selenium atom plays the role of the bridge. This group of molecules with the general formula $[XFe(CO)_3]_2$ (where X = S, RS, or RSe and R is an organic group), a typical example of which is $[C_2H_5SFe(CO)_3]_2$ (Fig. 3)[27], has attracted attention because here the concept of so called bent bonds was introduced to describe the metal–metal interactions. Indeed, in molecules of this group the formation of covalent bonds between metal atoms via a colinear overlapping of their atomic orbitals is impossible without a significant distortion from octahedral symmetry. Consequently Dahl[28] postulated an almost undistorted octahedral configuration of the metal atom, which forms a bond with another metal atom via a non-colinear overlapping of a pair of their axial orbitals, i.e. the bond is bent (Fig. 3).

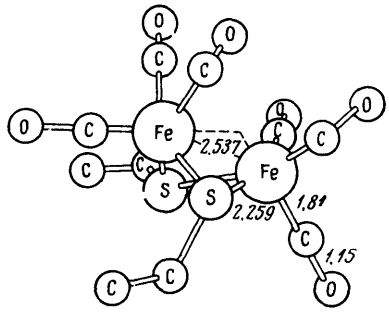


Figure 3. Geometry of the $[C_2H_5SFe(CO)_3]_2$ molecule.

The most interesting of the fields, developed by Dahl and coworkers, comprises work on the elucidation of the effect of the unpaired electrons on the molecular geometry of the complex. This is illustrated by the isomorphous complexes $Co_3(CO)_9S$ and $FeCo_2(CO)_9S$. The paramagnetic molecule of tricobaltenneacarbonyl sulphide[29] $Co_3(CO)_9S$ contains a triangle of Co atoms (Fig. 4) whose side has an average length of 2.64 Å; the S atom is a triple bridge and is located at equal distances (2.14 Å) from all the CO atoms. In the isomorphous complex $FeCo_2(CO)_9S$, which differs from $Co_3(CO)_9S$ by the replacement of a Co atom by an Fe atom, the average metal–metal bond length is 2.554 ± 0.007 Å,[30] i.e. it is shorter by 0.08 Å, although the covalent radius of iron is greater by 0.05 Å than the radius of cobalt. According to Dahl[30], this shortening is evidence of the effect of the unpaired electron on the molecular geometry of the complex. Indeed the replacement of one of the cobalt atoms in the paramagnetic $Co_3(CO)_9S$ molecule by an iron atom leads to a diamagnetic complex $FeCo_2(CO)_9S$ and strengthening of the metal–metal bonds; this shows that the unpaired electron in $Co_3(CO)_9S$ must be located in an antibonding molecular orbital.

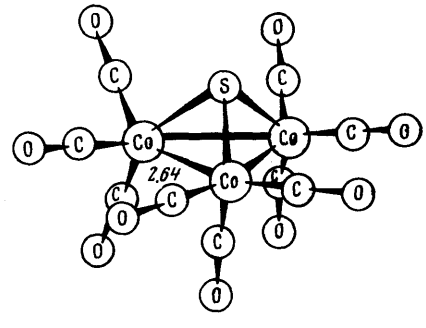


Figure 4. Geometry of the $Co_3(CO)_9$ molecule.

Finally, mention must be made of the structural work of Dahl and coworkers on organocobalt sulphur-containing complexes in which an attempt was made to determine the Co–Co bond order on the basis of quantum-chemical concepts used to analyse the structure of the anion $[Re_3Cl_{12}]^{-3}$ (see, for example, Wei and Dahl[31]).

Nowadays many workers are vigorously investigating the so called cluster compounds, which contain groups of a finite number of metal atoms. According to Cotton[8], the term "cluster" is usually understood as comprising compounds with finite closed groups of metal atoms, forming

triangles, for example $(\pi\text{-}C_5H_5Ni)_3(CO)_2$ (Fig. 5)[32], tetrahedra, for example $Rh_4(CO)_{12}$ (Fig. 6)[33], pentameric groups, for example $Fe_5(CO)_{15}C$ (Fig. 7)[34], and even octahedra, for example $Rh_6(CO)_{16}$ (Fig. 8)[35]. The wide interest in cluster compounds can be explained in the first place by their very unusual properties; one deals not with an individual transition metal atom but with a group, for which such firmly established concepts as, for example, the coordination number and atomic radius† are sometimes inapplicable, since instead of individual atoms one has to consider a fairly complicated collective electron system of a group of metal atoms. This factor permits the inclusion among complexes with covalent bonds only some of the cluster compounds; some of these, for reasons indicated above, can be treated only within the framework of the molecular orbital method, the application of which to such systems is valid and fruitful.

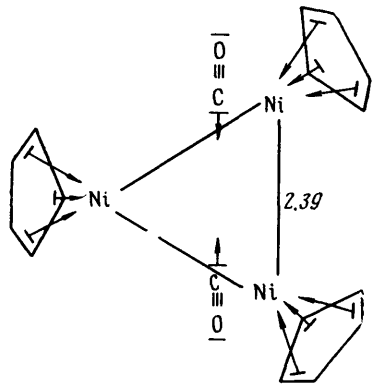


Figure 5. Trigonal group of metal atoms in the $(\pi\text{-}C_5H_5Ni)_3(CO)_2$ molecule.

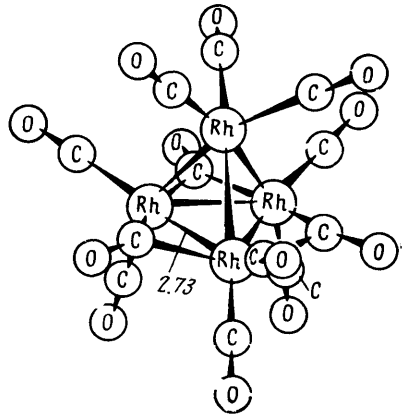


Figure 6. Tetrahedral grouping of metal atoms in the $Rh_4(CO)_{12}$ molecule.

† See the footnote on p. 791.

2. Heteropolymetallic Complexes

The number of π-complexes with bonds between transition metals belonging to different Groups‡, whose structures have been investigated, is small (Table 3) and studies of this kind have not been systematic.

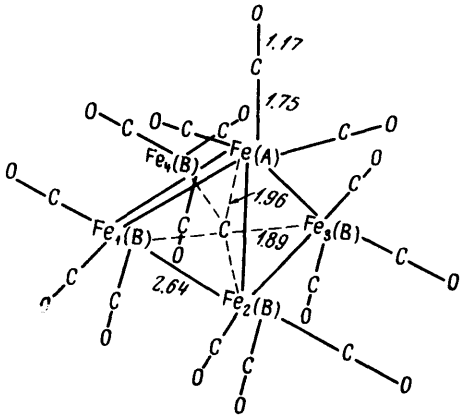


Figure 7. Pentameric grouping of metal atoms in the $Fe_5(CO)_{15}C$ molecule.

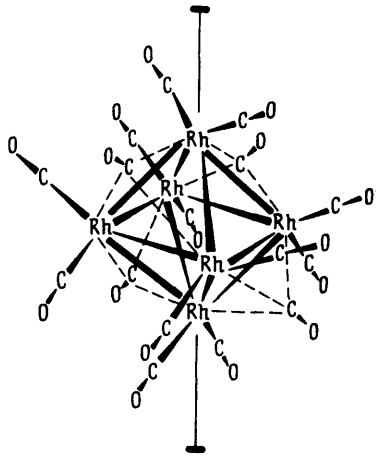


Figure 8. Octahedral grouping of metal atoms in the $Rh_6(CO)_{16}$ molecule.

The results of the investigations of heterodimetallic molecules such as $(\pi\text{-}C_5H_5)Mo(CO)_3\text{–}Mn(CO)_5$ (Fig. 9)[36], which are a combination of the monomeric fragments of dimeric homodimetallic molecules [in this case $[(\pi\text{-}C_5H_5)Mo(CO)_3]_2$ [37] and $Mn_2(CO)_{10}$ [15]] via a metal–metal

‡ Heteropolymetallic π-complexes of course include also compounds containing the same metal atoms with different electron configurations, but the metal–metal bond lengths in them are close to those found in homopolymetallic complexes.

bond. The equality of the Mo–Mn bond length (3.08 Å) in this molecule to half the sums of the Mo–Mo and Mn–Mn distances in dimeric molecules [(3.222 + 2.923)/2 = 3.072] indicates that in the formation of heterodimetallic complexes the interaction of monomeric fragments is "additive", i.e. takes place without appreciable changes in the nature of the orbitals of the metal atoms participating in the formation of the metal–metal bonds.

Table 3. Metal–metal bond lengths in heteropolymetallic π-complexes.

Bond	Bond length, Å	Sum of single bond covalent radii	Absolute change in bond length	Relative change in bond length, %
Fe–Mn	2.82	2.7_2	+0.10	+3.7
Fe–Pd*	2.59	2.8_3	−0.24	−8.5
Mo–Mn	3.08	2.9_6	+0.12	+4.1
Mo–Re	3.12	3.0_9	+0.03	+1.0
W–Mn	3.16	2.9_7	+0.19	+6.4
Pt–Co	2.61	2.7_2	−0.11	−4.0
Pt–Mn	2.74	2.8_1	−0.07	−2.5

*Bond "strengthened" by a bridging group.

Thus the type of interaction between covalently linked metal atoms in heteropolymetallic complexes is determined by the same factors as in the previously discussed homopolymetallic complexes.

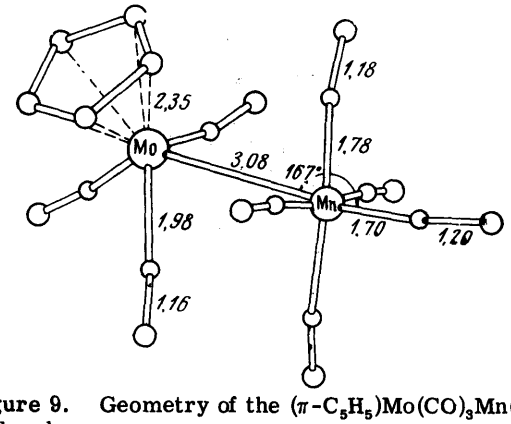


Figure 9. Geometry of the $(\pi\text{-}C_5H_5)Mo(CO)_3Mn(CO)_5$ molecule.

To illustrate this conclusion, we shall consider the pairs of compounds $(\pi\text{-}C_5H_5)Mo(CO)_3\text{–}M(CO)_5$ (M = Mn or Re) and $(\pi\text{-}C_5H_5)M(CO)_3Mn(CO)_5$ (M = Mo or W). Comparison of the metal–metal bond lengths (3.08 Å [36] and 3.12 Å [26]) with the sums of the single bond covalent radii (2.96 and 3.09 Å) for the first pair of compounds shows that the Mo–Mn bond (relative bond elongation Δ_{rel} = +4.1%, see Table 3) is somehwat weaker than the Mo–Re bond (Δ_{rel} = +1.0%). Comparison of the second pair of compounds shows that the W–Mn bond is somewhat weaker than Mo–Mn (Δ_{rel} = 6.4 and 4.1% respectively). Thus in the case of heteropolymetallic complexes too the metals of the second and third transition series from stronger bonds and the maximum tendency of this kind is shown by metals of the second transition series.

It is noteworthy that, although the molecules with metal–metal bonds discussed are not overcrowded in the usual sense of this term, certain details of their real conformations are in fact due to the interaction of the valence nonbonded atoms. Thus in the $(\pi\text{-}C_5H_5)Mo(CO)_3\text{–}Mn(CO)_5$ molecule [36] already discussed (Fig. 9) there is a considerable number of brief contacts between the carbonyl groups at the Mo and Mn atoms, i.e. the $(\pi\text{-}C_5H_5)Mo(CO)_3$ and $Mn(CO)_5$ fragments undergo mutual steric repulsion, which leads to a weakening of the metal–metal interaction.

B. COMPOUNDS WITH COVALENT BONDS BETWEEN TRANSITION METALS AND ELEMENTS OF GROUPS IB–IVB

The number of structural studies on compounds of this type has been small and they have been systematic only for compounds with direct bonds between transition metals and non-transition elements of Group IVB.

A characteristic feature of compounds with direct bonds between Group IB elements (copper, silver, and gold) and transition metals, for example $(C_6H_5)_3PAu\text{–}Mn(CO)_5$, [38] is the presence of phosphine or arsine ligands attached to the

Table 4. Covalent bonds between transition metal atoms and those of elements in Groups IB–IVB.

Bond	Metal–metal bond length, Å	Sum of single bond covalent radii, Å	Absolute change in bond length, Å	Relative change in bond length, %
Group IB element–transition metal				
Au–Mn	2.52–2.57	2.82	−(0.25–0.30)	8.9–10.6
Au–Co	2.50	2.73	−0.23	8.4
Au–W	2.69	3.0_3	-0.3_4	11.2
Cu–Mn	2.56	2.66	−0.10	3.8
Group IIB element–transition metal				
Hg–Fe	2.44–2.59	2.8_4	−(0.27–0.42)	9.4–14.7
Hg–Co	2.50–2.58	2.81	−(0.23–0.31)	8.2–11.0
Zn–Co	2.30	2.63	−0.33	12.5
Group IIIB element–transition metal				
In–Co	2.53–2.63	2.73	−(0.10–0.20)	3.7– 7.2
Group IVB element–transition metal				
Sn–Cr	2.85	2.86	−0.01	0.3
Sn–Mo	2.75	2.9_8	-0.2_3	7.7
Pb–Mo	2.90	3.0_4	-0.1_4	4.6
Sn–W	2.76–2.81	2.9_9	$-(0.1_8–0.2_3)$	6.0– 7.7
Ge–Mn	2.53–2.60	2.60	−(0–0.07)	0–3.0
Ge–Re	2.69	2.73	−0.04	0.2
Sn–Mn	2.63–2.74	2.78	−(0.04–0.15)	1.0– 5.3
Sn–Re	2.74	2.91	−0.17	5.8
Pb–Re	2.77	2.97	−0.20	6.7
Ge–Fe	2.36–2.40	2.5_6	$-(0.1_6–0.2_0)$	6.2– 7.8
Sn–Fe	2.46–2.75	2.7_4	−(0.01–0.28)	0.4–10.2
Sn–Ru	2.56–2.69	2.8_9	−(0.20–0.33)	6.9–11.4
Pb–Fe	2.71	2.8_9	-0.0_8	3.2
Si–Co	2.25–2.38	2.46	−(0.08–0.21)	3.2– 8.5
Sn–Co	2.66	2.69	−0.03	1.1
Sn–Jr	2.64	2.8_7	-0.2_3	8.0
Sn–Pd	2.56	2.8_9	-0.3_3	11.4
Sn–Pt	2.80	2.8_3	-0.0_3	10.6

*Pauling's radii [14] corresponding to a coordination number of 12 were employed for elements in Group IB–IIIB; the values for Group IVB elements were taken from Bokii and Struchkov [55] and those for transition metals from Andrianov et al. [13] see Table 2.

non-transition element. Groups such as $(C_6H_5)_3PAu$ and $(C_6H_5)_3SbCu$ have electronegativities similar to those of halogens[2]. This suggests[39] the possibility of an electronic d_π–d_π interaction between these groups and transition metals. As a result there is a transfer of non-bonding d electrons of the transition metal atom to the vacant d orbitals of the IB Group element and the stability of derivatives of the type $R_3P \rightarrow Au–Mn(CO)_5$ increases[40] as the electron-acceptor properties of the R substituents become more pronounced.

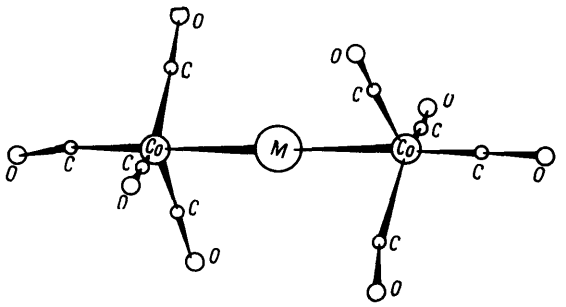


Figure 10. Molecules of the series $M[Co(CO)_4]_2$ (M = Hg or Zn).

The occurrence of d_π–d_π interaction is supported also by the fact that substitution reactions in derivatives of this kind involve carbonyl groups. Finally, comparison of the bond lengths between Group IB elements and transition metals with the sums of the single bond covalent radii (Table 4) shows that the bond lengths are appreciably shorter (by about 0.1–0.3 Å), which is evidence of an increase in the multiplicity of these bonds compared with ordinary covalent bonds.

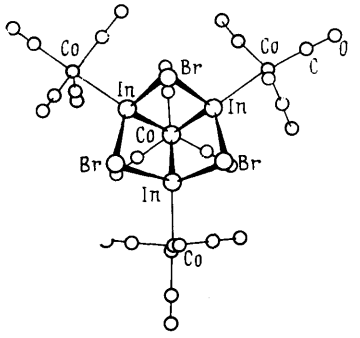


Figure 11. Geometry of the $In_3Br_3Co_4(CO)_{15}$ molecule.

An analogous situation is observed also for compounds with direct bonds between elements of Group IIB and transition metals, for example $M[Co(CO)_4]_2$ (M = Hg [41] or Zn,[42] Fig. 10). The significant shortening (by about 0.3–0.4 Å, Table 4) of these bonds also suggests their partial double bond character, caused[43] by the transfer of d electrons from the occupied orbitals of the transition metal to vacant orbitals of the IIB Group elements.

Amongst compounds with bonds between Group IIIB elements and transition metals, structural studies have been made[44] only on the product of the reaction of InBr and $Co_2(CO)_8$ having the composition $In_3Br_3Co_4(CO)_{15}$.

The molecule contains a buckled six-membered ring (Fig. 11) consisting of alternating In and Br atoms. Each indium atom is linked to a $Co(CO)_4$ group via a metal–metal bond with a length of 2.53–2.58 Å and the fourth cobalt atom (in a $Co(CO)_3$ group), which is different from the other cobalt atoms, forms bonds with all three indium atoms with a length of 2.57–2.63 Å. All these bonds are shorter than the sum of the single bond radii (2.73 Å).

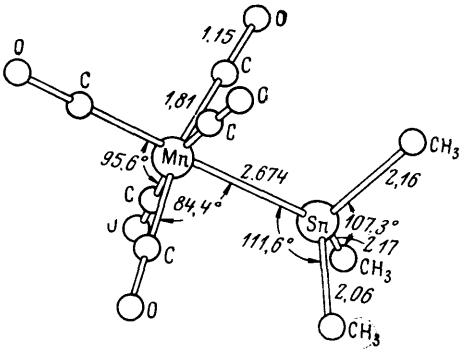


Figure 12. Bond lengths and valence angles in the $(CH_3)_3SnMn(CO)_5$ molecule.

We now come to the discussion of π-complexes with bonds between transition metals and non-transition Group IVB elements, a typical example of which is $(CH_3)_3Sn–Mn(CO)_5$ (Fig. 12);[45] this group of compounds has been most completely investigated. Examination of the metal–metal distances of these molecules reveals two striking facts: appreciable variability of the metal–metal bond lengths and a significant shortening of the bonds compared with the sums of the single bond covalent radii (Table 4). For example the Sn–Mn and Sn–Fe bond lengths vary in the ranges 2.63–2.74 and 2.47–2.75 respectively, while the sums of the radii are 2.78 and 2.74 Å.

Numerous studies of the infrared spectra of such series of compounds show that the stretching vibration frequencies of the carbonyl groups attached to the transition metal atoms are exceptionally sensitive to the nature of the substituent X at the atom of the non-transition Group IVB element. This effect has been treated in two different ways in the literature (see, for example, Refs. 46–48). According to the first treatment, the change in the nature of the σ bond between metal atoms on replacement of X (for example as a result of a change in the σ-donor properties of the ligands $X_3Sn–$, $X_2Sn<$, and $XSn\equiv$) leads to a change in the effective charge at the transition metal atom, which is reflected in a variation of the stretching vibration frequencies of the CO groups. For example, an increase in these frequencies on replacement of X = CH_3 by the more electronegative X = Cl in the series $X_3Sn–Mn(CO)_5$ (X = CH_3, Fig. 12) can be due to the more positive nature of the Mn atom in the latter case (in

other words a lower negative charge of the atom), which leads to a weakening of the dative d_π–p_π Mn–C bond and an increase in the multiplicity of the C–O bond.

In the treatment of the second type of effect of the substituent X consists in a change of the affinity of the vacant *d* orbitals of the non-transition Group IVB element for the non-bonding *d* electrons of the transition metal atom if one postulates the occurrence of d_π–d_π interaction in the metal–metal bond under consideration. Thus the two types of treatment are not mutually exclusive and require both σ-donor and π-acceptor properties of the ligands to be taken into account.

We are bound to admit that the problem of the occurrence of d_π–d_π interaction in metal–metal bonds is at present controversial, particularly owing to the lack of quantum-chemical calculations for this group of compounds, but there is much indirect spectroscopic[48] and chemical evidence in favour of such interaction.

The experimental data for interatomic metal–metal distances also indicate some increase in the bond multiplicity. For example, the length of the Mn–Mn bond varies in the range 2.63–2.74 Å and is much shorter than the sum of the single bond covalent radii (2.78 Å).

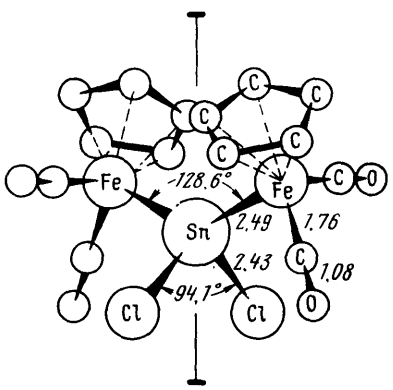


Figure 13. Bond lengths and valence angles in the $[(\pi\text{-}C_5H_5)Fe(CO)_2]_2SnCl_2$ molecule.

In another very fully investigated group of compounds with Sn–Fe bonds, it is possible to distinguish molecules of the series $[(\pi\text{-}C_5H_5Fe(CO)_2]_2SnX_2$, for example with X = Cl (Fig. 13).[49] Spectroscopic studies also show[50,51] a change in the stretching vibration frequencies of the CO group as a function of the properties of the substituent X. The Sn–Fe bonds gradually become shorter with increasing electronegativity of X, the length decreasing from 2.60 Å for X = CH_3 [52] to 2.49 Å for X = Cl,[49] while the sum of the single bond covalent radii is 2.75 Å. At the same time a gradual increase of the FeSnFe angle is observed: from 123.4° to 128.6°C on replacement of CH_3 by Cl. All these findings suggest that, with increase of the electronegativity of X, the multiplicity of the metal–metal bond also increases owing both to an enhancement of the d_π–d_π interaction and the hybridisation ($sp^3 \rightarrow sp^2$) of the tetrahedral atomic orbitals of the non-transition element participating in the metal–metal bond, in accordance with Bent's rule[53].

The experimental interatomic distances permit a comparison of the molecules of the series under consideration, differing both in the transition metal atoms, for example $(C_6H_5)_3Ge$–$M(CO)_5$ (where M = Mn or Re), and the atom of the non-transition Group IVB element, for example $(C_6H_5)_3A$–$Re(CO)_5$ (where A = Ge, Sn, or Pb).

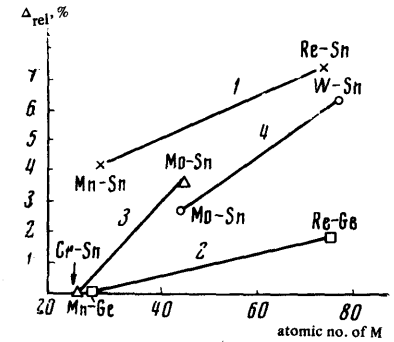


Figure 14. Variation of the relative shortening of metal–metal bonds with the atomic number of the transition metal in molecules with covalent bonds between transition metal atoms and those of a non-transition Group IVB element:
1) $(OC)_5MSn(C_6H_5)_3$; *2*) $(OC)_5M$–$Ge(C_6H_5)_3$;
3) $C_5H_5(CO)_3M$–$Sn(C_6H_5)_3$; *4*) $[C_5H_5M(CO)_3]_2Sn(C_6H_5)_2$.

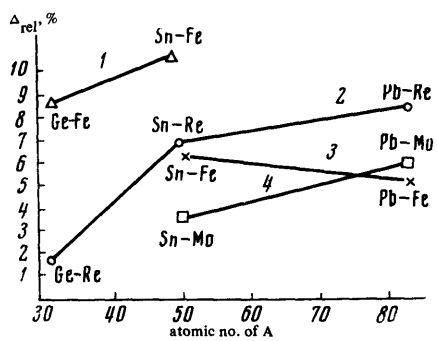


Figure 15. Variation of the relative shortening of metal–metal bonds with the atomic number of the transition metal in molecules with covalent bonds between transition metal atoms and those of a non-transition Group IVB element:
1) $[C_5H_5Fe(CO)_2]_2.ACl_2$; *2*) $(OC)_5Re$–$A(C_6H_5)_3$;
3) $[C_5H_5Fe(CO)_2]_2A(CH_3)_2$; *4*) $C_5H_5(CO)_3Mo$–$A(C_6H_5)_3$.

Fig. 14 presents plots of the relative shortening of the metal–metal bonds $\Delta_{rel} = \Delta_{abs}/\Sigma r$ with the atomic number of the transition metal showing that the overall tendency of the transition metal atoms of the second and third series to form more stable metal–metal bonds compared with their analogues in the first series is maintained also when they combine with a non-transition Group IVB element.

As regards molecules with different non-transition Group IVB elements, it is found that, within the limits of the available experimental data (Fig. 15), tin forms stronger bonds than germanium, while for lead no systematic trend has been observed.

III. COMPLEXES WITH METAL–DONOR BONDS

This group includes molecules with square planar coordination about the central metal atom, which has a d^8 valence configuration, for example $Rh(CO)_2[(CH_3CO)_2CH]$ [54] (Fig. 16). In crystals molecules of such compounds are distributed one on top of the other in parallel planes with metal–metal distances of 3.2–3.33 Å (while the distance equal to twice the covalent radius is 2.7–3.0 Å).

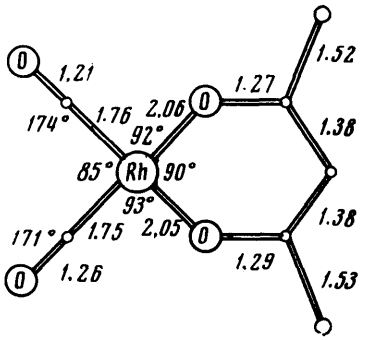


Figure 16. Geometry of the $Rh(CO)_2[(CH_3CO)_2CH]$ molecule.

Thus the coordination about the metal atom is increased to give a distorted octahedron as a result of the formation of the so called metal–donor or polymeric metal–metal bonds. It has been shown[3] that such metal–metal interaction, leading to the formation of an infinite one-dimensional polymetallic system, takes place as a result of the overlapping of the filled d_{z_2} orbital of one metal atom and the vacant p_z orbital of an adjacent atom. These bonds impart to the crystal certain properties of the metal, giving rise, in particular, to a sharp anisotropy of its electrical conduction and photoconduction. The metal–metal interaction of this type is probably not entirely covalent, so that crystals of compounds of this kind exhibit semiconductor properties to a greater extent than metallic properties.

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