BOND HYBRIDIZATION AND STRUCTURE IN THE METAL CARBONYLS

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CONTENTS

I. INTRODUCTION

The metal carbonyls occupy an unusual position in the broad field of transition metal complexes. These compounds may be regarded as coördination complexes formed between electron-donor carbon monoxide molecules and zerovalent transition metals. The resulting complexes, in contrast to the usual properties of coördination complexes, are electrically neutral, diamagnetic, and quite volatile. Another unusual feature of the metal carbonyls is that the coördination number is not such as to satisfy a stable geometrical configuration, as in the numerous octahedral complexes. Instead, the most important factor governing the coördination number seems to be the attainment of a closed shell of electrons. For example, the trigonal bipyramid structure is quite common within the metal carbonyls [Fe(CO)$_5$, Ru(CO)$_5$, Os(CO)$_5$, Co$_2$(CO)$_8$] but is rarely encountered elsewhere. It is this type of unusual behavior that has led to much of the interest in these compounds. In table 1 are listed the known metal carbonyls along with some of their physical properties.

The physical and chemical properties of the metal carbonyls have been well covered in previous reviews (2, 6, 89). This aspect of the present review will be brought up to date but otherwise will be held to a minimum. The more recent trend in the study of the metal carbonyls has involved the elucidation of their structures and the nature of the bonding. This is the phase which will be stressed in this review. An attempt has been made to review the literature up to January 1, 1955.

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TABLE 1
The known metal carbonyls and their properties

Cr (24)	Mn (25)	Fe (26)	Co (27)	Ni (28)
$Cr(CO)_6$: sublimes, colorless	$Mn_2(CO)_{10}$: m.p. 154-155°C., golden yellow	$Fe(CO)_5$: m.p. −20°C., b.p. 103°C., yellow $Fe_2(CO)_9$: decomposes at 100°C., golden yellow $Fe_3(CO)_{12}$: decomposes at 140°C., dark green	$Co_2(CO)_8$: m.p. 51°C., golden yellow $[Co(CO)_3]_n$: decomposes at 60°C., jet black	$Ni(CO)_4$: m.p. −25°C., b.p. 43°C., colorless
Mo (42)	Tc (43)	Ru (44)	Rh (45)	Pd (46)
$Mo(CO)_6$: sublimes, colorless		$Ru(CO)_5$: m.p. −22°C., colorless $Ru_2(CO)_9$: orange $Ru_3(CO)_{12}$: green	$Rh_2(CO)_8$: m.p. 76°C. (decomposes), orange $[Rh(CO)_3]_n$: red $[Rh_4(CO)_{11}]_m$: black	
W (74)	Re (75)	Os (76)	Ir (77)	Pt (78)
$W(CO)_6$: sublimes, colorless	$Re_2(CO)_{10}$: m.p. 177°C., colorless	$Os(CO)_5$: m.p. −15°C., colorless $Os_2(CO)_9$: m.p. 224°C., bright yellow	$Ir_2(CO)_8$: sublimes, yellow-green $[Ir(CO)_3]_n$: decomposes 210°C., yellow	

TABLE 2
Bond distances in the metal carbonyls

Carbonyl	R_{M-C}	R_{C-O}	Method	Reference	R_{M-C} (calculated)*
	Å.	Å.			
$Ni(CO)_4$...............	1.84 ± 0.03	1.15 ± 0.03	X-ray	(55)	1.92
	1.82 ± 0.03	1.15	Electron diffraction	(9)	
$Fe(CO)_5$................	1.84 ± 0.03	1.15 ± 0.04	Electron diffraction	(31)	1.94
$Cr(CO)_6$...............	1.92 ± 0.04	1.16 ± 0.05	Electron diffraction	(10)	1.94
$Mo(CO)_6$..............	2.08 ± 0.04	1.15 ± 0.05	Electron diffraction	(10)	2.06
$W(CO)_6$................	2.06 ± 0.04	1.13 ± 0.05	Electron diffraction	(10)	2.07
$Fe_2(CO)_9$..............	1.9 ± 0.05 1.8 ± 0.05 (bridge)	1.15 ± 0.05 1.3 ± 0.05 (bridge)	X-ray	(72)	1.94
$HCo(CO)_4$.............	1.83 ± 0.02 1.75 ± 0.08 (COH)	1.15 ± 0.05	Electron diffraction	(31)	1.93
$H_2Fe(CO)_4$............	1.84 ± 0.03 1.79 ± 0.04 (COH)	1.15 ± 0.05	Electron diffraction	(31)	1.94

* Covalent radii taken from page 135 of reference 60.

II. NATURE OF BONDING

In table 2 are given bond-length data for some of the metal carbonyls and hydrocarbonyls. The internuclear distances observed for these compounds have led to much discussion of the nature of the bonding involved (17, 60, 71). In this discussion of bonding in polyatomic molecules it is convenient to use the concept of localized molecular orbitals. This permits a comparison of the properties of an "atom-pair" bond in a series of related molecules, while also allowing a
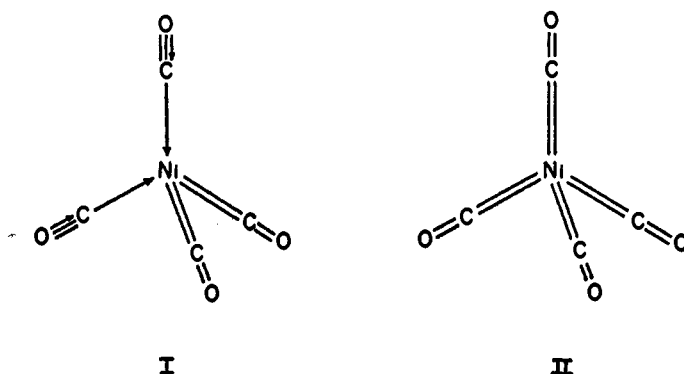
FIG. 1. Structure and bonding of nickel tetracarbonyl, Ni(CO)₄

description of these bonds in the familiar σ and π designation. Three groups of "atom-pair" bonds are considered: (A) the carbonyl bonds, (B) the metal–carbon bonds, and (C) the metal–metal bonds.

A. THE CARBONYL BONDS

The carbon–oxygen internuclear distance in the metal carbonyls has consistently been observed to be 1.15 Å. (see table 2). This distance, being intermediate between the carbon–oxygen distance in formaldehyde (1.225 Å.) and that in carbon monoxide (1.128 Å.), has led many investigators to the conclusion that the bond order is intermediate between the C=O double bond (formaldehyde) and the C≡O triple bond (carbon monoxide). Additional support for this was gained from force constant data, the carbonyl stretching force constants being 12.3×10^5, 15.89×10^5, and 18.6×10^5 dynes/cm. for formaldehyde, nickel tetracarbonyl, and carbon monoxide, respectively. This intermediate bond order was represented by resonance among such structures as I in figure 1. Nyholm and Short (68) point out that a comparison of the force constant and bond length in nickel tetracarbonyl with these values for formaldehyde is not justified, since the hybridization of the carbon atom in the two cases differs. Thus, in formaldehyde the carbon bonding orbital is an sp^2 hybrid, whereas in nickel tetracarbonyl it is an sp hybrid. This increase in s-character in the carbon–oxygen bond leads to an increase in bond strength and therefore a smaller internuclear distance. The carbonyl bonds in nickel tetracarbonyl should then be compared with those in such compounds as ketene, carbon dioxide, carbon suboxide, etc., in which the carbon bonding orbitals are sp hybrids. Such a comparison reveals a striking similarity, as is shown in table 3. From this it was concluded that the completely double-bonded structure (II) best described the molecule. A similar argument was presented earlier (58, 90) to explain the internuclear distances in such molecules as ketene and the metal carbonyls. The change in hybridization was taken into account, but bond polarity was taken as the criterion of bond strength. Walsh (91) was able to calculate the "per cent polarity" of the carbonyl bond in a series of compounds from ionization potentials of a non-bonding p-electron of the oxygen atom. This ionization potential

TABLE 3

Properties of the carbonyl bond

Compound	R_{C-O}		$k \times 10^{-5}$		ϵ_{C-O}*
	Value	Reference	Value	Reference	
	$\overset{\circ}{A}.$		*dynes/cm.*		*kcal./mole*
H_2CO................	1.225	(1)	12.3	(56)	163.8
CH_2CO..............	1.16 ± 0.02	(11)	15.5	(38)	181.0
COS.................	1.1637	(86)	15.2	(33)	191.6
CO_2.................	1.1632	(1)	15.5	(16)	192.0
$Ni(CO)_4$.............	1.15 ± 0.02	(1)	15.89	(20)	(196)†
BH_3CO..............	1.131	(34)	17.3	(19)	(218)†
CO..................	1.13078	(32)	18.55	(16)	257.3

* Based on thermodynamic data taken from reference 75. The value 171.7 kcal./mole was used for the heat of sublimation of carbon.
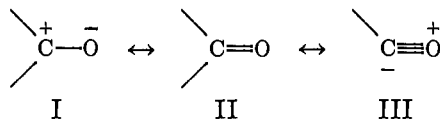
† Estimated from a plot of bond energy *versus* force constant.

was found to be inversely related to the bond polarity. A comparison of these polarities with internuclear distances and force constants shows that the bond strength increases as the polarity decreases. It was concluded (58, 90) that the use of covalent-ionic resonance to describe the carbonyl bond was incorrect, since this should lead to an increase in both bond polarity and bond strength. While such a conclusion is unnecessary, perhaps even undesirable,[1] the bond polarity–bond strength relationship is very useful in predicting the effect of certain factors on the carbonyl. Three such factors deserve special consideration: (1) carbon atom hybridization, (2) ring strain, and (3) inductive effects.

1. Carbon atom hybridization

It has been shown (61) that the absolute electron affinity of an atomic orbital increases considerably with an increase in s character. Thus the greater electron affinity of an sp hybrid orbital compared with an sp^2 hybrid orbital should provide a less polar and therefore stronger carbonyl bond. This is the argument used by Walsh to explain the stronger carbonyl bonds in ketene, carbon dioxide, and metal carbonyls as compared to those in aldehydes and ketones. The magnitude of this effect can be seen from table 3.

[1] The observation of the inverse relationship between bond polarity and bond strength should properly be considered in agreement with the covalent-ionic resonance formulation of the valence-bond theory. Consider the usual resonance structures:

$$\underset{I}{\overset{+}{\underset{}{C}}-\overset{-}{O}} \quad \leftrightarrow \quad \underset{II}{C=O} \quad \leftrightarrow \quad \underset{III}{\overset{+}{C}\equiv\overset{-}{O}}$$

The polarity and bond length of these three structures decrease in the order I, II, III. Any effect which would enhance the importance of structure I would lead to a weaker and more polar bond. Such an effect would be the addition of electron-releasing substituents. Contrarily, any effect enhancing the importance of structure III would lead to a less polar and stronger carbonyl bond. Such effects would be the addition of electron-attracting substituents or internal strain (see sections 2 and 3 of the following discussion).

2. Ring strain

This factor could properly be treated under the previous section (section 1). It is discussed separately here because the hybridization changes are of such different magnitude.

It has been observed by many investigators that the characteristic carbonyl vibration frequency of cyclic ketones is a function of the ring strain. These frequencies increase with an increase in ring strain. Thus, the carbonyl frequencies in cyclohexanone, cyclopentanone, and cyclobutanone are 1714, 1744, and 1774 cm.$^{-1}$, respectively.[2] This may be explained as the effect of a rehybridization of the carbon hybrid orbitals with a change in interbond angles. Consider the carbon atom in cyclohexanone to which the oxygen is bonded. In this molecule there is no strain and the three σ-bonding orbitals of the carbon may be considered as equivalent sp^2 hybrids. With a decrease in the $\angle$ CCC from 120° (as in cyclopentanone or cyclobutanone) a rehybridization occurs. This gives the external σ-bonding orbital, directed toward the oxygen, more s-character and the σ-bonding orbitals directed toward the carbon atoms more p-character (18). This increase in s-character increases the electron affinity of the external bonding orbital, decreasing the bond polarity and therefore increasing the bond strength. This increase in bond strength is shown by the increasing frequencies in the series cyclohexanone, cyclopentanone, cyclobutanone.

3. Inductive effects

Substitution of electron-attracting groups for the hydrogen atoms of formaldehyde should cause a decrease in the bond polarity and therefore an increase in bond strength. This is observed, the carbonyl frequencies of formaldehyde, phosgene, carbonyl fluorochloride, and carbonyl fluoride being 1743, 1827, 1868, and 1928 cm.$^{-1}$, respectively (66).

This concept of partial triple-bond character from the valence-bond theory has been put on a more quantitative basis in the molecular orbital theory. Moffitt (61) has been able to calculate the π-bond order for several of the electronic states of carbon monoxide and carbon dioxide. A plot of this calculated π-bond order *versus* internuclear distance is shown in figure 2. A very interesting feature of this curve is the sharp descent and point of inflection between 1.21 and 1.13 Å. This implies a large change in bond strength and internuclear distance, with small changes in π-bond order in this region. By the assumption of localized molecular orbitals, this curve can be extended to gain a better understanding of the carbonyl bonds in more complicated molecules. Thus, the carbon–oxygen distance of 1.15 Å. in the metal carbonyls corresponds to a π-bond order of 1.45. It is of interest that the carbon–oxygen distance of 1.225 Å. in formaldehyde corresponds to a π-bond order of 1.06, so that the use of that bond as the normal C≡O double bond has more basis than has been attributed to it by some authors.

The carbonyl bond in such metal carbonyls as nickel tetracarbonyl or iron pentacarbonyl is then very similar to that in carbon dioxide but somewhat

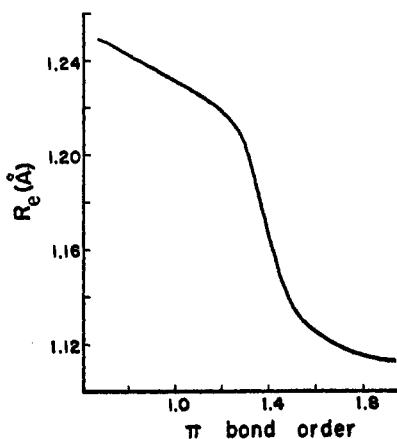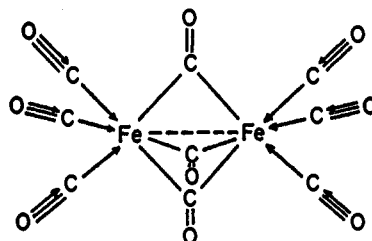---

[2] Spectra determined in the liquid state.

FIG. 2. Internuclear distance plotted against π-bond order for carbon-oxygen bonds
FIG. 3. Structure of $Fe_2(CO)_9$

stronger (see table 3). However, it is still necessary to consider the bond as having partial triple-bond character.

Interestingly enough, another type of carbonyl bond is encountered in the metal carbonyls. An x-ray study (72) of $Fe_2(CO)_9$ showed the molecule to have the structure shown in figure 3. The $\angle FeCFe$ of the bridging carbonyl groups was found to be 87°. According to the previous discussion the bridging carbonyl bond would be expected to be similar to that in cyclobutanone. This similarity is shown in the infrared spectrum of the compound (80). The spectrum shows an intense band at 1828 cm.$^{-1}$ in addition to the expected bands at 2034 and 2080 cm.$^{-1}$ The band at 1828 cm.$^{-1}$ was assigned as a bridging carbonyl stretching frequency. The corresponding frequency in cyclobutanone is 1774 cm.$^{-1}$ The infrared spectra of $Co_2(CO)_8$ (13), $[Co(CO)_3]_x$ (14), and $Fe_3(CO)_{12}$ (79) also contain frequencies which have been attributed to bridging carbonyl groups.

B. THE METAL–CARBON BONDS

It may be concluded from the previous discussion that the carbonyl bonds in the metal carbonyls have a bond order of about 2.5. Accordingly, a metal–carbon bond order of about 1.5 would be expected. Internuclear distances are in complete accord with this (see table 2). This partial double-bond character is achieved by utilization of the d-orbital electrons of the metal in π-bonding. This type of bonding has been called "dative π-bonding" (15) and was used to explain the relative acid strengths of the acids p-$R_3MC_6H_4COOH$ (where M is carbon, silicon, germanium, or tin and R is methyl and ethyl).

This metal–carbon double-bond character is particularly appealing in the metal carbonyls because it removes an otherwise high negative charge from the central metal. Such a negative charge is contrary to the tendency of metals to lose electrons and form positive ions. In this respect, the metal–carbon bonds in the cyanide complexes are expected to be similar to those in the metal car-

TABLE 4

Properties of metal–carbon bonds

| Bond | Compound | R_{M-C} | | $k \times 10^{-5}$[†] | ϵ_{M-C}[§] |
		Observed[*]	Calculated[**]		
		Å.	Å.	dynes/cm.	kcal./mole
Zn—C..............	Zn(CH₃)₂	—	2.02	2.39	38.6
Cd—C..............	Cd(CH₃)₂	—	2.18	2.05	30.8
Hg—C..............	Hg(CH₃)₂	2.23	2.21	2.45	23.9
Ge—C..............	Ge(CH₃)₄	1.98	1.99	2.72	—
Sn—C..............	Sn(CH₃)₄	2.18	2.18	2.37	50.9
Pb—C..............	Pb(CH₃)₄	2.29	2.31	1.94	40.3
As—C..............	As(CH₃)₃	1.98	1.98	2.44	—
Sb—C..............	Sb(CH₃)₃	2.13	2.18	2.09	—
Bi—C..............	Bi(CH₃)₃	2.23	2.29	1.75	—
Ni—C..............	Ni(CO)₄	1.82	1.92	2.52[‡]	95[¶]
Fe—C..............	Fe(CO)₅	1.84	1.94	—	89[¶]

[*] Taken from reference 1.
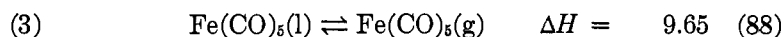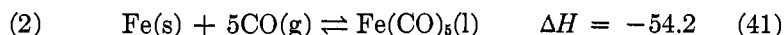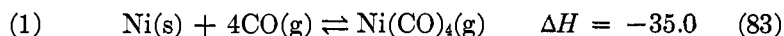[**] Covalent radii from page 135 of reference 60.
[†] Taken from reference 77 with the exception of the value for the Ni—C bond.
[‡] Reference 20.
[§] Thermodynamic data taken from reference 75.
[¶] Obtained by assumption of a carbonyl bond energy of 196 kcal./mole (see table 3).

bonyls. Insufficient experimental data make a comparison of the metal–carbon bonds in these two types of complexes difficult. However, a comparison of the metal–carbon bonds in the carbonyls with those in the metal alkyls can be made. Some of the relevant bond properties are presented in table 4. The bond energies of the metal alkyls were calculated using the carbon–hydrogen bond energy from methane, with most of the data taken from the tables of the National Bureau of Standards (75). Heats of vaporization were determined from the boiling points by the assumption of a Trouton's constant of 21 for those metal alkyls for which these data were lacking. The heats of formation of tin tetramethyl and lead tetramethyl were taken from the recent work of Lippincott and Tobin (56). Other data used are shown in equations 1, 2, and 3.

(1) $Ni(s) + 4CO(g) \rightleftharpoons Ni(CO)_4(g)$ $\Delta H = -35.0$ (83)

(2) $Fe(s) + 5CO(g) \rightleftharpoons Fe(CO)_5(l)$ $\Delta H = -54.2$ (41)

(3) $Fe(CO)_5(l) \rightleftharpoons Fe(CO)_5(g)$ $\Delta H = 9.65$ (88)

A carbon–oxygen bond energy of 196 kcal./mole was used in both cases (see table 3). The surprisingly large bond-energy values of the carbonyls compared with the low values of the single-bonded alkyls support the idea of double-bond character in the metal carbonyls. The fact that the alkyl derivatives of the transition metals have never been isolated has been attributed to very weak metal–carbon bonds in those compounds (49). These would necessarily be single bonds. The existence and relative stability of the carbonyls and cyanide complexes of these metals is indicative that stronger metal–carbon bonds are involved.

It is of interest that the bond energy is larger in nickel tetracarbonyl than in iron pentacarbonyl. The π-bonding orbitals of nickel in nickel tetracarbonyl are

sp^3 hybrids and those of iron in iron pentacarbonyl are dsp^3 hybrids. On Pauling's scale of bond strength these have the values 2.000 and 2.724,[3] respectively. If the metal–carbon bonds were single bonds, then one would expect those in iron pentacarbonyl to be stronger. However, if metal–carbon double bonds are assumed, the reverse would be expected. In the tetrahedral configuration the nickel has $3d$-electrons available for π-bonding at all four positions. The iron in a trigonal bipyramidal configuration has $3d$-electrons available for π-bonding at only four of the five positions. One would therefore expect stronger metal–carbon bonds in nickel tetracarbonyl than in iron pentacarbonyl. This is in agreement with the observed bond energies and is indicative of partial double-bond character in the metal–carbon bonds. This same reasoning would also explain the lack of bond shortening in the octahedral metal carbonyls [$Cr(CO)_6$, $Mo(CO)_6$, and $W(CO)_6$], in which π-bonds can be formed at only three of the six positions.

From the previous discussion it is quite evident that the metal–carbon bonds in these compounds have partial double-bond character. It is also very likely that the amount of double-bond character varies appreciably among the different carbonyls because of variations in the hybridization of the central metal atom. Thus, one would expect the amount of double-bond character of the metal–carbon bond to decrease in the series $Ni(CO)_4$, $Fe(CO)_5$, $Cr(CO)_6$. It has been shown that the properties of the metal–carbon bond agree with this. A similar decrease in bond order would be expected in the terminal metal–carbon bonds of the series $Co_2(CO)_8$, $Fe_2(CO)_9$, $Mn_2(CO)_{10}$. Unfortunately, there are insufficient data to provide a check for this.

It should be pointed out that not all the data are explicable on the basis of metal–carbon double bonds. For example, the nickel–carbon stretching force constant in $Ni(CO)_4$ is comparable to those of the metal–carbon single bonds in the metal alkyls (see table 4). Also, the iron–carbon distances in $Fe_2(CO)_9$ have been reported as 1.8 Å. in the bridging groups and 1.9 Å. in the terminal groups (72). The reported experimental error was ±0.05. Thus the bridging Fe—C bonds which are necessarily single bonds are reported shorter than the terminal Fe—C bonds, which supposedly have some double-bond character. This discrepancy is probably not significant because of the limited accuracy of the data. A carbon–oxygen distance in the bridging carbonyl of 1.3 Å. was also reported, while the previous discussion of the carbonyl bond would indicate a value of <1.2 Å.

The need of more experimental work along this line is apparent. Further structural and thermochemical studies are very important to a better understanding of these metal–carbon bonds.

C. THE METAL–METAL BONDS

Metal–metal covalent bonds are rarely encountered in polynuclear complexes, which tend to polymerize through bridging groups. In the polynuclear carbonyls,

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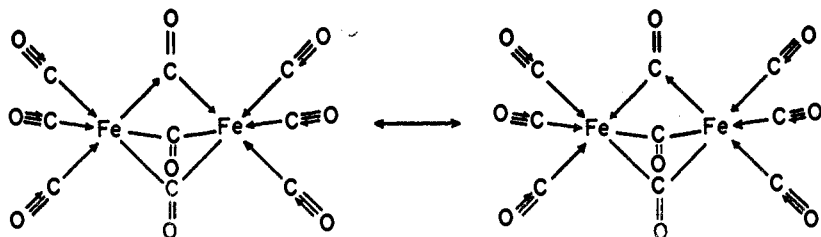[3] This is a weighted average of 2.937 for the axial and 2.249 for the equatorial bonds; see reference 24.

FIG. 4. Resonance explanation of the diamagnetism of $Fe_2(CO)_9$

however, metal–metal bonds are assumed to be present in the bridged molecules and are necessarily present in the non-bridged molecules.

$Fe_2(CO)_9$ has the unusual structure shown in figure 3. Each iron atom, having an even number of electrons and forming three covalent bonds, is left with an unpaired electron after bonding with the carbonyl groups. These odd electrons must have their spins coupled in order to account for the observed diamagnetism of the complex (5). The most logical explanation of this spin coupling is that of bond formation between the metal atoms. The iron–iron distance of 2.46 Å. is compatible with this idea. Resonance forms such as those in figure 4 have been suggested as an alternative explanation (50). However, Ewens (30) has pointed out that this is tantamount to the assumption of a covalent metal–metal bond with ionic character. The only other explanation is that of spin coupling without bond formation. This involves the assumption that the singlet state of the molecule lies lower than the triplet state. In view of Hund's rule, this seems much less likely than bond formation. Similar metal–metal bonds are proposed in the bridged molecule $Co_2(CO)_8$ (13). It is very likely that they also occur in other polynuclear carbonyls; however, there are yet insufficient data to verify this.

The metal–metal bonds in $Mn_2(CO)_{10}$ and $Re_2(CO)_{10}$ are better defined. Molecular weight determinations show these carbonyls to be dimeric (7, 42), while the infrared spectra indicate that there are no bridging carbonyl groups. The dimerization must then occur through metal–metal bonds.

It would be quite interesting to compare the properties of these localized metal–metal bonds with those of the metallic bond. Unfortunately, this comparison cannot be made, because the former have not been characterized. A unique opportunity for the study of such bonds is offered by the polynuclear carbonyls. Similar bonds are found in such species as Zn_2, Cd_2, and Hg_2, but these materials are not nearly so suitable for study. Especially useful information could be obtained from thermochemical and force constant studies.

III. HYBRIDIZATION AND STRUCTURE

The stereochemistry of a covalent complex is a result of the type of hybrid bond orbitals involved. A structure determination is then indicative of the hybridization. Conversely, a deduced hybridization allows one to predict the structure.

By the use of group theory one can find the set (or sets) of atomic orbitals which, when hybridized, will yield a particular arrangement of bonding orbitals.

TABLE 5

Coördination number and effective atomic number of some metal carbonyls and derivatives

Metal	Atomic Number	Carbonyl	Number of Electrons Donated	Effective Atomic Number
Cr...........................	24	$Cr(CO)_6$	12	36
Fe...........................	26	$Fe(CO)_5$	10	36
		$Fe(CO)_4H_2$	10	36
		$Fe(CO)_2(NO)_2$	10	36
Co...........................	27	$Co(CO)_4H$	9	36
		$Co(CO)_3NO$	9	36
Ni...........................	28	$Ni(CO)_4$	8	36

This treatment has been carried out and the results tabulated for structures involving d-, s-, and p-orbitals and coördination numbers from 2 to 8 (52). Recent calculations have extended this treatment to include f-orbitals in structures with coördination numbers from 2 to 9 (81). The hybridizations and corresponding structures which are most important in the study of the metal carbonyls are: sp^3-tetrahedral, dsp^3-trigonal bipyramidal, and d^2sp^3-octahedral.

The simple mononuclear carbonyls and their derivatives are in general agreement with this theory. However, several unusual features arise with the polynuclear carbonyls, and for that reason the two groups will be treated separately.

A. MONONUCLEAR CARBONYLS

In these carbonyls the tendency of the central metal atom to attain the electronic configuration of an inert gas is the factor which governs the coördination number of the metal. This tendency toward a stable electronic configuration is shown in table 5 for some of the more common metal carbonyls and derivatives. The term "effective atomic number" was devised by Sidgwick (82) and is merely the number of electrons of the metal atom plus the number donated by the entering groups.

Nickel tetracarbonyl is a colorless liquid boiling at 43.2°C. It is diamagnetic (70) and has a dipole moment of 0.3 Debye (87). An electron diffraction study showed the molecule to be tetrahedral with the Ni–C–O groups linear (9). The reported nickel–carbon and carbon–oxygen distances are 1.82 Å. and 1.15 Å., respectively. The infrared (20) and Raman (21) spectra have been shown to agree with this structure. Moreover, the same structure was recently obtained by an x-ray study (55).

This structure is just that to be expected from theory. The ground state of nickel is a ^3F state with the outer electronic configuration $3d^84s^2$. Only 42 kcal./mole are required to excite the nickel to the ^1S state with a $3d^{10}$ configuration (62). The vacant 4s- and 4p-orbitals are hybridized, resulting in four equivalent sp^3 hybrid bonding orbitals directed to the corners of a tetrahedron. Each entering carbon monoxide molecule donates a pair of electrons in the formation of σ-bonds along these tetrahedral directions.

The corresponding tetracarbonyls of palladium and platinum have not been isolated; however, infrared spectra of carbon monoxide chemisorbed on these

metals indicate that they do exist (28). More work is required before any conclusions can be drawn.

The structure and hybridization of iron pentacarbonyl is of particular interest because of the rare occurrence of pentacoördinated compounds and the existence of two almost equally probable structures. Either of these two structures, the trigonal bipyramid and the tetragonal pyramid, can be obtained from dsp^3 hybridization. Symmetry arguments cannot predict which is the more favorable. From energy considerations, Daudel and Bucher (23) concluded that the trigonal bipyramid should occur only if the d-orbital involved in the hybridization is of higher energy than the s- and p-orbitals. This is known to be the case with such molecules as phosphorus pentafluoride and phosphorus pentachloride, in which the hybridization of the central atom is $3d3s3p^3$. They contended that if the d-orbital were lower in energy than the s- and p-orbitals, then the tetragonal pyramid structure should be the more favorable. This argument has been used in support of the tetragonal pyramid structure for the complex $NiBr_3 \cdot 2P(C_2H_5)_3$.
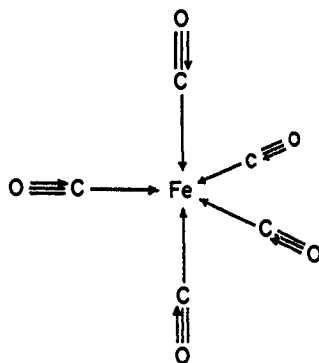

FIG. 5. Structure of iron pentacarbonyl, Fe(CO)$_5$

This structure was deduced from dipole moment and magnetic data (51, 67). The hybridization assumed was $3d4s4p^3$; however, $3d^24s4p^2$ is equally plausible and would be expected to yield a tetragonal pyramid structure. The only molecules for which the tetragonal pyramid structure has been definitely proven are bromine pentafluoride and iodine pentafluoride (12, 37, 59, 84). The hybridization expected in these two cases is of the unusual type $nd\ (n + 1)s\ np^3$. Here, of course, the d-orbital is of higher energy than the s- and p-orbitals, so that the tetragonal pyramid structure is not in agreement with the conclusions of Daudel and Bucher.

Iron pentacarbonyl is a colorless liquid boiling at 103°C. It is also diamagnetic (5, 70). Two dipole moment measurements have been reported for this molecule. The values obtained were 0.64 Debye (4) and 0.81 Debye (35). Bergmann and Engel (4) interpreted their observed dipole moment as an indication of a tetragonal pyramid structure. However, an electron diffraction study (31) showed the molecule to have the trigonal bipyramidal structure shown in figure 5. The iron-carbon and carbon-oxygen distances are 1.84 and 1.15 Å., respectively, and the

Fe–C–O grouping is linear. An attempted determination of the Raman spectrum of the molecule was unsuccessful because of photodecomposition of the sample (25). However, a tentative assignment of the observed infrared bands is in agreement with this structure (80). The structure, although it could not have been unambiguously predicted, is in agreement with the general theory of directed valence.

The ground state of iron is a ^5D state with the outer electronic configuration $3d^64s^2$. Excitation to the ^1D state with configuration $3d^8$ leaves vacant one $3d$- and the $4s$- and $4p$-orbitals for dsp^3 hybridization. The structures of the other pentacarbonyls, ruthenium pentacarbonyl and osmium pentacarbonyl, have not been determined. It is very likely that they also have the trigonal bipyramidal configuration.

The hexacarbonyls of chromium, molybdenum, and tungsten are colorless crystals which sublime at room temperature. Chromium hexacarbonyl and molybdenum hexacarbonyl have been found to be diamagnetic (53). All three have been shown to have octahedral structures by both the x-ray diffraction (76) and electron diffraction (10) techniques. The infrared spectra are in accord with this structure (39, 78). Here again the structures are those to be expected from the general theory of directed valence. For example, consider chromium hexacarbonyl. Chromium in the ground state has the outer electron configuration $3d^54s^1$. Excitation to the ^1H state with a $3d^6$ configuration leaves vacant two d-orbitals and the $4s$- and $4p$-orbitals for d^2sp^3 hybridization. This hybridization is known to yield an octahedral structure.

The utilization of the d-orbital electrons in dative π-bond formation in these molecules has already been discussed. These π-bonds do not alter the molecular configuration, but are assumed to fit into the σ-bond framework. The number of π-bonds which can be formed in any particular hybridization and structure can be determined by the use of group theory methods. These values are included in the tabulation by Kimball (52). The number of π-bonds are four in the tetrahedral and trigonal bipyramid structures and three in the octahedral structure. Observed bond distances in the metal carbonyls show the effect of these variations in double-bond character.

B. THE POLYNUCLEAR CARBONYLS

Polynuclear complexes are those which contain more than one central metal atom. Structurally, they may be considered to be built up from the polyhedra of the mononuclear complexes. The structural picture is somewhat complicated by the alternative possibilities of joining these polyhedra at apices, edges, and faces. Thus, the junction of two octahedra at an apex would be the structural picture of a complex such as $(MX_5)_2$, in which there is an M—M bond. Two octahedra joined at an edge would represent a complex such as $(MX_5)_2$, in which two bridging X groups appear. Finally, two octahedra joined at a face would represent a complex such as M_2X_9, in which three bridging X groups are present.

A wide variety of polynuclear complexes occurs in the metal carbonyls. Structural determinations for such large polyatomic molecules are very difficult by

TABLE 6

Characteristic carbonyl frequencies of the metal carbonyls

Carbonyl	Terminal Carbonyl Frequencies	Bridged Carbonyl Frequencies	Carbonyl	Terminal Carbonyl Frequencies	Bridged Carbonyl Frequencies
	$cm.^{-1}$	$cm.^{-1}$		$cm.^{-1}$	$cm.^{-1}$
Ni(CO)₄	2043, 2050		[Co(CO)₄]ₙ	2037, 2067	1866
Fe(CO)₅	1994, 2028		[Fe(CO)₄]₃	2029, 2052	1830, 1860
Cr(CO)₆	2000		HCo(CO)₄	2049, 2066	
Mo(CO)₆	2000		H₂Fe(CO)₄	2026, 2043	
W(CO)₆	1997		Mn₂(CO)₁₀	1988, 2010, 2050	
Co₂(CO)₈	2034, 2054, 2077	1859	Re₂(CO)₁₀	1973, 2015, 2078	
Fe₂(CO)₉	2034, 2080	1828			

the usual methods of x-ray and electron diffraction. However, the vibrational spectra are very useful in the investigation of these structures. There are several reasons for this: (*1*) the symmetry of the structures simplifies the spectra. For example, of the 54 fundamental vibrations of the molecule $Fe_2(CO)_9$, only 16 frequencies are expected in the infrared spectrum. (*2*) The masses and interactions of the atoms are such that the observed frequencies are characteristic of "atom-pair" vibrations (see table 6). Thus one can select bands corresponding to "carbonyl stretching vibrations" or "metal–carbon stretching vibrations." (*3*) Many of these molecules contain bridging carbonyl groups in which the C—O bond is comparable to that in strained cyclic ketones. These groups give characteristic vibrational frequencies which differ from that of the non-bridging carbonyl groups. Thus the presence or absence of bridging carbonyl groups can be readily ascertained from the infrared or Raman spectra. These aspects of the structural problem will be discussed in connection with the individual cases.

The only polynuclear carbonyl which has been studied by a diffraction technique is $Fe_2(CO)_9$. An x-ray study (72) revealed the very interesting structure shown in figure 3. This structure is that which results from the junction of two octahedra at a face. The electronic configuration of iron which would be expected to yield such a structure is shown in table 7. Promotion of one 4s-electron into a 3d-orbital leaves two 3d-orbitals and the 4s-orbital half-filled and the 4p-orbitals vacant. These are hybridized to yield an octahedral arrangement of bonding orbitals, of which three form covalent bonds (bridging groups) and the other three form coördinate covalent bonds. There is, then, an unpaired 3d-electron on each iron atom, so that an Fe—Fe bond is assumed to account for the observed diamagnetism (5) of the complex. There are left two pair of 3d-electrons on each iron for dative π-bonding with the terminal carbonyl groups.

The infrared spectrum (80) of this complex contains three intense peaks at 2080 cm.⁻¹, 2034 cm.⁻¹, and 1828 cm.⁻¹ The two high-frequency bands have been assigned to stretching vibrations of the terminal carbonyl groups. The band at 1828 cm.⁻¹ is attributed to a stretching vibration of the bridging carbonyl groups. This is precisely the spectrum to be expected from the results of a vibrational analysis of the structure described above (80).

The appearance of an infrared band in the spectrum of $Fe_2(CO)_9$ correspond-

TABLE 7

Hybridization and structure of dinuclear carbonyls

	Configuration 3d 4s 4p			State	Energy *	Carbonyl	Dinuclear Structure
					kcal./mole		
Mn				^6S	0.00		
				^4F	128.59	$Mn_2(CO)_{10}$	
				^2H	181.22	$Mn_2(CO)_{10}$	
Fe				^5D	0.00		
				^5F	19.81	$Fe_2(CO)_9$	
Co				^4F	0.00		
				^4F	9.96	$Co_2(CO)_8$	
				^2D	78.61	$Co_2(CO)_8$	
Cu				^2S	0.00	$Cu_2(CO)_6$	
				^4P	111.55	$Cu_2(CO)_6$	

* These energy values are with respect to the ground state of the metal and are taken from reference 62.

ing to a bridging carbonyl vibration and the agreement of the structure with the theory of directed valence has led to further investigations of the polynuclear carbonyls by this method. In table 7 two plausible structures for the molecule $Co_2(CO)_8$ are shown. These arise from the same hybridization and bonding orbital configuration of the separate metal atoms. In one case the two trigonal bipyramids are joined at an equatorial edge, resulting in two bridging carbonyl groups. The other structure is obtained by junction of two trigonal bipyramids at an equatorial position, corresponding to a metal–metal bond. Both of these structures belong to the point group D_{2h}. Several other structures are possible in this particular case because of non-equivalence of the apical and equatorial positions of the trigonal bipyramid. Thus, by junction at the apical positions one could obtain either a D_{3h} (eclipsed form) or a D_{3d} (staggered form) structure. The sharing of an apical-equatorial edge could yield either a C_{2h} or a C_{2v} structure. Vibrational analyses for these various structures have been carried out (13). It was found that two of the structures were compatible with the observed infrared spectrum. These two structures are shown in figure 6, and consist of two trigonal bipyramids joined at an edge. The presence of bridging carbonyls is confirmed by the appearance of an intense band at 1858 cm.$^{-1}$ Unfortunately,
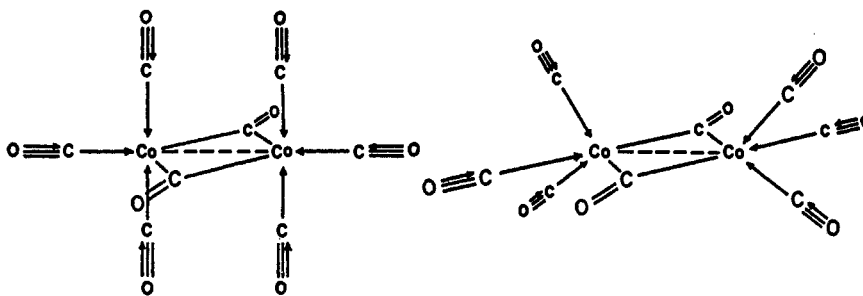
FIG. 6. Structures of $Co_2(CO)_8$

the infrared spectrum is unable to distinguish between these two structures. However, polarization work in the Raman method should allow one to select the correct structure.

The structural problem has a simpler explanation in the case of $Mn_2(CO)_{10}$. The hybridizations and resultant structures derived from theory are shown in table 7. In the first case the structure is that of two octahedra joined at an edge. The structure contains two bridging carbonyl groups and belongs to the point group D_{2h}. The other structure is that obtained by the junction of two octahedra at an apex and has the symmetry D_{4h}. Vibrational analyses of these two structures yield the following results: For the D_{2h} model one would expect to observe in the infrared spectrum four frequencies corresponding to terminal carbonyl stretching vibrations and one frequency corresponding to a bridged carbonyl stretching vibration. For the D_{4h} model, only three frequencies of the terminal carbonyl stretching vibrations are expected in the infrared. $Mn_2(CO)_{10}$ has recently been prepared and the infrared spectrum, along with that of $Re_2(CO)_{10}$, reported (7). The infrared spectra of these two carbonyls both contain three intense bands in the region of 2000 cm.$^{-1}$ and no absorption in the 1800 cm.$^{-1}$ region characteristic of bridging carbonyl groups. This indicates that the D_{4h} structures without bridging carbonyl groups are correct for these two carbonyls.

It is somewhat surprising to find that the correct structure for $Mn_2(CO)_{10}$ is the one without bridging carbonyls. In both cobalt and manganese more energy is required for electronic excitation to the states which result in non-bridging structures than to those which yield bridges. Also, one would expect more energy to be regained by bond formation in the bridged molecules. Yet in $Co_2(CO)_8$ the bridged structure is obtained, while the non-bridging structure is obtained in $Mn_2(CO)_{10}$. However, there is an additional factor to be considered. In the structures without bridges, molecule formation is attained by the combination of metal and carbon monoxide molecules, as such. In the formation of the bridged molecules, however, additional energy must be supplied to bring about a rehybridization of the carbon atom in the carbon monoxide molecules that form the bridge. That is, if the entering carbon monoxide groups are to form covalent bonds with both metal atoms, the two bonding electrons must singly occupy hybrid orbitals directed toward those metal atoms. Such hybrid orbitals would have slightly more p-character than the familiar sp^2 hybrids.

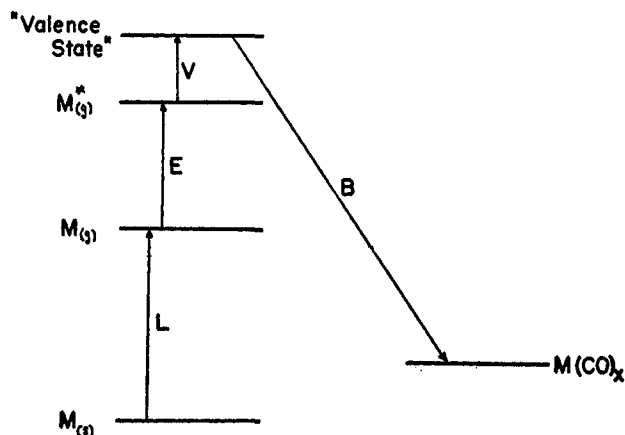Unfortunately, the energy necessary for this rehybridization is not known;

FIG. 7. Energy steps in molecule formation

however, an approximate value can be obtained by a consideration of the relevant energies. In complex formation there are several energy steps. Those steps related to the metal atom are shown in figure 7. In this diagram L is the heat of sublimation of the metal, E is the electronic excitation energy, V is the valence state excitation energy,[4] and B is the energy regained in bond formation. In addition, there is the rehybridization energy of the carbon monoxide molecules which form the bridges. In the following discussion this energy term will be called R. Consider the two alternative structures depicted in table 7 for $Co_2(CO)_8$. The value of L is the same for both structures. The E values differ by 137.2 kcal./mole,[5] being larger for the non-bridged structure. The values of V are assumed to be equal, since the hybridization is the same in each case. The B values cannot be directly calculated; however, bond-energy considerations indicate a value about 40 kcal./mole larger for the bridged structure. Finally, R is assumed to be negligible for the non-bridged structure. Since the bridged structure is known to be the stable form, the following inequality must be true:

$$2R < (L + E + V - B)_{\text{non-bridged}} - (L + E + V - B)_{\text{bridged}}$$
$$2R < 137.2 + 40$$
$$R < 88.6 \text{ kcal./mole}$$

Similar considerations for the alternative structures of $Mn_2(CO)_{10}$ lead to the following inequality:

$$2R > (L + E + V - B)_{\text{non-bridged}} - (L + E + V - B)_{\text{bridged}}$$
$$2R > 107.2 + 40$$
$$R > 73.6 \text{ kcal./mole}$$

These crude calculations set the limit of this rehybridization energy between 73 and 89 kcal./mole. This energy value should be useful in the prediction of the

[4] For a discussion of the valence state and these energy steps, see page 195 of reference 18.

[5] There are two metal atoms in each structure. This value is $2(78.61 - 9.96)$ (see table 7).

molecular structures of other polynuclear carbonyls. Unfortunately, the atomic energy levels are not yet known for some of the metals which form these carbonyls. However, these energy considerations do permit a prediction of the molecular structure of the recently isolated complex $Cu_2(CO)_6$ (74). The electronic configurations, energy levels, and structures are shown in table 7. In the first model, two tetrahedra are joined at an apex in an ethane-like structure. The second is obtained by an edge junction of two tetrahedra and results in two bridging carbonyl groups. In this case, the two large energy terms (E and R) both favor the non-bridged structure. Thus the ethane-like structure should be correct.

The higher members of these dinuclear carbonyls have not been studied structurally. It is very likely that $Ru_2(CO)_9$ and $Os_2(CO)_9$ have the same structure as $Fe_2(CO)_9$. However, there is more uncertainty with $Rh_2(CO)_8$ and $Ir_2(CO)_8$. Here the presence or absence of bridging groups will depend on the energies of the relevant electronic states. Unfortunately these energies are not known, so that the structures cannot be predicted.

There are two other polynuclear carbonyls that have been fairly well characterized. Iron tetracarbonyl is a dark green crystalline solid, soluble in non-polar solvents. It has been found to be diamagnetic (5, 22). The molecular weight, as determined from the freezing-point depression of $Fe(CO)_5$, corresponds to a trimeric structure (40). The infrared spectrum has been interpreted to favor the structure shown in figure 8 (79). This structure is obtained by an edge junction of two trigonal prisms to the opposite edges of a tetrahedron. The central iron atom forms four covalent bonds by utilization of tetrahedral d^3s hybrid orbitals. The electronic configuration of the iron atom before hybridization is $3d^74s^1$. The end iron atoms form trigonal prism d^2sp^3 hybrid orbitals from a $3d^8$ electron configuration. This arrangement allows four coördinate covalencies and two covalencies at each of the end iron atoms. The resulting molecule has no unpaired electrons, a situation which is in agreement with magnetic data.

Cobalt tricarbonyl is a black, crystalline compound which has a molecular weight corresponding to the tetramer (47). The infrared spectrum of the compound in n-hexane solution is particularly simple. There are two strong bands in the terminal carbonyl region and one very sharp, intense band in the bridged carbonyl region. This is indicative of either a very symmetrical tetrameric molecule or a lower degree of polymerization. There are several reasons for favoring
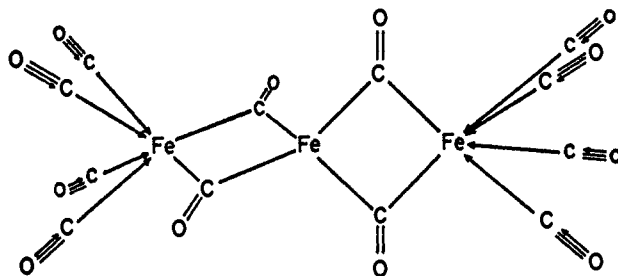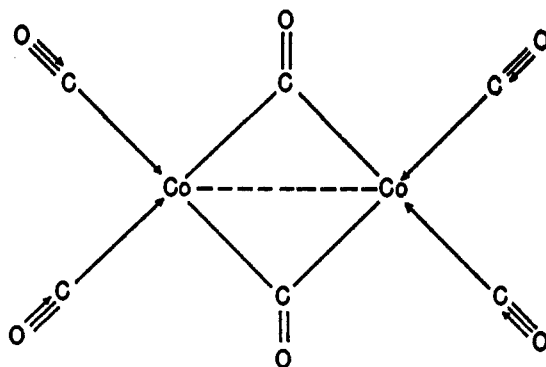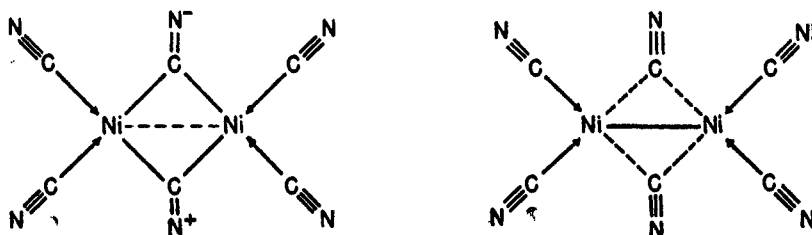

FIG. 8. Structure of $[Fe(CO)_4]_3$

FIG. 9. Dimeric structure of cobalt tricarbonyl

FIG. 10. Structures and bonding of $[Ni(CN)_3]_2^{-4}$

the latter. (1) From theory one would expect a dimeric molecule such as that shown in figure 9. The hybridization at each cobalt is dsp^2, resulting in a square planar bonding configuration. These two square planes are joined at an edge resulting in two bridged carbonyls. (2) The above structure is in perfect agreement with the observed infrared spectrum. No tetrameric structure has been found which is in accordance with the infrared data. (3) The isoelectronic ion $Ni(CN)_3^-$ is dimeric, with square planar nickel and bridging cyano groups (figure 10). It should be pointed out that the solvent used in the molecular weight determination was iron pentacarbonyl (47). This substance not only is decomposed by visible light and oxygen but could conceivably form a complex with the cobalt tricarbonyl. Such properties of the solvent could easily lead to wrong conclusions about the molecular weight of the solute.

The other polynuclear carbonyls have not been studied structurally. These include $[Ru(CO)_4]_3$, $[Rh(CO)_3]_n$, $[Ir(CO)_3]_n$, and $[Rh_4(CO)_{11}]_m$. Further experimental study of all the polynuclear carbonyls is needed for a better understanding of these very interesting complexes.

C. DERIVATIVES OF THE METAL CARBONYLS

There are several sets of inorganic complexes which are closely related to the metal carbonyls. These include the hydrocarbonyls, nitrosocarbonyls, cyanocarbonyls, carbonyl halides, and heavy metal derivatives. This relation is of particular importance in those cases for which the different groups are isoelectronic with carbon monoxide.

1. The hydrocarbonyls

The known hydrocarbonyls are $H_2Cr(CO)_5$ (73), $HMn(CO)_5$ (7), $H_2Fe(CO)_4$, $HCo(CO)_4$, $HRh(CO)_4$ (46), $HIr(CO)_4$ (45), and $[HNi(CO)_3]_2$ (3). Of these, only $H_2Fe(CO)_4$ and $HCo(CO)_4$ have been well characterized.

$H_2Fe(CO)_4$ is a pale yellow liquid which decomposes rapidly above $-10°C$. An alkaline solution is a fairly strong reducing agent, as shown by equation 4 (44).

$$(4) \qquad 3Fe(CO)_4^- \rightleftharpoons [Fe(CO)_4]_3 + 6e^- \qquad E^0 = 0.74 \text{ v.}$$
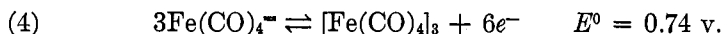
It has been found to be a weak dibasic acid. The acid dissociation constants are $K_1 = 4 \times 10^{-5}$ and $K_2 = 4 \times 10^{-14}$ (43, 54). An electron diffraction study has shown a tetrahedral arrangement of the carbonyls about the iron atom. The position of the hydrogens could not be directly determined; however, the linear Fe–C–O groups exclude binding to the carbons in an aldehydic linkage (31).
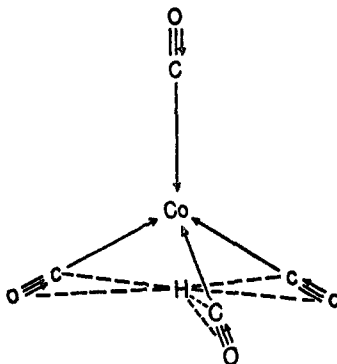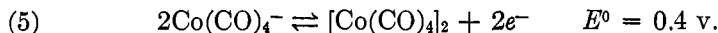

FIG. 11. Structure of $HCo(CO)_4$

$HCo(CO)_4$ is also a pale yellow liquid that is thermally unstable. It also has reducing properties, as shown by equation 5 (44).

$$(5) \qquad 2Co(CO)_4^- \rightleftharpoons [Co(CO)_4]_2 + 2e^- \qquad E^0 = 0.4 \text{ v.}$$

$HCo(CO)_4$ is a strong acid comparable in strength to nitric acid (43). The carbonyls have been found to be tetrahedrally arranged about the cobalt (31, 65). In this case the infrared spectrum reveals no band that can be attributed to a vibrational motion of the hydrogen atom. This is demonstrated by the fact that the infrared spectra of $HCo(CO)_4$ and $DCo(CO)_4$ are identical (85). If any of the observed bands in the spectrum of the hydrocarbonyl are due to vibrations involving the hydrogen, they should be shifted in the spectrum of the deutero-carbonyl. The proton magnetic resonance spectrum of $HCo(CO)_4$ reveals a chemical shift (δ) of -1.55 referred to H_2O (36). According to the usual interpretation of the chemical shift, this indicates an unusually high electron density about the proton. An explanation for this high electron density is offered by a recent structural description of the molecule (27). These authors describe a structure such as that shown in figure 11. In this description the hydrogen atom

lies on the C_3 axis and is bound by a seven-centered molecular orbital (M.O.) to the three carbonyl groups which lie off this C_3 axis. The odd d-electron of the cobalt pairs with the electron from the hydrogen atom in a non-bonding orbital. Thus, the hydrogen atom is effectively immersed in a sea of negative charge, a situation which would explain the negative chemical shift. This description is quite similar to the three-center molecular orbitals recently proposed for the boron hydrides (26). In this connection, it should be noted that the bridge hydrogens in diborane have a more negative chemical shift than the terminal protons (69) and are also more acidic.

This multicentered molecular orbital description seems to be a step in the right direction, but there are several points which await a satisfactory explanation. (1) The molecule, as depicted, belongs to the point group C_{3v}. The seven-centered molecular orbital and the d_{z^2} atomic orbital of the cobalt both belong to the A_1 representation of that point group. They should, if energetically feasible, mix in the formation of a somewhat more delocalized molecular orbital involving eight nuclear centers. Instead of this, there was assumed to be no interaction between the cobalt and the hydrogen.[6] (2) How does one reconcile a high electron density at the proton with strong acidic character? (3) Why is there no isotope shift observed in the infrared spectra of $HCo(CO)_4$ and $DCo(CO)_4$? This shift has been observed for the bridge hydrogen vibrations of pentaborane (48).

The anions of these hydrocarbonyls are structurally related to the metal carbonyls. Thus, $Co(CO)_4^-$ and $Fe(CO)_4^=$ are isoelectronic with $Ni(CO)_4$. All three have tetrahedral structures. Similarly, $Mn(CO)_5^-$ and $Cr(CO)_5^=$ are isoelectronic with $Fe(CO)_5$, so that one might expect a trigonal bipyramidal structure. It is of interest that $Ni(CO)_3^-$ is isoelectronic with $Cu(CO)_3$ and both have been reported to be dimeric (3, 74).

2. The nitrosocarbonyls

The two known nitrosocarbonyls are $Fe(NO)_2(CO)_2$ and $Co(NO)(CO)_3$. Both have been shown to have a tetrahedral arrangement of groups about the central metal (8). In order to explain the hybridization involved, it is assumed that there is an electron transfer from the nitric oxide molecule to the metal atom. The entering group is then regarded as the nitrosyl ion (NO^+), which is isoelectronic with carbon monoxide. Also, $Fe(NO)_2(CO)_2$ and $Co(NO)(CO)_3$ are isoelectronic with $Ni(CO)_4$, so that the tetrahedral structures for these molecules are not surprising.

3. The cyanocarbonyls

The CN^- group is also isoelectronic with carbon monoxide, so that it is of interest to compare the cyanocarbonyls and cyanides with the carbonyls. For example, the complex ions $Mn(CN)_6^{-5}$, $Fe(CN)_6^{-4}$, $Co(CN)_6^{-3}$, $Fe(CN)_5(CO)^{-3}$,

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[6] *Note added in proof:* Molecular orbital calculations show that the cobalt participates only to a small extent in the bonding because of unfavorable energy conditions. (W. F. Edgell and G. Gallup: J. Am. Chem. Soc. **77**, 5762 (1955)).
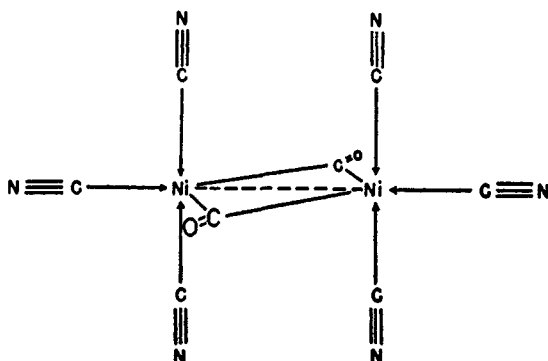
FIG. 12. Structure of $[Ni(CN)_3CO]_2^{-4}$

$Mn(CN)_5(NO)^{-3}$, and $Fe(CN)_5(NO)^{-2}$ are all isoelectronic with $Cr(CO)_6$. All seven are diamagnetic and octahedral. Similarly, $Ni(CN)_4^{-4}$, $Cu(CN)_4^{-3}$, $Zn(CN)_4^{-2}$, and $Ni(CN)_2(CO)_2^{-2}$ are isoelectronic with $Ni(CO)_4$. All are tetrahedral and diamagnetic.

Of special interest in this connection are the two recently characterized complexes of univalent nickel. $K_2Ni(CN)_3$ is a red, diamagnetic, crystalline compound. An x-ray study (63) has shown the ion to be dimeric, with bridging cyanide groups. The authors proposed structure I of figure 10. An infrared study (29) has indicated that a more satisfactory description would be that of structure II in figure 10. The dotted lines between the metal atoms and the bridged carbon atoms represent "half-bonds" similar to those in the bridges of $Al_2(CH_3)_6$ and B_2H_6. This bridged structure is similar to the structure proposed for the isoelectronic cobalt tricarbonyl (14).

The other complex of univalent nickel is $K_2Ni(CN)_3CO$. This complex has been shown to be diamagnetic (64), and the anion is assumed to be dimeric. It is quite probable that the structure is analogous to that of $Co_2(CO)_8$, since the two are isoelectronic. This structure is shown in figure 12.

4. The carbonyl halides

The known carbonyl halides are listed in table 8. These compounds are quite similar in volatility and solubility to the metal carbonyls, a fact which indicates that they are covalent complexes rather than ionic. Further support for this is gained from the fact that stabilities increase from chloride to iodide.

It is quite interesting to consider these structures along the lines previously discussed for the carbonyls. The complexes $Mn(CO)_5X$, $Re(CO)_5X$, $Fe(CO)_4X_2$, and $Os(CO)_4X_2$ would be expected to have octahedral structures resulting from d^2sp^3 hybridization of the metal ion. This would result in geometrical isomerism (cis-trans) for the latter two. Similarly the complexes $M(CO)_2X_2$ would be expected to have tetrahedral structures for M = iron, ruthenium, and osmium and square planar structures for M = platinum. There is more uncertainty in the case of the other carbonyl halides. Much more additional information is required for an understanding of the structure of these molecules.

TABLE 8

Metal carbonyl halides

Mn	Fe	Co	Ni	Cu
$Mn(CO)_5X$	$Fe(CO)_5X_2$ $Fe(CO)_4X_2$ $[Fe(CO)_3X_2]_3$ $Fe(CO)_2X_2$ $Fe(CO)_2I$	$Co(CO)I_2$	—	$Cu(CO)X$
Tc	**Ru**	**Rh**	**Pd**	**Ag**
—	$Ru(CO)_2X_2$ $Ru(CO)Br$	$[Rh(CO)_2X]_2$	$[Pd(CO)Cl_2]_n$	—
Re	**Os**	**Ir**	**Pt**	**Au**
$Re(CO)_5X$	$Os(CO)_4X_2$ $Os(CO)_3X_2$ $Os(CO)_2X_2$ $[Os(CO)_4X]_2$	$Ir(CO)_3X$ $Ir(CO)_2X_2$	$Pt(CO)_2Cl_2$ $[Pt(CO)X_2]_2$	$Au(CO)Cl$

TABLE 9

Heavy metal derivatives

Type	Metal	Type	Metal
$M Fe(CO)_4$ $M Co(CO)_4$	Cd, Hg Tl	$M [Co(CO)_4]_2$ $M [Co(CO)_4]_3$	Zn, Cd, Hg, Sn, Pb Ga, In, Tl

5. Heavy metal derivatives

The known heavy metal derivatives of $H_2Fe(CO)_4$ and $HCo(CO)_4$ are summarized in table 9. $HgFe(CO)_4$ is a stable yellow substance insoluble in both polar and non-polar solvents. It is unaffected by acids. $CdFe(CO)_4$ is quite similar, except that it reacts with acids to liberate $H_2Fe(CO)_4$. The evidence seems to indicate long-chain polymers with alternating mercury (or cadmium) and iron atoms. Whether the linkage is through metal–metal bonds or bridging carbonyls is yet to be determined. However, energy considerations would favor the structure with metal–metal bonds. Such a structure is shown in figure 13 for $HgFe(CO)_4$. $CdFe(CO)_4$ would be similarly depicted. Here the mercury utilizes linear sp hybrid orbitals and the iron uses d^2sp^3 octahedral orbitals in the bonding.

In contrast the metal derivatives of $HCo(CO)_4$ seem to be quite similar in properties to the polynuclear carbonyls. They are soluble in non-polar solvents and insoluble in water and can be sublimed. The expected structures would be similar to that shown for $HgFe(CO)_4$, except that the molecules are monomeric. The structure expected for $Zn[Co(CO)_4]_2$, $Cd[Co(CO)_4]_2$, and $Hg[Co(CO)_4]_2$ is shown in figure 14. The cobalt uses dsp^3 trigonal bipyramidal bonding orbitals. The same configuration of the bonding orbitals about the cobalt would be ex-
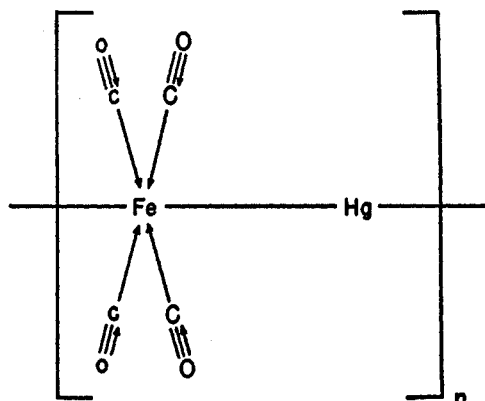
FIG. 13. Structure of HgFe(CO)₄
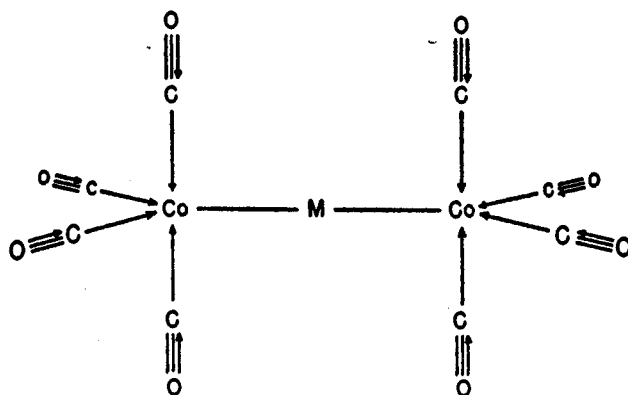
FIG. 14. Structure of M[Co(CO)₄]₂; M = zinc, cadmium, or mercury

pected for the other heavy metal derivatives. However, for Sn[Co(CO)₄]₂ and Pb[Co(CO)₄]₂ the molecule would probably be bent, as in the tin dialkyls. A trigonal sp^2 configuration would be expected at the central metal for Ga[Co(CO)₄]₃, In[Co(CO)₄]₃, and Tl[Co(CO)₄]₃.

In all of these heavy metal derivatives there are alternative structures involving bridged carbonyl groups. The presence or absence of these bridging carbonyls could readily be determined from vibrational spectra. Such studies would probably allow one to select correct structures for these molecules.

IV. SUMMARY AND CONCLUSIONS

It has been shown that the metal carbonyls can best be understood as coördination complexes between electrically neutral particles. As such, the structures of the mononuclear carbonyls and their derivatives are those to be expected from the familiar theory of directed valence. The structures of the polynuclear carbonyls and heavy metal derivatives are somewhat more complicated but can also be derived from this theory. Linkage of the monomer units by metal–metal

bonds or alternatively by bridging carbonyl groups is shown to be dependent on the energy of the relevant electronic states of the metal.

The bonding in these compounds is especially suitable for treatment by the method of localized molecular orbitals. Empirical correlations of "atom-pair" bonds in these molecules with those in other compounds have been made. The results are very helpful in gaining a better understanding of the nature of the bonding in the metal carbonyls. It is concluded that the carbon–oxygen bonds are quite similar to those in ketene and carbon dioxide. The metal carbon bonds have partial double-bond character due to dative π-bonding.

The need for further experimental study, both structural and thermochemical, has been emphasized.

V. References

(1) Allen, P. W., and Sutton, L. E.: Acta Cryst. 3, 46 (1950).
(2) Anderson, J. S.: Quart. Revs. (London) 1, 331 (1947).
(3) Behrens, H., and Lohofer, F.: Z. Naturforsch. 8b, 691 (1953).
(4) Bergmann, E., and Engel, L.: Z. physik. Chem. B13, 232 (1931).
(5) Berkman, S., and Zocher, H.: Z. physik. Chem. 124, 318 (1926).
(6) Blanchard, A. A.: Chem. Revs. 21, 3 (1937).
(7) Brimm, E. O., Lynch, M. A., and Sesny, W. J.: J. Am. Chem. Soc. 76, 3831 (1954).
(8) Brockway, L. O., and Anderson, J. S.: Trans. Faraday Soc. 33, 1233 (1937).
(9) Brockway, L. O., and Cross, P. C.: J. Chem. Phys. 3, 828 (1935).
(10) Brockway, L. O., Ewens, R. V. G., and Lister, M. W.: Trans. Faraday Soc. 34, 1350 (1938).
(11) Broun, T., and Livingstone, R. L.: J. Am. Chem. Soc. 74, 6084 (1952).
(12) Burke, T. G., and Jones, E. A.: J. Chem. Phys. 19, 1611 (1951).
(13) Cable, J. W., Nyholm, R. S., and Sheline, R. K.: J. Am. Chem. Soc. 76, 3373 (1954).
(14) Cable, J. W., and Sheline, R. K.: Unpublished results.
(15) Chatt, J., and Williams, A. A.: J. Chem. Soc. 1954, 4403.
(16) Cottrell, T. L.: The Strengths of Chemical Bonds, p. 276. Academic Press, New York (1954).
(17) Coulson, C. A.: Valence, p. 216. Oxford University Press, London (1952).
(18) Coulson, C. A., and Moffitt, W.: Phil. Mag. 40, 1 (1949).
(19) Cowan, R. D.: J. Chem. Phys. 18, 1101 (1950).
(20) Crawford, B. L., and Cross, P. C.: J. Chem. Phys. 6, 525 (1938).
(21) Crawford, B. L., and Horwitz, W.: J. Chem. Phys. 16, 147 (1948).
(22) Cutforth, H. G., and Selwood, P. W.: J. Am. Chem. Soc. 65, 2414 (1943).
(23) Daudel, R., and Bucher, A.: J. chim. phys. 42, 6 (1945).
(24) Duffey, G. H.: J. Chem. Phys. 17, 196 (1949).
(25) Duncan, A. B. F., and Murray, J. W.: J. Chem. Phys. 2, 636 (1934).
(26) Eberhardt, W. H., Crawford, B. L., and Lipscomb, W. N.: J. Chem. Phys. 22, 989 (1954).
(27) Edgell, W. F., and Magee, C. B.: "The Infrared Spectra of Cobalt Hydrocarbonyl and Cobalt Carbonyl Nitrosyl," presented at the 127th National Meeting of the American Chemical Society, Cincinnati, Ohio, March 31, 1955; Chem. Eng. News 33, 1652 (1955).

(28) EISCHENS, R. P., PLISKIN, W. A., AND FRANCIS, S. A.: J. Chem. Phys. **22**, 1786 (1954).

(29) EL SAYED, M., AND SHELINE, R. K.: Unpublished results.

(30) EWENS, R. V. G.: Nature **161**, 530 (1948).

(31) EWENS, R. V. G., AND LISTER, M. W.: Trans. Faraday Soc. **35**, 681 (1939).

(32) GILLIAM, O. R., JOHNSON, C. M., AND GORDY, W.: Phys. Rev. **78**, 140 (1950).

(33) GLOCKLER, G., AND TUNG, J. Y.: J. Chem. Phys. **13**, 388 (1945).

(34) GORDY, W., RING, H., AND BURG, A. B.: Phys. Rev. **74**, 243 (1948).

(35) GRAFFUNDER, W., AND HEYMANN, E.: Z. physik. Chem. **B15**, 377 (1932).

(36) GUTOWSKY, H. S.: Private communication.

(37) GUTOWSKY, H. S., AND HOFFMANN, C. J.: J. Chem. Phys. **19**, 1259 (1951).

(38) HALVERSON, F., AND WILLIAMS, V. Z.: J. Chem. Phys. **15**, 522 (1947).

(39) HAWKINS, N. J., MATTRAW, H. C., SABOL, W. W., AND CARPENTER, D. R.: Paper submitted for publication.

(40) HIEBER, W., AND BECKER, E.: Ber. **63**, 1405 (1930).

(41) HIEBER, W., BEHRENS, H., AND TELLER, U.: Z. anorg. u. allgem. Chem. **249**, 26 (1942).

(42) HIEBER, W., AND FUCHS, H.: Z. anorg. u. allgem. Chem. **248**, 256 (1941).

(43) HIEBER, W., AND HUBEL, W.: Z. Naturforsch. **7b**, 322 (1952).

(44) HIEBER, W., AND HUBEL, W.: Z. Naturforsch. **7b**, 323 (1952).

(45) HIEBER, W., AND LEGALLY, H.: Z. anorg. u. allgem. Chem. **245**, 321 (1940).

(46) HIEBER, W., AND LEGALLY, H.: Z. anorg. u. allgem. Chem. **251**, 96 (1943).

(47) HIEBER, W., MUHLBAUER, F., AND EHMANN, E. A.: Ber. **65**, 1090 (1932).

(48) HROSTOWSKI, H. J., AND PIMENTEL, G. C.: J. Am. Chem. Soc. **76**, 998 (1954).

(49) JAFFE, H. H., AND DOAK, G. O.: J. Chem. Phys. **21**, 196 (1953).

(50) JENSEN, K. A., AND ASMUSSEN, R. W.: Z. anorg. u. allgem. Chem. **252**, 233 (1944).

(51) JENSEN, K. A., AND NYGAARD, B.: Acta Chem. Scand. **3**, 474 (1949).

(52) KIMBALL, G.: J. Chem. Phys. **8**, 188 (1940).

(53) KLEMM, W., JACOBI, H., AND TILK, J.: Z. anorg. u. allgem. Chem. **201**, 1 (1931).

(54) KRUMHOLTZ, P., AND STETTINER, H. M. A.: J. Am. Chem. Soc. **71**, 3035 (1949).

(55) LADELL, J., POST, B., AND FANKUCHEN, I.: Acta Cryst. **5**, 795 (1952).

(56) LINNETT, J. W.: Quart. Revs. (London) **1**, 85 (1947).

(57) LIPPINCOTT, E. R., AND TOBIN, M. C.: J. Am. Chem. Soc. **75**, 4141 (1953).

(58) LONG, L. H., AND WALSH, A. D.: Trans. Faraday Soc. **43**, 342 (1947).

(59) LORD, R. C., LYNCH, M. A., SCHUMB, W. C., AND SLOWINSKI, E. J.: J. Am. Chem. Soc. **72**, 522 (1950).

(60) MOELLER, T.: *Inorganic Chemistry*, p. 702. John Wiley and Sons, Inc., New York (1954).

(61) MOFFITT, W.: Proc. Roy. Soc. (London) **196A**, 524 (1949).

(62) MOORE, C. E.: *Atomic Energy Levels*, Vol. II. U. S. Government Printing Office, Washington, D. C. (1952).

(63) NAST, R., AND PFAB, W.: Naturwissenschaften **39**, 300 (1952).

(64) NAST, R., AND ROOS, H.: Z. anorg. u. allgem. Chem. **272**, 242 (1953).

(65) NATTA, G., AND CORRADINI, P.: Atti. accad. nazl. Lincei, Rend. classe sci. fis., mat. e nat. **15**, 248 (1953); Chem. Abstracts **48**, 13328 (1954).

(66) NIELSEN, A. H., BURKE, T. G., WOLTZ, P. J. H., AND JONES, E. A.: J. Chem. Phys. **20**, 596 (1952).

(67) NYHOLM, R. S.: Chem. Revs. **53**, 285 (1953).

(68) NYHOLM, R. S., AND SHORT, L. N.: J. Chem. Soc. **1953**, 2670.

(69) OGG, R. A.: J. Chem. Phys. **22**, 1933 (1954).

(70) OXLEY, A. E.: Proc. Cambridge Phil. Soc. **16**, 102 (1910).

(71) PAULING, L.: *The Nature of the Chemical Bond*, p. 251. Cornell University Press, Ithaca, New York (1945).

(72) POWELL, H. M., AND EWENS, R. V. G.: J. Chem. Soc. **1939**, 286.

(73) RHOMBERG, M. G., AND OWEN, B. B.: J. Am. Chem. Soc. **73**, 5904 (1951).

(74) ROBINSON, P. L., AND STAINTHORPE, K. R.: Nature **153**, 24 (1944).

(75) ROSSINI, F. D.: *Selected Values of Chemical Thermodynamic Properties*. U. S. Government Printing Office, Washington, D. C. (1952).
(76) RUDORF, W., AND HOFMANN, U.: Z. physik. Chem. **B28**, 351 (1935).
(77) SHELINE, R. K.: J. Chem. Phys. **18**, 602 (1950).
(78) SHELINE, R. K.: J. Am. Chem. Soc. **72**, 5761 (1950).
(79) SHELINE, R. K.: J. Am. Chem. Soc. **73**, 1615 (1951).
(80) SHELINE, R. K., AND PITZER, K. S.: J. Am. Chem. Soc. **72**, 1107 (1950).
(81) SHIRMAZAN, M. G., AND DYATKINA, M. E.: J. Phys. Chem. (U.S.S.R.) **27**, 491 (1953).
(82) SIDGWICK, N. W.: J. Chem. Soc. **123**, 725 (1923).
(83) SPICE, J. E., STAVELEY, L. A. K., AND HARROW, G. A.: J. Chem. Soc. **1955**, 100.
(84) STEPHENSON, C. V., AND JONES, E. A.: J. Chem. Phys. **20**, 1830 (1952).
(85) STERNBERG, H. W., WENDER, I., FRIEDEL, R. A., AND ORCHIN, M.: J. Am. Chem. Soc. **75**, 2717 (1953).
(86) STRANDBERG, M. W. P., WENTINK, T., AND KYHL, R. L.: Phys. Rev. **75**, 270 (1949).
(87) SUTTON, L. E., AND BENTLEY, J. B.: Nature **130**, 314 (1932).
(88) TRAUTZ, M., AND BADSTUBNER, W.: Z. Elektrochem. **35**, 799 (1929).
(89) TROUT, W. E.: J. Chem. Education **14**, 453 (1937).
(90) WALSH, A. D.: J. Am. Chem. Soc. **68**, 2408 (1946).
(91) WALSH, A. D.: Trans. Faraday Soc. **43**, 158 (1947).