

STRUCTURE AND PROPERTIES OF METAL CARBONYLS

Composition and Effective Atomic Number of Metal Carbonyls and the Nature of the Metal-Carbon-Oxygen Bond

For this discussion metal carbonyls shall be defined as compounds composed of a metal and carbon monoxide; there are two types, monomeric and polymeric carbonyls (table 1). Some metal carbonyls exist only as monomers, for example, $\text{Ni}(\text{CO})_4$; some only as polymers, for example, $\text{Co}_2(\text{CO})_8$; and some both as monomers and polymers, for example, $\text{Fe}(\text{CO})_5$ and $\text{Fe}_3(\text{CO})_{12}$. Some metal carbonyls are known to undergo substitution reactions in which carbonyl groups are replaced by other groups (table 2).

TABLE 1.—*Monomeric and polymeric metal carbonyls (atomic numbers in parentheses)*

Cr(24)	Mn(25)	Fe(26)	Co(27)	Ni(28)
$\text{Cr}(\text{CO})_6$	$\text{Mn}_2(\text{CO})_{10}$	$\text{Fe}(\text{CO})_5$ $\text{Fe}_2(\text{CO})_9$ $\text{Fe}_3(\text{CO})_{12}$	$\text{Co}_2(\text{CO})_8$ $\text{Co}_4(\text{CO})_{12}$	$\text{Ni}(\text{CO})_4$
Mo(42)	Tc(43)	Ru(44)	Rh(45)	Pd(46)
$\text{Mo}(\text{CO})_6$		$\text{Ru}(\text{CO})_5$ $\text{Ru}_2(\text{CO})_9$ $\text{Ru}_3(\text{CO})_{12}$	$\text{Rh}_2(\text{CO})_8$ $\text{Rh}_4(\text{CO})_{12}$	
W(74)	Re(75)	Os(76)	Ir(77)	Pt(78)
$\text{W}(\text{CO})_6$	$\text{Re}_2(\text{CO})_{10}$	$\text{Os}(\text{CO})_5$ $\text{Os}_2(\text{CO})_9$	$\text{Ir}_2(\text{CO})_8$ $\text{Ir}_4(\text{CO})_{12}$	

The systematization of this array of compounds is facilitated by the concept of the Effective Atomic Number (E.A.N.). The E.A.N. is the name given to the total number of electrons that enter into the configuration of the central atom of the complex compound. If it is assumed that each $[:\text{C}=\text{O}:]$ group donates one pair of electrons to the central atom, the E.A.N. of Ni in $\text{Ni}(\text{CO})_4$, for instance, is 36; that is, 28 (atomic number of Ni) plus 2×4 (electrons donated by the four CO groups). Thus, the E.A.N. of Ni in $\text{Ni}(\text{CO})_4$ is equal to the atomic number of krypton, which is the inert gas of the completed atomic period in which Ni is situated. As may be seen from

table 1, the principle governing the composition of all known monomeric carbonyls is this attainment of an E.A.N. equal to the atomic number of an inert gas. The same principle is also operative in the substituted carbonyls (table 2), where each $[:\text{C}=\text{N}-\text{R}]$, $[:\text{PCl}_3]$, and $[:\text{P}(\text{C}_6\text{H}_5)_3]$ group is assumed to donate two electrons and each $[:\text{N}=\ddot{\text{O}}:]$ and $[:\text{C}-\text{OH}]$ group three electrons.

TABLE 2.—*Some substituted carbonyls*

Fe	Co	Ni
$\text{Fe}(\text{CO})_4(\text{CN-R})$		$\text{Ni}(\text{CN-R})_4$
$\text{Fe}(\text{CO})_3(\text{CN-R})_2$		$\text{Ni}(\text{CO})(\text{CN-R})_3$
$\text{Fe}(\text{CO})_3(\text{SbCl}_3)_2$		$\text{Ni}(\text{PCl}_3)_4$
$\text{Fe}(\text{CO})_4[\text{P}(\text{C}_6\text{H}_5)_3]$		$\text{Ni}(\text{CO})_3[\text{P}(\text{C}_6\text{H}_5)_3]$
$\text{Fe}(\text{CO})_3[\text{P}(\text{C}_6\text{H}_5)_3]_2$		$\text{Ni}(\text{CO})_2[\text{P}(\text{C}_6\text{H}_5)_3]_2$
$\text{Fe}(\text{CO})_2(\text{NO})_2$	$\text{Co}(\text{CO})_3(\text{NO})$	
$\text{Fe}(\text{CO})_2(\text{COH})_2$	$\text{Co}(\text{CO})_3(\text{COH})$	$\text{Ni}_2(\text{CO})_4(\text{COH})_2$

The composition of the polymeric carbonyls also conforms to the principle of E.A.N., this fact may be deduced as follows (*126*⁵): Table 1 shows that where the "monomer" has an E.A.N. of 35, for example, $\text{Co}(\text{CO})_4$ in $\text{Co}_2(\text{CO})_8$ or $\text{Fe}(\text{CO})_{4.5}$ in $\text{Fe}_2(\text{CO})_9$, the polymeric carbonyl contains two metal atoms; where the E.A.N. of the "monomer" is 34, for example, $\text{Fe}(\text{CO})_4$ in $\text{Fe}_3(\text{CO})_{12}$, the polymeric carbonyl contains three metal atoms; and where it is 33, for example, $\text{Co}_4(\text{CO})_{12}$, the polymeric carbonyl contains four metal atoms. This relation between the atomic number of the next inert gas (G), the atomic number of the metal (M), the number of metal atoms, and the number of carbonyl groups is expressed by the following formula for any metal carbonyl of the general form $(\text{M})_x(\text{CO})_y$

$$G - M - 2y/x - x + 1 = 0$$

The concept of E.A.N. not only correlates the compositions of metal carbonyls on a formal basis but also implies a relationship between carbonyls and inert gases. This relationship, according to Blanchard (*11*), manifests itself in the volatilities of metal carbonyls as demonstrated in table 3.

There are not many compounds known with molecular weights as high as 171 or 342 that boil at 46° or sublime at room temperature.

⁵ Italicized numbers in parentheses refer to items in bibliography at the end of this report.

TABLE 3.—Volatilities of metal carbonyls

Compound	Molecular weight	Volatility
Ni(CO) ₄ ----	171	Boiling point, 46° C.
Fe(CO) ₅ ----	196	Boiling point, 102° C.
Co ₂ (CO) ₈ ----	342	Sublimes at room temperature in a current of CO.
Fe ₃ (CO) ₁₂ ----	504	Sublimes at 60°–70° C. at 10 ⁻⁵ mm. Hg.

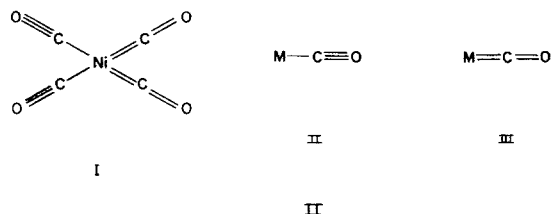
Until recently the nature of the metal-carbon-oxygen linkage in metal carbonyls could not be explained satisfactorily. As far as force constant and bond distance are concerned, the C—O bond in metal carbonyls is closer to that in carbon monoxide than to that in formaldehyde (table 4).

Some investigators considered the carbonyl group in metal carbonyls to be a slightly modified carbon monoxide molecule coordinately bonded to the metal (120). Others believed that the C—O bond was intermediate between a double bond, as in formaldehyde, and a triple bond, as in carbon monoxide, and that a metal carbonyl such as Ni(CO)₄ should be regarded as a resonance hybrid of structures such as I (34).

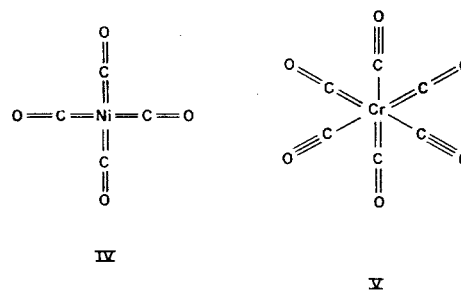
Nyholm and Short (101) first questioned the validity of comparing the force constants of the carbonyl groups of nickel carbonyl and formaldehyde. They pointed out that different types of sigma bonds are formed by the carbon atoms in these two cases. In nickel carbonyl the sigma bond is formed from a carbon sp hybrid orbital, whereas in formaldehyde it is formed from a carbon sp² hybrid orbital. In ketene carbonyl, on the other hand, the sigma bond is formed from a carbon sp hybrid orbital, and Nyholm and Short suggested that the carbonyl group in metal carbonyls should be considered ketenelike. Table 4 shows that the carbonyl group in nickel carbonyl is indeed similar to that in ketene as far as bond distance and force constant are concerned.

The smaller bond distance and higher force constant of the metal carbonyl as compared with that of ketene carbonyl indicate that the bond order in metal carbonyl is higher than that

in ketene carbonyl. We may explain this fact by regarding the metal-carbon-oxygen linkage as a resonance hybrid of structures II and III.

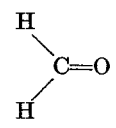


In II the C—O bond is similar to that in carbon monoxide, and in III it is similar to that in ketene. In both II and III the C—O and M—C sigma bonds are formed from carbon sp hybrid orbitals. To express the type of bonding in the M—C—O linkage by a single-structural formula, one probably would choose III (32). However, this formulation has certain disadvantages. For example, although one can write a double-bond structure for Ni(CO)₄, a similar structure for Fe(CO)₅ or Cr(CO)₆ is not possible. Chromium, for example, has only six electrons in its valence shell and therefore can only form a maximum of three double bonds, as shown in structure V. A comparison of IV and V may lead to the conclusion that the

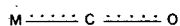


average bond order of the C—O bond in V is considerably higher than that in IV and that one should expect a higher stretching frequency for the carbonyl group in V. Actually, the two stretching frequencies are very close: 2,000 cm.⁻¹ for chromium and 2,060 cm.⁻¹ for nickel carbonyl. These figures indicate that the car-

TABLE 4.—Bond distances and force constants of carbonyl groups

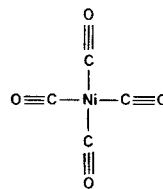
	:C=O:	Ni—C=O:		H ₂ C=C=O
Bond distance A.-----	1.13	1.15	1.21	1.17
Force constant, (10 ⁵ dynes cm. ⁻¹)-----	18.6	15.9	12.1	14.5

bonyl groups in $\text{Cr}(\text{CO})_6$ are very similar to those in $\text{Ni}(\text{CO})_4$. A possible way to express this similarity by appropriate structural formulas would be to write the $\text{M}-\text{C}-\text{O}$ linkage as shown in VI to indicate a bond order inter-

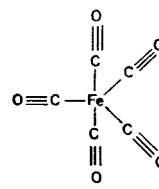


VI

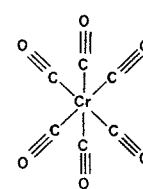
$\text{Fe}(\text{CO})_5$, and $\text{Cr}(\text{CO})_6$ are expressed by structures VII, VIII, and IX.



VII



VIII



IX

mediate between II and III. However, to express the fact that the carbonyl groups in the various metal carbonyls and also within the same metal carbonyl are equivalent, we shall use structure II. Thus, for example, $\text{Ni}(\text{CO})_4$,

This notation does *not* imply a pure carbon-oxygen triple bond, but a bond intermediate between a ketenic carbonyl and carbon monoxide.

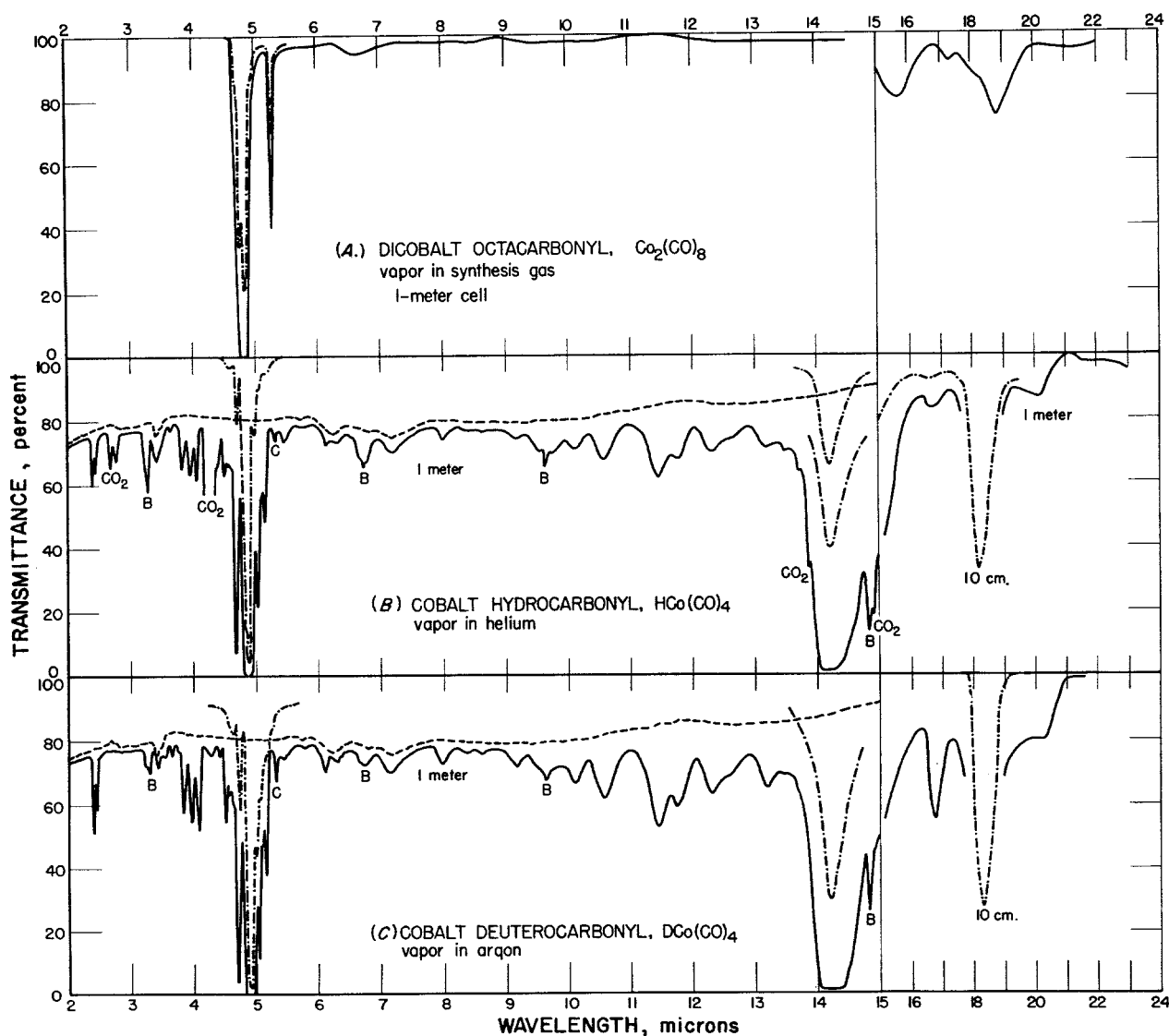


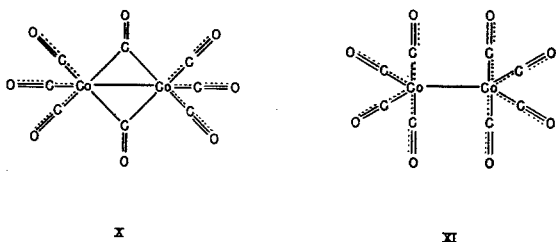
FIGURE 1.—Infrared Spectra of Cobalt Carbonyls in the Gaseous State.

Spectra and Structures of Cobalt Carbonyls

The infrared spectra of the metal carbonyls are simple, indicating a high degree of symmetry. The number of possible configurations is therefore limited and permits an insight into the structure of these molecules.

Dicobalt Octacarbonyl, $\text{Co}_2(\text{CO})_8$

The infrared spectrum of dicobalt octacarbonyl has been reported by Brimm and Lynch (16) and Cable, Nyholm, and Sheline (23). Structures X (5, 16, 23) and XI (136)



have been suggested for dicobalt octacarbonyl, where X is similar to the known structure of iron enneacarbonyl $\text{Fe}_2(\text{CO})_9$ (113, 121). Cable, Nyholm, and Sheline have proposed specific structures, like structure X, and have tested them by the principles of group theory. The structure assigned to the molecule was a combination of two trigonal bipyramids joined at an edge (23).

The infrared spectra of dicobalt octacarbonyl in the gas phase and in solution are shown in figures 1 and 2.

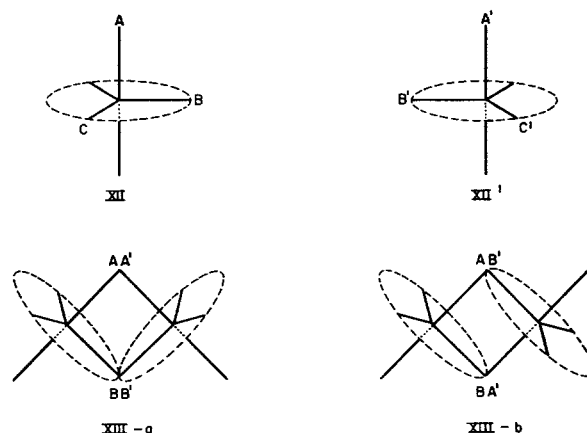
A gas sample of dicobalt octacarbonyl was prepared as follows: A handful of glass beads was placed in a 12-liter, round-bottomed flask. The flask was fitted with a rubber stopper containing an inlet and outlet tube provided with stopcocks and was purged with synthesis gas ($1\text{CO}+1\text{H}_2$) from which all traces of $\text{Fe}(\text{CO})_5$ had been removed by passage through cold sulfuric acid and two liquid-nitrogen traps. Without interrupting the gas current, the stopper was removed, 3 g. of dicobalt octacarbonyl was placed in the flask, the stopper was inserted, and the purging was continued for 2 hours. The inlet and outlet tubes were now closed, and the flask was shaken to disperse the dicobalt octacarbonyl. After 2 days, a gas sample was withdrawn which, according to published vapor-pressure data²⁸, contained 0.72 mg. (0.002 millimole) of dicobalt octacarbonyl per liter.

When the pressure of carbon monoxide is insufficient, dicobalt octacarbonyl decomposes into the tetramer and carbon monoxide. It was therefore not possible to obtain a gas sample of dicobalt octacarbonyl by simply evaporating the solid into an evacuated gas cell. The strongest bands in the vapor spectrum are three bands centered at $2,053\text{ cm}^{-1}$ and a single band at $1,876\text{ cm}^{-1}$. The same bands in solution

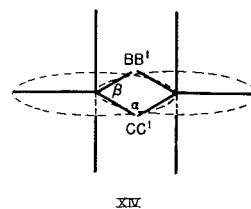
spectra occur at lower frequencies (table 5). These bands have been assigned to the terminal and bridge carbonyl groups, respectively, of $\text{Co}_2(\text{CO})_8$ (16, 23).

The possibility that two or more molecular forms are responsible for the two sets of bands was investigated by determining the spectrum (1) in the vapor state and (2) in solution over a wide range of concentrations. The relative intensities of the bands did not change, strengthening the postulation of the existence of bridge carbonyl groups.

The configuration around each cobalt atom in dicobalt octacarbonyl is probably that of a trigonal bipyramid, and the Co—Co bond is formed from two unhybridized *d* orbitals (23). Assuming a bipyramidal configuration around each cobalt, three structures can be derived (XIII-a, XIII-b, and XIV) by joining the two bipyramids XII and XII'.

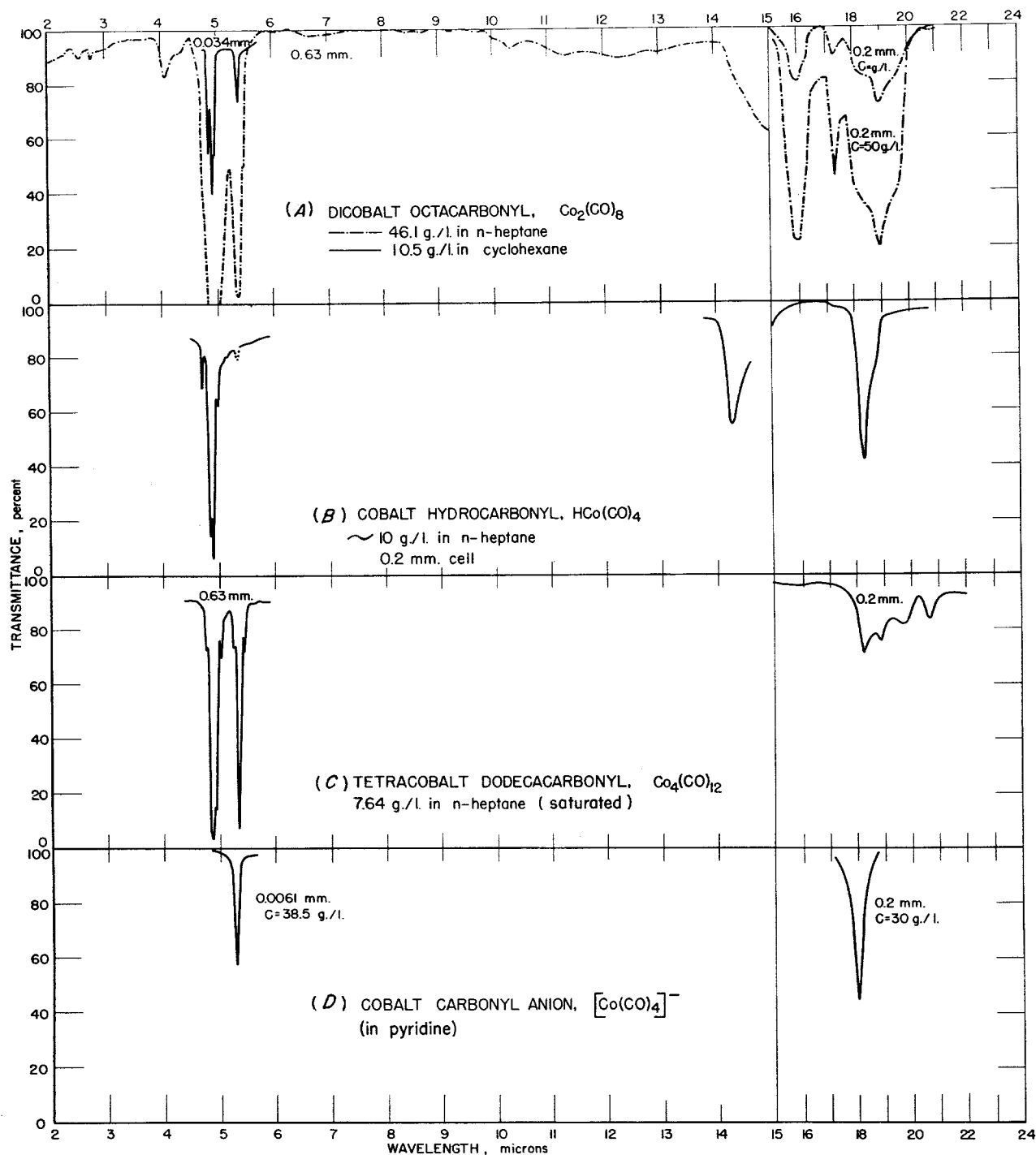


is obtained by connecting A to A' and B to B', structure XIII-b by connecting A to B' and B to A'. Structure XIV, chosen by Cable,



Nyholm, and Sheline as the most probable structure, is obtained by connecting B to B' and C to C'. Cable, Nyholm, and Sheline suggested structure XIII-b as a possible alternative to XIV (23). The shared groups in XIII-a, XIII-b, and XIV represent the bridge carbonyls.

Structure XIV can be eliminated for the following reasons. The angles α and β in XIV are 60° and 120° , respectively. Assuming that



(A) 0.007 g. per liter in $1\text{CO}+1\text{H}_2$; —, about 700 mm.; ---, about 280 mm. (B) 0.1 g. per liter in helium at about 700 mm.; —, 1-meter cell; ---, 1.0-cm. cell; ----, 1-meter cell blank; impurities; "B" is benzene, "C" is dicobalt octacarbonyl. (C) Sample consisted of 65 percent deuterocarbonyl and 35 percent hydrocarbonyl; spectra run under same conditions as (B).

FIGURE 2.—Infrared Spectra of Cobalt Carbonyls in Solution.

the metal-to-bridge carbon distance in dicobalt octacarbonyl is the same as that determined in $\text{Fe}_2(\text{CO})_9$, that is, 1.80 Å. (113), then the Co—Co distance is 1.80 Å., which is considerably smaller than 2.50 Å., the sum of the

covalent radii of two cobalt atoms. Opening the angle α to 90° would make the Co—Co distance 2.54 Å., but it would also reduce the angle β to 90° and thereby destroy the trigonal bipyramid configuration around the cobalt.

TABLE 5.—Infrared spectra of cobalt carbonyls (cm.⁻¹)

HCo(CO) ₄ solution	HCo(CO) ₄ gas	Co ₂ (CO) ₈ gas	Co ₂ (CO) ₈ solution	[Co(CO) ₄] ⁻ solution	Co ₄ (CO) ₁₂ solution
	1 4,184				
	1 4,090				
	2 2,941				
	2 2,825				
	2 2,740				
	1 2,614				
	1 2,525				
	1 2,451		2 2,475		
	1 2,208		3 2,326		
	4 2,179				
	4 2,151				
	5 2,126				
2,119 ¹			4 2,105		4 2,110
2,070 ⁴					
2,053 ⁶	4 2,066	6 2,079	6 2,068		6 2,058
2,030 ⁶	6 2,049	6 2,053	6 2,041		4 2,030
		6 2,037	6 2,024		
1,996 ¹	5 2,010	4 2,000	7 1,992		1 1,996
	5 1,981				
1,957 ⁴	4 1,961				4 1,905
1,934 ⁴	8 1,934	5 1,876	5 1,860	6 1,883	6 1,873
	2 1,938		4 1,825		1 1,838
	2 1,635				
	2 1,393				
	2 1,250				
	2 1,089				
	2 989		2 970		
	1 945				
	8 872		2 890		
	1 849				
	1 812		9 809		
	4 787				
	1 758				
	4 742				
	4 729				
700 ⁸	6 704	5 641	5 627		
	2 599		4 617		
578 ⁹		1 578	8 578		
546 ⁵	5 548	4 551	7 552	5 555	1 549
532 ⁴		5 531	5 528		4 529
	2 495		4 510		4 483

1 Medium.
2 Weak.
3 Weak shoulder.
4 Shoulder.
5 Strong.

6 Very strong.
7 Strong shoulder.
8 Medium shoulder.
9 Very weak.

Thus, only structures XIII-a and XIII-b need be considered. In either structure the trigonal bipyramidal configuration is retained, the angles α and β are 90°, and the Co—Co distance 2.54 Å. if a Co—C distance of 1.8 Å. is assumed. A slight deformation of the angle α from 90° to 87° and of β from 120° to 123° is sufficient to reduce the Co—Co distance to 2.5 Å., a distance small enough to account for the pairing

of the spins of the two unpaired electrons, as in the case of Fe₂(CO)₉ (113, 121).

A group-theory analysis shows that XIII-a (C_{2v} symmetry) produces five terminal and two bridge carbonyl stretching frequencies, whereas XIII-b (C_{2h} symmetry) produces three terminal and one bridge carbonyl stretching vibrations (table 6). Since the spectrum of dicobalt octacarbonyl shows a maximum of three bands assignable to terminal stretching and one band assignable to bridge carbonyl stretching, structure XIII-b is strongly supported.

The symmetry of model XIII-a prescribes 8 Co—C stretching and 25 bending frequencies which are infrared active, whereas model XIII-b prescribes only 5 Co—C stretching and 15 bending, infrared-active frequencies. The long wavelength spectrum of dicobalt octacarbonyl exhibits only three bands and two band shoulders. By analogy with Fe(CO)₅ (121) and Ni(CO)₄ (34), the strong bands at 641 and 531 cm.⁻¹ are probably Co—C stretching and Co—C—O bending, respectively.

The high frequency (1,876 cm.⁻¹) of bridge carbonyls in dicobalt octacarbonyl may be explained in terms of ring strain (23, 121) or by the presence of a type of hyperconjugation similar to that operative in phosgene (136). In phosgene, the carbonyl stretching frequency is increased and the bond length (37, 145) decreased in comparison with formaldehyde, a fact that cannot be explained by ring strain.

To further characterize the presumed bridge carbonyl structure, intensity measurements were made on the assigned absorption bands. The absolute intensity for the Co₂(CO)₈ bridge carbonyl band at 1,860 cm.⁻¹ (cyclohexane solution) is 4.0 × 10⁴ l.mole⁻¹ cm.⁻² per carbonyl, and the extinction coefficient is 680 l.mole⁻¹ cm.⁻¹ per carbonyl, assuming two carbonyls are present. These values compare reasonably well with intensities of strongly absorb-

TABLE 6.—Vibrations of Co₂(CO)₈

XIII, trigonal bipyramids, eclipse form, D _{3h}					XIII, trigonal bipyramids, staggered form, D _{3d}					XIII-a cis trigonal bipyramid, C _{2v}					XIII-b trans trigonal bipyramid, C _{2h}				
Class	R	IR	Modes	Designation	Class	R	IR	Modes	Designation	Class	R	IR	Modes	Designation	Class	R	IR	Modes	Designation
A ₁ '	+	-	7	$\nu_1-\nu_7$	A _{1g}	+	-	7	$\nu_1-\nu_7$	A ₁	+	+	15	$\nu_1-\nu_{15}$	A _g	+	-	15	$\nu_1-\nu_{15}$
A ₁ ''	-	-	2	$\nu_8-\nu_9$	A _{1u}	-	-	2	$\nu_8-\nu_9$	A ₂	+	-	8	$\nu_{16}-\nu_{23}$	A _u	-	+	10	$\nu_{16}-\nu_{23}$
A ₂ '	-	-	1	ν_{10}	A _{2g}	-	-	1	ν_{10}	B ₁	+	+	14	$\nu_{24}-\nu_{37}$	B _g	+	-	9	$\nu_{24}-\nu_{37}$
A ₂ ''	-	+	6	$\nu_{11}-\nu_{16}$	A _{2u}	-	+	6	$\nu_{11}-\nu_{16}$	B ₂	+	+	11	$\nu_{38}-\nu_{48}$	B _u	-	+	14	$\nu_{38}-\nu_{48}$
E'	+	+	8	$\nu_{17}-\nu_{24}$	E _g	+	+	8	$\nu_{17}-\nu_{24}$										
E''	+	-	8	$\nu_{25}-\nu_{32}$	E _u	-	+	8	$\nu_{25}-\nu_{32}$										
IR active modes:					IR active modes:					IR active modes:					IR active modes:				
Apical CO stretch.....					Apical CO stretch.....					Bridge CO stretch.....					Bridge CO stretch.....				
Equatorial CO stretch.....					Equatorial CO stretch.....					Terminal CO stretch.....					Terminal CO stretch.....				
Co—C stretch.....					Co—C stretch.....					Co—C stretch.....					Co—C stretch.....				
Co—C—O bend.....					Co—C—O bend.....					Co—C—O bend.....					Co—C—O bend.....				
1					1					2					1				
2					2					5					3				
3					3					8					5				
8					8					25					15				

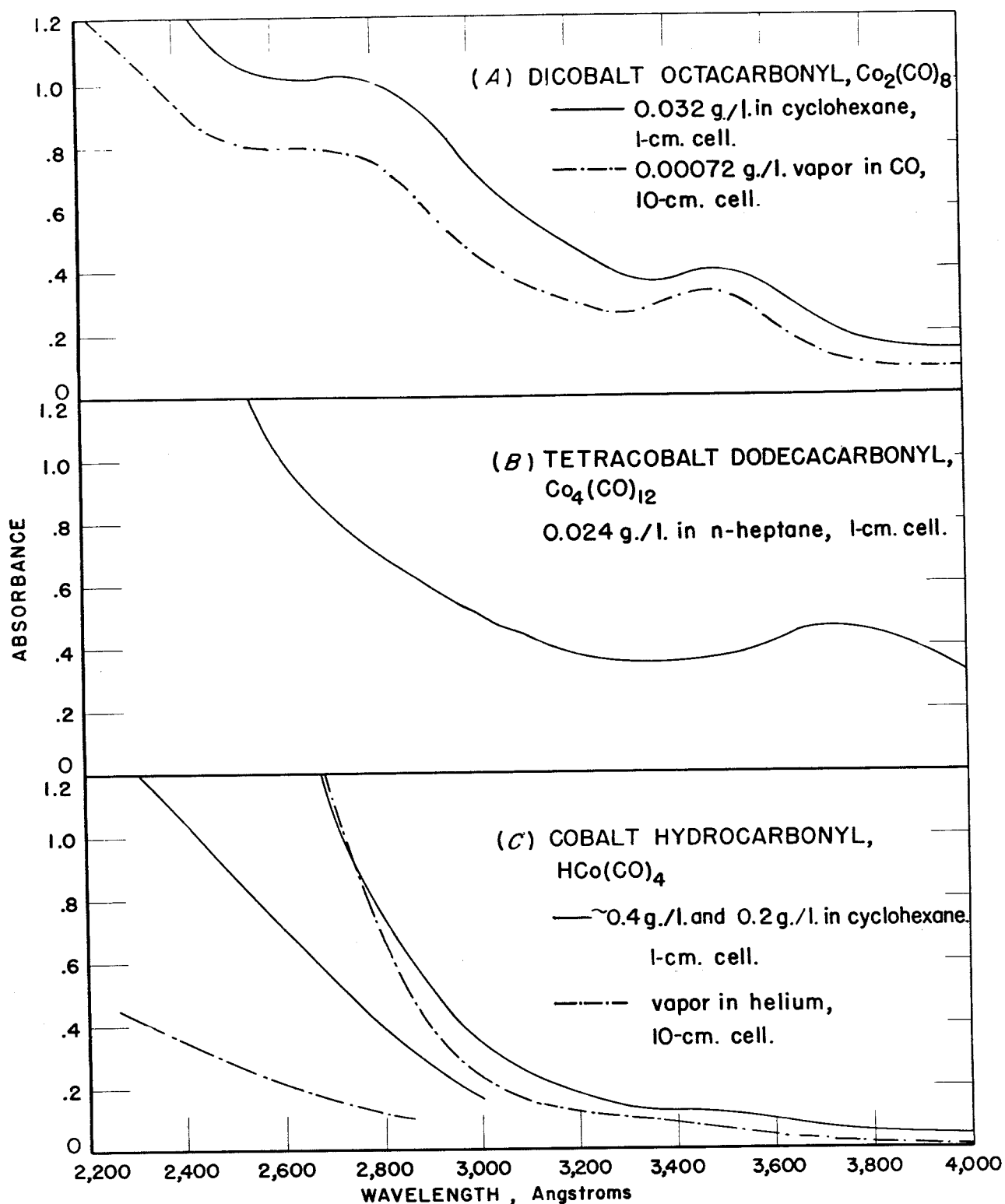


FIGURE 3.—Ultraviolet Spectra of Cobalt Carbonyls in the Gaseous and Solution States.

ing organic carbonyl groups (73), particularly those in conjugated systems.

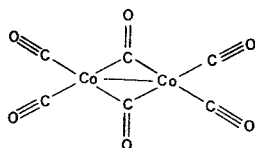
The ultraviolet spectrum of a cyclohexane solution of $\text{Co}_2(\text{CO})_8$, figure 3, shows two ab-

sorption bands at 3500 and 2800 Å., which have been reported by Hieber and Hofmann (61) and by Cable, Nyholm, and Sheline (23). The spectrum of the gaseous state, figure 3, is

similar except that the band maxima are shifted to shorter wavelengths. In spite of the instability of dicobalt octacarbonyl to ultraviolet light and to oxygen dissolved in solvents, the molar extinctions that were found compare favorably with those measured by Hieber. For example, at 3500 Å. in cyclohexane our value is 4300, and his value in n-heptane is 4900. The broad band at 2800 Å. is the band attributed by Cable to bridge carbonyl. This assignment seems plausible; cobalt hydrocarbonyl does not have the same band. However, $\text{Co}_4(\text{CO})_{12}$, which exhibits the bridge carbonyl band in infrared, does not have a 2800 Å. band (fig. 3). Thus, the assignment of the 2800 Å. band to bridge carbonyl in the ultraviolet spectrum of dicobalt octacarbonyl is in doubt.

TETRACOBALT DODECACARBONYL $\text{Co}_4(\text{CO})_{12}$

This cobalt carbonyl is believed to be a tetramer, $[\text{Co}(\text{CO})_3]_4$ (64), and a structure corresponding to this composition has been suggested (41). Cable and Sheline (24) have pointed out that the solvent used in the molecular-weight determination (64) was iron pentacarbonyl. This substance not only is decomposed by visible light and oxygen but could conceivably form a complex with the cobalt carbonyl. Such properties of the solvent could easily lead to wrong conclusions about the molecular weight of the solute. Cable and Sheline proposed structure XV as the one in best agreement with the observed infrared spectrum (fig. 2,



XV

table 5). In this structure the hybridization of each cobalt is dsp^2 , resulting in a square planar bonding configuration. These two square planes are joined at an edge, resulting in two bridge carbonyls. Structure XV is further supported by the fact that the ratio of areas under the bands compared with the same ration in $\text{Co}_2(\text{CO})_8$ (fig. 2) indicates a ratio of 2:1 for terminal-to-bridge carbonyl.

Tetracobalt dodecacarbonyl was prepared as follows:

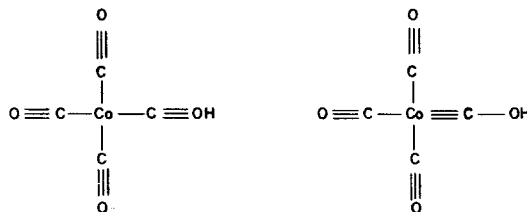
In an Erlenmeyer flask provided with a sidearm and a ground joint was placed 3 g. of dicobalt octacarbonyl, 75 ml. of cyclopentane, and some boiling chips. A slow current of nitrogen was passed through the sidearm, and the flask was attached to a reflux condenser

(provided with a mercury seal) and heated for 24 hours in a glycerine bath at 48°–52° C. Without interruption of the nitrogen steam, the flask was detached from the condenser, the cyclopentane solution was decanted, and the residue was washed several times with n-heptane by decantation. Finally, 75 ml. of n-heptane was added, the flask was stoppered, and the contents of the flask were allowed to stand in an atmosphere of nitrogen for 48 hours, during which time the flask was occasionally shaken to insure saturation of the n-heptane solution. Ten milliliters of the saturated n-heptane solution contained 0.0764 g. (0.1335 millimole) of tetracobalt dodecacarbonyl, as determined by a gasometric method described previously for the determination of dicobalt octacarbonyl (133).

COBALT HYDROCARBONYL, $\text{HCo}(\text{CO})_4$, AND COBALT DEUTEROCARBONYL $\text{DCo}(\text{CO})_4$

The hydrocarbonyls and deuterocarbonyls were prepared in a current of helium and argon, respectively (132). The gas samples contained approximately 0.5 millimole per liter of the hydrocarbonyl and deuterocarbonyl, respectively. A mass spectrometric analysis of the deuterocarbonyl showed that it contained 65 percent deuterocarbonyl and 35 percent hydrocarbonyl.

Ewens and Lister proposed structure XVI for cobalt hydrocarbonyl (42). On the basis of electron-diffraction data, they assumed a tetrahedral configuration for XVI, but were unable to establish the location of the hydrogen. Syrkin and Dyatkina suggested structure XVII (136).



XVI

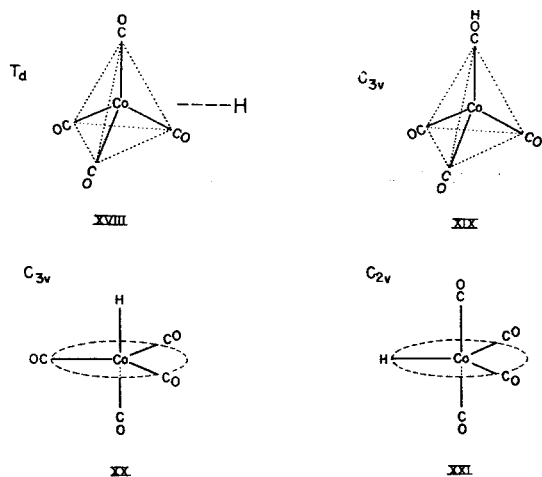
XVII

The infrared spectrum of cobalt hydrocarbonyl in the gas phase through the KBr region is given in figure 1; frequencies of the bands are listed in table 7. Many weak bands are apparent throughout the spectrum. The carbonyl band, 2,049 cm^{-1} with shoulder at 2,066 cm^{-1} , is the strongest band in the spectrum. Other strong bands at 704 cm^{-1} and 548 cm^{-1} are probably assignable to $\text{Co}-\text{C}$ stretching and $\text{Co}-\text{C}-\text{O}$ bending, respectively.

Cobalt deuterocarbonyl was prepared to investigate the location of the hydrogen atom in cobalt hydrocarbonyl. Whether the hydrogen is bonded to oxygen, carbon, or cobalt, the absorption band(s) due to this bond should shift by a predictable frequency interval upon

substitution of deuterium for hydrogen. The spectrum of cobalt deuterocarbonyl contained a band at 599 cm.^{-1} more intense than a weak, broad band at this position for the hydrocarbonyl. However, the band was not reproducible, and the spectra of hydrocarbonyl and deuterocarbonyl were otherwise identical.

The symmetries of various possible molecular configurations for cobalt hydrocarbonyl have been investigated. The group-theory results for four possible molecular models (structures XVIII, XIX, XX, and XXI) have been tabulated (table 7). Structures XX and XXI pre-



dict too many carbonyl stretching frequencies and are eliminated from further consideration. Since the spectrum is very similar to that of $\text{Ni}(\text{CO})_4$, support is given to structure XVIII, the tetrahedral form (hydrogen location unknown), as being the structure of cobalt hydrocarbonyl. In $\text{Ni}(\text{CO})_4$ only one carbonyl stretching vibration is infrared active. The only observed band is a very sharp one at $2,060\text{ cm.}^{-1}$. This value agrees with the $2,050\text{ cm.}^{-1}$ reported by Crawford and Cross (34). With the resolution available at that time, they

found a half-band width about four times as large as our half-band width at the same transmittance. However, the cobalt hydrocarbonyl band at $2,049\text{ cm.}^{-1}$ has a shoulder, which indicates the possible presence of two infrared-active carbonyl stretching modes. The band and shoulder are split into separate bands in the solution spectrum (fig. 2). Structure XIX, symmetry C_{3v} , predicts the observed two carbonyl stretching modes, but the OH stretching mode, which also exists, is not observed. The infrared evidence indicates that the hydrogen may be bound to one or more of the oxygens strongly enough to produce two infrared-active carbonyl stretching modes, but not strongly enough to produce an observable OH frequency. Thus, the spectrum indicates a structure intermediate between XVIII and XIX.

Proton Magnetic Resonance of $\text{HCo}(\text{CO})_4$

Measurements were made in both the liquid and solid phases at temperatures near the melting point, -25° C. (55). A proton resonance was observed in the sample, confirming the presence of hydrogen.

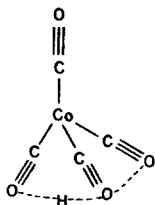
Some information regarding the nature of the bond to hydrogen was obtained from the position of the proton resonance, which depends on the electron environment of the hydrogen nucleus (83). The resonance position was measured with respect to acetone by a sample-interchange method, with 30 c.p.s. modulation and oscilloscope display of the resonances. The chemical shift δ -value (83) was found to be -1.55 ± 0.20 , referred to H_2O . This large negative value indicates a much greater electron density about the hydrogen nucleus than is found when hydrogen is bound to oxygen or carbon atoms. Such high electron density could occur if the hydrogen were bound to the cobalt by a rather ionic bond with a hydridelike character.

TABLE 7.—Vibrations of $\text{HCo}(\text{CO})_4$

Structure III symmetry, T_d tetrahedron					Structure IV symmetry, C_{3v} $\text{Co}(\text{CO})_3\text{COH}$					Structure V symmetry, C_{3v} trigonal bipyramid H on apex					Structure VI symmetry, C_{3v} trigonal bipyramid H on equator				
Class	R	IR	Modes	Designation	Class	R	IR	Modes	Designation	Class	R	IR	Modes	Designation	Class	R	IR	Modes	Designation
A_1	+	—	2	$\nu_1-\nu_2$	A_1	+	+	7	$\nu_1-\nu_7$	A_1	+	+	7	$\nu_1-\nu_7$	A_1	+	+	9	$\nu_1-\nu_9$
A_2	—	—	0	—	A_2	—	—	1	ν_8	A_2	—	—	1	ν_8	A_2	+	—	3	$\nu_{10}-\nu_{12}$
E	+	—	2	$\nu_3-\nu_4$	E	+	+	8	$\nu_9-\nu_{16}$	E	+	+	8	$\nu_9-\nu_{16}$	B_1	+	+	6	$\nu_{13}-\nu_{18}$
F_1	—	—	1	ν_5											B_2	+	+	6	$\nu_{19}-\nu_{24}$
F_2	+	+	4	$\nu_6-\nu_9$															
IR active modes (F_2):					IR active modes (A_1, E):					IR active modes (A_1, E):					IR active modes:				
CO stretch..... 1					CO stretch..... 2					CO stretch..... 3					CO stretch..... 4				
Co-C stretch..... 1					Co-C stretch..... 2					Co-C stretch..... 3					Co-C stretch..... 4				
Co-C-O bend..... 2					Co-C-O bend..... 9					Co-C-O bend..... 7					Co-C-O bend..... 10				
					OH stretch..... 1					Co-H stretch..... 1					Co-H stretch..... 1				
					OH bend..... 1					Co-H bend..... 1					Co-H bend..... 2				

If the hydrogen nucleus were bound strongly to the cobalt, one might expect the hydrogen resonance to be split into $2I(\text{Co})+1$ or 8 components by the electron exchange coupling of the nuclear moments (54). Actually, no evidence of broadening or splitting was found; the apparent width of the hydrogen resonance in the liquid was limited instrumentally at 0.05 to 0.10 oersted. However, any one of several factors could account for the absence of splitting (54). One of the most likely is a fast chemical exchange of the hydrogens.

On the basis of molecular orbital calculations, Edgell and Gallup (39) proposed structure XXII for cobalt hydrocarbonyl, where the hy-

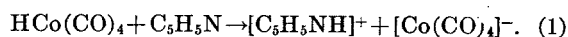


XXII

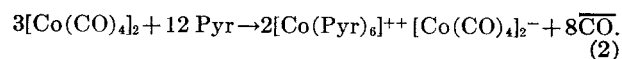
drogen is embedded in one face of the tetrahedron on the figure axis. The hydrogen is considered immersed in a sheath of negative charge due to the π -electrons of the carbonyl groups, an assumption which agrees with the findings from the proton magnetic resonance spectrum (139).

Cobalt Carbonyl Anion, $[\text{Co}(\text{CO})_4]^-$

When cobalt hydrocarbonyl is dissolved in pyridine, pyridinium cation and cobalt carbonyl anion are formed (equation (1)) (159):



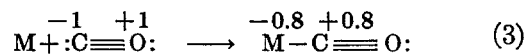
The anion is also obtained when dicobalt octacarbonyl is treated with pyridine (equation (2)) (158):



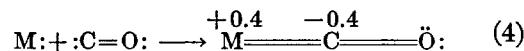
Cobalt carbonyl anion XXIII resembles nickel carbonyl in that it contains four carbonyl groups; it differs from nickel carbonyl by having a charge of -1 . As in nickel carbonyl, the metal-carbon bonds in cobalt carbonyl anion presumably are sp^3 hybrid bonds.

The infrared spectrum of cobalt carbonyl anion (fig. 2) shows only one band in the carbonyl stretching region, as does the spectrum of nickel carbonyl. The rest of the spectrum is

also simple; only one other strong band, at 555 cm^{-1} , is found. The carbonyl band, at $1,883 \text{ cm}^{-1}$, is assignable to carbonyl stretching even though it is located in a lower frequency region than the corresponding band ($2,060 \text{ cm}^{-1}$) in nickel carbonyl. This difference in the CO frequency between nickel carbonyl and cobalt carbonyl anion may be explained according to Brimm and Lynch (16) on the basis of Pauling's principle of electrical neutrality (104), which states that the charge of the central atom in a complex is essentially zero. Assuming a value of 1.6 for the electron negativity of nickel and cobalt and a value of 2.5 for that of carbon (124), one finds from the correlation between electronegativity and percent ionic character (105) that the metal-carbon bond is about 20 percent ionic and that the single bond



imparts a charge of -0.8 (equation (3)), whereas the metal-carbon double bond



imparts a charge of $+0.4$ (equation (4)) to the metal atom. Since the principle of electrical neutrality requires that the charge on the metal atom be zero, the average bond order of the metal-carbon bonds will be between 1 and 2. This average bond order may be calculated from (16)

$$+0.4x - 0.8(4-x) = 0, \quad (5)$$

where x equals the number of double bonds and $4-x$ the number of single bonds. Equation (5) is an algebraic expression of the postulation that the sum of single and double bonds should impart a charge of zero to the metal atom. Equation (5) yields 2.67 for x ; thus, of the four metal-carbon bonds, 2.67 are double and 1.33 are single. The average metal-carbon bond order in nickel carbonyl is therefore 1.67, and the average carbon-oxygen bond order is 2.33. Application of this method to $\text{Fe}(\text{CO})_5$, for instance, gives the same average bond order (2.33) for the carbon-oxygen bond in $\text{Fe}(\text{CO})_5$. This result is in good agreement with the fact that infrared-active carbonyl stretching fundamentals in $\text{Fe}(\text{CO})_5$ and $\text{Ni}(\text{CO})_4$ occur in the same region; that is, at $2,033$ and $2,012 \text{ cm}^{-1}$ for $\text{Fe}(\text{CO})_5$ and $2,060 \text{ cm}^{-1}$ for $\text{Ni}(\text{CO})_4$. Shelton and Pitzer (121) reported two fundamentals at $1,993$ and $2,028 \text{ cm}^{-1}$ for $\text{Fe}(\text{CO})_5$. The latter, which is much the stronger of the two, was found to consist of two strong bands at $2,012$ and $2,033 \text{ cm}^{-1}$, with the former being the stronger. These two bands are hereby