[CONTRIBUTION FROM BUREAU OF MINES, SYNTHETIC FUELS RESEARCH BRANCH]

Spectra and Structures of Cobalt Carbonyls[1]

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The spectra and structures of cobalt hydrocarbonyl, dicobalt octacarbonyl, cobalt carbonyl anion and tetracobalt dodecacarbonyl have been studied. The hydrogen of cobalt hydrocarbonyl is very weakly bound to the rest of the molecule, as shown by infrared spectra and nuclear magnetic resonance studies. The infrared spectrum of cobalt carbonyl anion indicates that the structure is tetrahedral; an explanation is given for the considerable long wave length shift of the carbonyl frequency. From the spectra of dicobalt octacarbonyl the structure proposed is a *trans* configuration of two trigonal bipyramids joined at the edge such that apical and equatorial carbonyls are shared as bridge carbonyls. The infrared spectrum of tetracobalt dodecacarbonyl is somewhat simpler than that of dicobalt octacarbonyl; the spectrum indicates a structure which also contains bridge carbonyls.

Introduction

The following three cobalt carbonyls are known: cobalt hydrocarbonyl, $HCo(CO)_4$, dicobalt octacarbonyl, $Co_2(CO)_8$ and tetracobalt dodecacarbonyl, $Co_4(CO)_{12}$. In addition, the stable cobalt carbonyl anion $[Co(CO)_4]^{-1}$ exists in solution.[2] Structure investigations by electron diffraction have been reported for cobalt hydrocarbonyl[3] and by infrared for dicobalt octacarbonyl.[4a,5] The present investigation was carried out in connection with catalysis studies to obtain further information concerning the structures of these metal carbonyls.

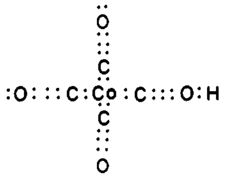
Cobalt Hydrocarbonyl, $HCo(CO)_4$

TABLE I

INFRARED SPECTRA OF COBALT CARBONYLS

m = medium; s = strong; sh = shoulder; v = very; and w = weak.

$HCo(CO)_4$ soln., (cm.$^{-1}$)	$HCo(CO)_4$ gas, (cm.$^{-1}$)	$Co_2(CO)_8$ gas, (cm.$^{-1}$)	$Co_2(CO)_8$ solution, (cm.$^{-1}$)	$[Co(CO)_4]^-$ soln., (cm.$^{-1}$)	$Co_4(CO)_{12}$ soln., (cm.$^{-1}$)
	4184 (m)				
	4090 (m)				
	2941 (w)				
	2825 (w)				
	2740 (w)				
	2614 (m)				
	2525 (m)				
	2451 (m)		2475 (w)		
	2208 (m)		2326 (wsh)		
	2179 (sh)				
	2151 (sh)				
2119 (m)	2126 (s)		2105 (sh)		2110 (sh)
2070 (sh)					
2053 (vs)	2066 (sh)	2079 (vs)	2068 (vs)		2058 (vs)
2030 (vs)	2049 (vs)	2053 (vs)	2041 (vs)		2030 (sh)
		2037 (vs)	2024 (vs)		
1996 (m)	2010 (s)	2000 (sh)	1992 (ssh)		1996 (m)
	1981 (s)				
1957 (sh)	1961 (sh)				1905 (sh)
1934 (sh)	1934 (ms)	1876 (s)	1860 (s)	1883 (vs)	1873 (vs)
	1828 (w)		1825 (sh)		1838 (m)
	1635 (w)				
	1393 (w)				
	1250 (w)				
	1089 (w)				
	989 (w)		970 (w)		
	945 (m)				
	872 (ms)		890 (w)		
	849 (m)				
	812 (m)		809 (vw)		
	787 (sh)				
	758 (m)				
	742 (sh)				
	729 (sh)				
700 (ms)	704 (vs)				
		641 (s)	627 (s)		
	599 (w)		617 (sh)		
578 (vw)		578 (m)	578 (ms)		
546 (s)	548 (s)	551 (sh)	552 (ssh)	555 (s)	549 (m)
532 (sh)		531 (s)	528 (s)		529 (sh)
	495 (w)		510 (sh)		483 (sh)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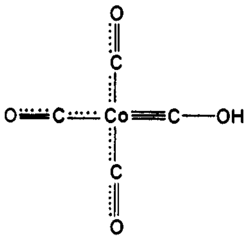
II

Infrared Spectra of $HCo(CO)_4$ and $DCo(CO)_4$.—Ewens and Lister proposed structure I for cobalt hydrocarbonyl.[3] On the basis of electron-diffraction data, they assumed a tetrahedral configuration for I but were unable to establish the location of the hydrogen. Syrkin and Dyatkina, taking into account Pauling's concept of the double-bond character of the metal–carbon bond, suggested structure II.[6a] In II and the following structures presented in this paper the bonds are written as $\mathrm{M}\overset{....}{=}\mathrm{C}\overset{....}{\equiv}\mathrm{O}$ to indicate fractional bond order as a result of resonance between the two forms, (A) $\mathrm{M{=}C{=}\ddot{O}}$: and (B) $\mathrm{M \leftarrow C{\equiv}O}$:. Resonance form (A) contains a doubly bonded $C{=}O$ group which is similar to that in ketene in that the σ bond is an sp hybrid bond.[7] Resonance form (B) contains a triply bonded $C{\equiv}O$ group similar to that in carbon monoxide. Thus, the $\mathrm{C}\overset{....}{\equiv}\mathrm{O}$ group in

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[1] Article not copyrighted.

[2] I. Wender, H. W. Sternberg and M. Orchin, THIS JOURNAL, **74**, 1216 (1952).

[3] R. V. G. Ewens and M. W. Lister, *Trans. Faraday Soc.*, **35**, 681 (1939).

[4] E. O. Brimm and M. A. Lynch, Jr., (a) "Estimated Bond Order in Metal Carbonyls," presented at the 121st meeting of the A.C.S. in Buffalo, N. Y., March, 1952, *Chem. Eng. News*, **30**, 1388 (1952); (b) private communication.

[5] J. W. Cable, R. S. Nyholm and R. K. Sheline, THIS JOURNAL, **76**, 3373 (1954).

[6] (a) Y. K. Syrkin and M. E. Dyatkina, "Structure of Molecules and the Chemical Bond," Interscience Publishers, Inc., New York, N. Y., 1950, p. 366; (b) p. 365; (c) p. 170.

[7] R. S. Nyholm and L. N. Short, *J. Chem. Soc.*, 2670 (1953).

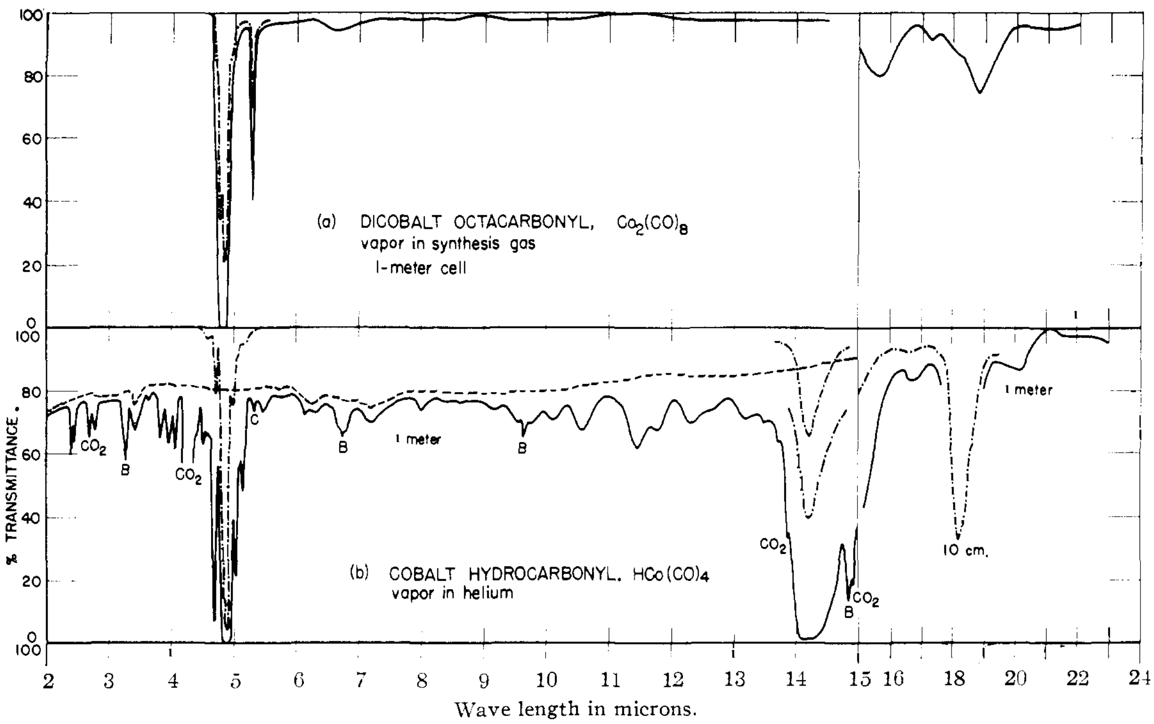


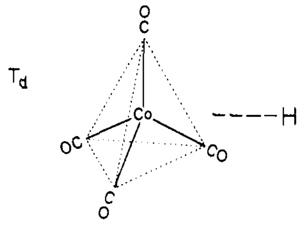
Fig. 1.—Infrared spectra of cobalt carbonyls in the gaseous state: (a) 0.1 g./l. in 1:1 CO + H_2; ——, about 700 mm.; –.– about 280 mm. (b) 0.1 g./l. in helium, at about 700 mm.; ——, one-meter cell, –.–, 1.0 cm. cell; ------, one-meter cell blank; impurities: "B" is benzene, "C" is dicobalt octacarbonyl.

metal carbonyls may be pictured as resonating between a ketenic-type carbonyl group with bond order 2 and a carbon monoxide-type carbonyl group with bond order 3. Molecular spectroscopy does not differentiate between a ketenic and a carbon monoxide-type carbonyl; both frequencies lie in the "triple-bond region," although the bond order may be closer to 2 than to 3.

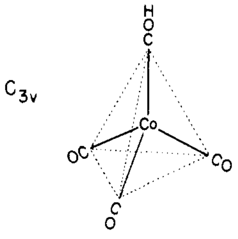
The infrared spectrum of cobalt hydrocarbonyl, an unstable gas, was in part reported previously.[8] The spectrum of the gas through the KBr region is given in Fig. 1; frequencies of the bands are listed in Table I. A large number of weak bands are apparent throughout the spectrum. The carbonyl band, 2049 cm.$^{-1}$ with shoulder at 2066 cm.$^{-1}$, is the strongest band in the spectrum. Other strong bands at 704 and 548 cm.$^{-1}$ are probably assignable to Co–C stretching and Co–C–O bending, respectively.

Cobalt deuteriocarbonyl 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. There was found in the spectrum of cobalt deuteriocarbonyl a band at 599 cm.$^{-1}$ that is more intense than a weak, broad band at this position for the hydrocarbonyl. But the band was not reproducible and the spectra of hydro- and deuteriocarbonyl were otherwise identical.[9]

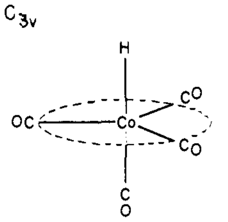
The symmetry properties of various possible molecular configurations for cobalt hydrocarbonyl have been investigated. The group theory results for four possible molecular models (structures III, IV, V, VI) have been tabulated (Table II). Structures V and VI predict too many stretching frequencies and are eliminated from further consideration. Since the spectrum is very similar to that of $Ni(CO)_4$, support is given to structure III, the tetrahedral form (hydrogen location unknown), as being the structure of cobalt hydrocarbonyl. In $Ni(CO)_4$ only one carbonyl stretching vibration is infrared-active. The only observed band is a very



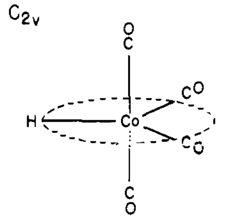
III



IV



V



VI

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(8) H. W. Sternberg, I. Wender, R. A. Friedel and M. Orchin, THIS JOURNAL, **75**, 2717 (1953).

(9) W. F. Edgell, private communication, is presently investigating this apparent anomaly.

TABLE II

VIBRATIONS OF $HCo(CO)_4$

Structure																			
III					IV					V					VI				
Symmetry																			
T_d tetrahedron					C_{3v} $Co(CO)_3COH$					C_{3v} trigonal bipyramid H on apex					C_{2v} trigonal bipyramid H on equator				
Class	R	IR	Modes	Desig.	Class	R	IR	Modes	Desig.	Class	R	IR	Modes	Desig.	Class	R	IR	Modes	Desig.
A_1	+	−	2	ν_1-ν_2	A_1	+	+	7	ν_1-ν_7	A_1	+	+	7	ν_1-ν_7	A_1	+	+	9	ν_1-ν_9
A_2	−	−	0		A_2	−	−	1	ν_8	A_2	−	−	1	ν_8	A_2	+	−	3	ν_{10}-ν_{12}
E	+	−	2	ν_3-ν_4	E	+	+	8	ν_9-ν_{16}	E	+	+	8	ν_9-ν_{16}	B_1	+	+	6	ν_{13}-ν_{18}
F_1	−	−	1	ν_5											B_2	+	+	6	ν_{19}-ν_{24}
F_2	+	+	4	ν_6-ν_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

sharp one at 2060 cm.$^{-1}$.[10] However, the cobalt hydrocarbonyl band at 2049 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 IV, symmetry C_{3v}, predicts the observed two carbonyl stretching modes, but the OH stretching mode is not observed. The infrared evidence indicates that the hydrogen may be close enough to one or more of the oxygens to produce two infrared-active carbonyl stretching modes, but not bound strongly enough to produce an observable OH frequency. Thus, the spectrum indicates a structure intermediate between III and IV.

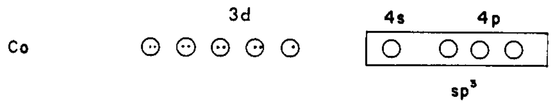
Ultraviolet Spectrum of $HCo(CO)_4$.—The spectra of the gaseous state of a cyclohexane solution of cobalt hydrocarbonyl are given in Fig. 3. The solution spectrum shows evidence of decomposition to form dicobalt octacarbonyl, as reported by Hieber,[11] in spite of precautions (see Experimental). However, the spectrum of gaseous hydrocarbonyl is free of contaminants. The spectrum has no absorption band in the spectral region investigated.

Proton Magnetic Resonance of $HCo(CO)_4$.—The resonance measurements and interpretations were kindly made by Dr. H. S. Gutowsky and coworkers at the University of Illinois, Department of Chemistry and Chemical Engineering. Because of its instability,[8] the sample of freshly prepared $HCo(CO)_4$ was delivered frozen in Dry Ice. And for the same reason, measurements were made of both the liquid and solid phases at temperatures near the melting point, −25°, in the cryostat and spectrometer described previously.[12] 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.[13] 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[12] was -1.55 ± 0.20, referred to H_2O. The 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. This high electron density could occur if the hydrogen were bound to the cobalt by a rather ionic bond with hydride-like character.

If the hydrogen nucleus were bound strongly to the cobalt, one might expect the hydrogen resonance to be split into $2I(Co) + 1$ or 8 components by the electron exchange coupling of the nuclear moments.[14] 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. But any one of several factors could account for the absence of the splitting.[14] One of the most likely is that there is a fast chemical exchange of the hydrogens.

To summarize the experimental evidence it is now obvious that the H in $HCo(CO)_4$ is very weakly bound. The negative character of the hydrogen is opposite to what one might expect from the production of protons in aqueous solution.[15] An electronic configuration consistent with a tetrahedral arrangement of the four carbonyl groups and the weakly bound hydrogen in $HCo(CO)_4$ is



where the carbons are bonded by the four hybrid orbitals and hydrogen by the unhybridized 3d orbital of cobalt.

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[10] This value agrees with the 2050 cm.$^{-1}$ reported by Crawford and Cross, *J. Chem. Phys.*, **6**, 525 (1938). 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.

[11] W. Hieber and K. K. Hofmann, *Z. anorg. allgem. Chem.*, **270**, 49 (1952).

[12] H. S. Gutowsky, L. H. Meyer and R. E. McClure, *Rev. Sci. Instr.*, **24**, 644 (1953).

[13] L. H. Meyer, A. Saika and H. S. Gutowsky, THIS JOURNAL, **75**, 4567 (1953).

[14] H. S. Gutowsky, D. W. McCall and C. P. Slichter, *J. Chem. Phys.*, **21**, 279 (1953).

[15] The same kind of structure probably exists in iron hydrocarbonyl, $H_2Fe(CO)_4$, so that the first and second ionization constants reported for the iron hydrocarbonyl by Krumholz and Stettiner [THIS JOURNAL, **71**, 3035 (1949)] may not reflect the actual structure of the molecule in the gaseous state.

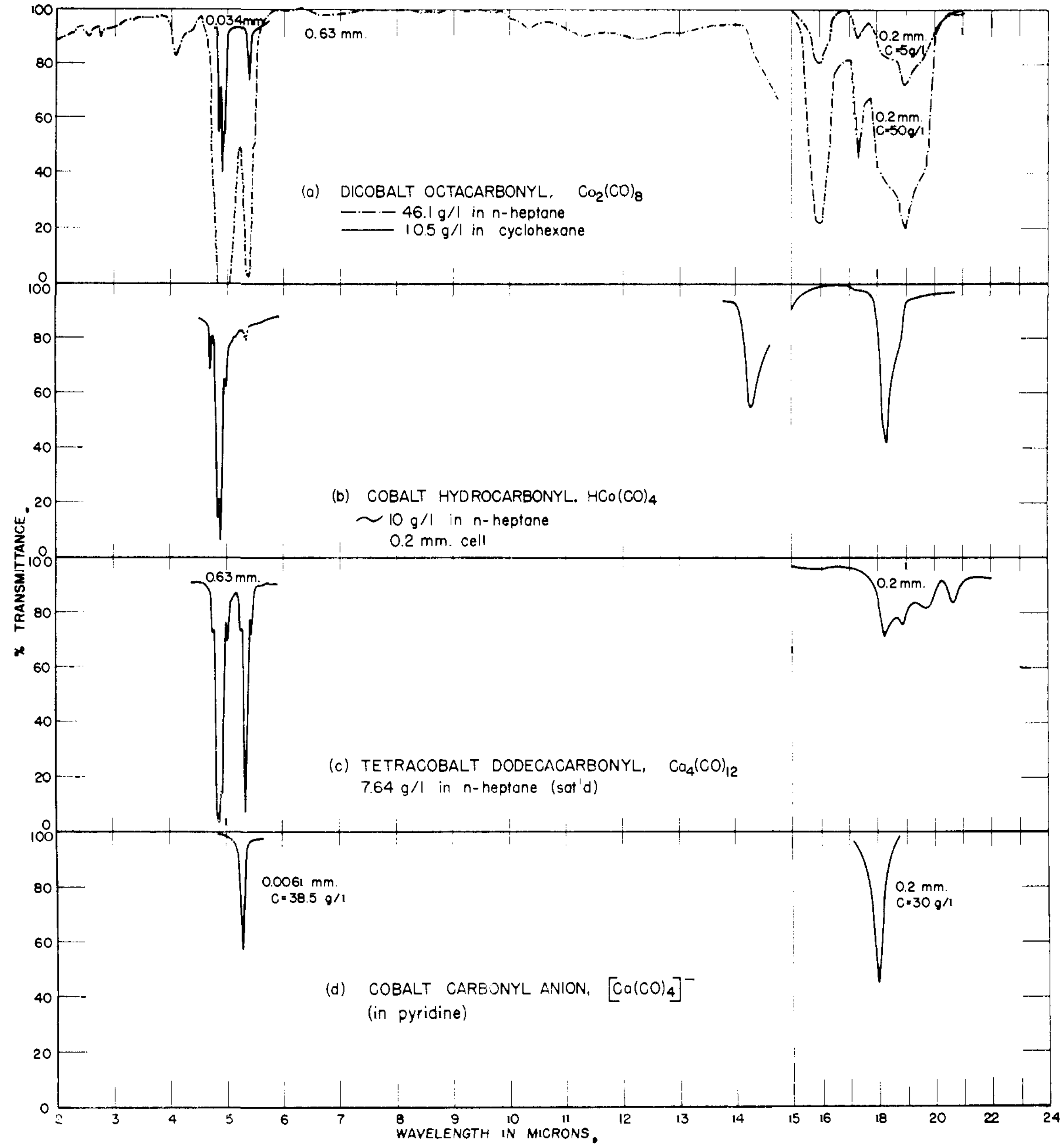


Fig. 2.—Infrared spectra of cobalt carbonyls in solution.

Cobalt Carbonyl Anion, $[Co(CO)_4]^-$

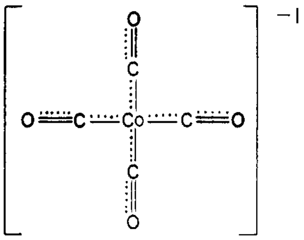
Infrared Spectra of $[Co(CO)_4]^-$.—When cobalt hydrocarbonyl is dissolved in pyridine, pyridinium cation and cobalt carbonyl anion are formed[16]

$$HCo(CO)_4 + C_5H_5N \longrightarrow [C_5H_5NH]^+ [Co(CO)_4]^-$$

The anion is also obtained when dicobalt octacarbonyl is treated with pyridine[17]

$$3[Co(CO)_4]_2 + 12Pyr \longrightarrow 2[Co(Pyr)_6]^{++}[Co(CO)_4]_2^- + 8\overline{CO} \quad (2)$$

Cobalt carbonyl anion (VII) resembles nickel carbonyl in that it contains four carbonyl groups and differs from nickel carbonyl by having a charge of −1. It is reasonable to assume that, as in nickel carbonyl, the metal–carbon bonds in cobalt carbonyl anion are sp³ hybrid bonds.



VII

The infrared spectrum of cobalt carbonyl anion (Fig. 2) shows only one band in the carbonyl

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(16) I. Wender, H. W. Sternberg and M. Orchin, This Journal, **75**, 3041 (1953).

(17) I. Wender, H. W. Sternberg and M. Orchin, *ibid.*, **74**, 1216 (1952).

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 1883 cm.$^{-1}$, is assignable to carbonyl stretching in spite of the fact that it is located in a lower frequency region than the corresponding band (2060 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,[4] on the basis of Pauling's principle of electrical neutrality, which states that the charge of the central atom in a complex is essentially zero.[18] Assuming a value of 1.6 for the electronegativity of nickel and cobalt[19] and a value of 2.5 for that of carbon, it follows from the correlation between electronegativity and per cent. ionic character[20] that the metal–carbon bond is about 20% ionic and that the single bond

$$\mathrm{M} + \overset{-1}{:\mathrm{C}}\equiv\overset{+1}{\mathrm{O}:} \longrightarrow \overset{-0.8}{\mathrm{M}}—\overset{+0.8}{\mathrm{C}}\equiv\mathrm{O}: \qquad (3)$$

imparts a charge of −0.8 (equation 3) while the metal–carbon double bond

$$\mathrm{M}: + :\mathrm{C}=\ddot{\mathrm{O}}: \longrightarrow \overset{+0.4}{\mathrm{M}}=\overset{-0.4}{\mathrm{C}}=\ddot{\mathrm{O}}: \qquad (4)$$

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 according to the equation[4b]

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

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 amount of single and double bonds should be such as to impart a charge of zero to the metal atom. Solving equation 5, we obtain 2.67 for x; thus, of the four metal–carbon bonds, 2.67 are double and 1.33 are single bonds. The average metal–carbon bond order in nickel carbonyl is therefore 1.67 and the average carbon–oxygen bond order 2.33. Application of this method to $Fe(CO)_5$, for instance, gives the same average bond order (2.33) for the carbon–oxygen bond in $Fe(CO)_5$. This result is in good agreement with the fact that infrared-active carbonyl stretching fundamentals in $Fe(CO)_5$ and $Ni(CO)_4$ occur in the same region, *i.e.*, at 2033 and 2012 cm.$^{-1}$ for $Fe(CO)_5$[21] and 2060 cm.$^{-1}$ for $Ni(CO)_4$. Table III presents a summation of infrared-active carbonyl stretching frequencies for several metal carbonyls. To illustrate an empirical similarity in carbonyl spectra, Table III also includes the combination band, in each carbonyl, nearest the terminal carbonyl frequency. The frequency interval from the lowest terminal frequency (Δ value) is nearly constant.

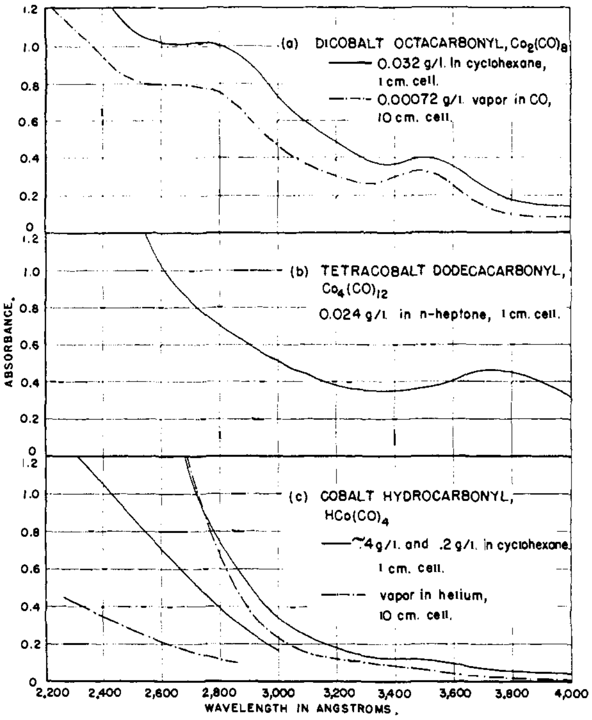

Fig. 3.—Ultraviolet spectra of cobalt carbonyls, in the gaseous and solution states.

TABLE III

INFRARED-ACTIVE CARBONYL STRETCHING FREQUENCIES OF VARIOUS METAL CARBONYLS; NEAREST COMBINATION BAND WITH FREQUENCY INTERVAL (Δ) FROM THE LOWEST TERMINAL CARBONYL FREQUENCY

	$HCo(CO)_4$ gas, (cm.$^{-1}$)	$Co_2(CO)_8$ gas, (cm.$^{-1}$)	$Fe(CO)_5$ gas, (cm.$^{-1}$)	$Ni(CO)_4$ gas, (cm.$^{-1}$)	$[Co(CO_4)]^-$ pyridine soln. (cm.$^{-1}$)	$Co_4(CO)_{12}$ heptane soln. (cm.$^{-1}$)
Terminal carbonyl frequencies	2066 2049[a]	2079 $\underline{2053}$ 2037	2033[b] $\underline{2012}$[b]	2060[c]	$\underline{1883}$	$\underline{2058}$ 2030
Bridge carbonyl frequency		1876				1873
Nearest combination band	2010	2000	1976	2022		1996
Δvalue	39	37	36	38		34

[a] Most intense band is underlined. [b] Bands at 2028 and 1993 cm.$^{-1}$ were reported and assigned as fundamentals by Sheline and Pitzer, ref. 21. [c] Crawford and Cross, ref. 10, reported the fundamental at 2050 cm.$^{-1}$. In the liquid phase, our value for the fundamental is 2047 cm.$^{-1}$; a value of 2045 cm.$^{-1}$ was reported by Margoshes, *et al.*, *J. Chem. Phys.*, **22**, 381(1954).

Applying the Pauling principle in the case of cobalt carbonyl anion (VII) and taking into account the fact that the number of single and double bonds must be adjusted so as to dissipate a charge of −1 from the cobalt atom, we arrive at equation 6

$$-1 + 0.4x - 0.8(4 - x) = 0 \qquad (6)$$

It follows from (6) that of the four cobalt–carbon bonds, 3.5 are double and 0.5 are single bonds, which leads to bond orders of 1.87 and 2.13 for

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(18) L. Pauling, *J. Chem. Soc.*, 1461 (1948).

(19) N. V. Sidgwick, "The Chemical Elements and Their Compounds," Vol. 1, Oxford, New York, N. Y., 1950, p. XVIII.

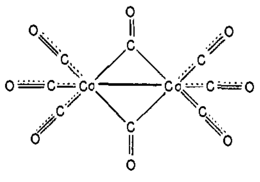
(20) L. Pauling, "The Nature of the Chemical Bond," Cornell University Press, Ithaca, New York, 1948, p. 70.

(21) R. K. Sheline and K. S. Pitzer, THIS JOURNAL, **72**, 1107 (1950), reported two fundamentals at 1993 and 2028 cm.$^{-1}$. We find that the latter, which is much the stronger of the two, actually consists of two strong bands at 2012 and 2033 cm.$^{-1}$, with the former being the stronger. These two bands are therefore probably the two infrared-active fundamentals. The 1993 cm.$^{-1}$ band is probably a combination band, which we find at 1976 cm.$^{-1}$ (see Table III).

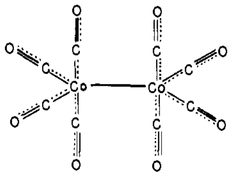
the Co–C and C–O bonds, respectively. The predicted lower bond order of the carbonyl bond in cobalt anion (2.13) as compared with the bond order in nickel carbonyl (2.33)[4b] is in good agreement with the observed lower frequency of the carbonyl band in cobalt carbonyl anion (1883 cm.$^{-1}$) as compared with that of nickel carbonyl (2060 cm.$^{-1}$). The band at 555 cm.$^{-1}$ is probably a Co–C–O bending vibration, analogous to that in $Ni(CO)_4$ at 545 cm.$^{-1}$.[10]

Dicobalt Octacarbonyl, $Co_2(CO)_8$

Infrared Spectra. Bridge Carbonyl Structure.—The infrared spectrum of dicobalt octacarbonyl has been reported by Brimm and Lynch,[4a] Sternberg, Wender, Friedel and Orchin,[8] and Cable, Nyholm and Sheline.[5] Structures VIII,[4a,5,22] and IX[6b] have been suggested for dicobalt octacarbonyl, where VIII is similar to the known structure of iron enneacarbonyl,[21,23] $Fe_2(CO_9)$. Cable, Nyholm and Sheline have proposed specific structures, of the form of structure VIII, 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.[5]



VIII



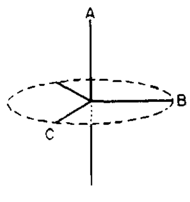
IX

The infrared spectra of dicobalt octacarbonyl in the gas phase and in solution are shown in Figs. 1 and 2. The strongest bands in the vapor spectrum are three bands centered at 2053 cm.$^{-1}$ and a single band at 1876 cm.$^{-1}$. The same bands in solution spectra occur at lower frequencies (Table I). These bands have been assigned to the terminal and bridge carbonyl groups, respectively, of $Co_2(CO)_8$.[4a,5]

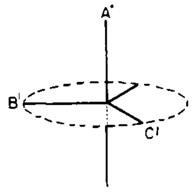
The possibility that two or more molecular forms are responsible for the two sets of bands was investigated by determining the spectrum of the vapor state and of solutions over a wide range of concentrations. The relative intensities of the bands did not change in either case. These results strengthen the postulate of bridge carbonyls.

That the ratio of bridge carbonyls to terminal carbonyls in dicobalt octacarbonyl is 2:6 was demonstrated as follows.[24] One mole of dicobalt octacarbonyl treated with excess acetylene liberated 2 moles of carbon monoxide. The spectrum of the resulting compound, $Co_2(CO)_6C_2H_2$, showed that the bridge carbonyl band at 1876 cm.$^{-1}$ had disappeared, while the bands corresponding to the terminal carbonyl groups remained.

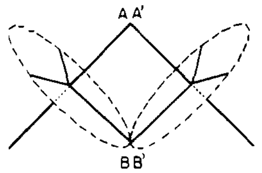
It is reasonable to assume that the configuration around each cobalt atom in dicobalt octacarbonyl is that of a trigonal bipyramid and that the Co–Co bond is formed from two unhybridized d orbitals.[5] On the assumption of a bipyramidal configuration around each cobalt, three structures can be derived (XIa, XIb and XIII) by joining the two bipyramids X and X′. Structure XIa is obtained by connecting A to A′ and B to B′, and structure XIb by connecting A to B′ and B to A′. Structure XII, considered by Cable, Nyholm and Sheline[5] and chosen by them as the most probable structure, is obtained by connecting B to B′ and C to C′.[25] The shared groups in XIa, XIb and XII represent the bridge carbonyls.



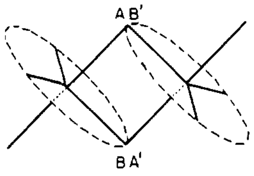
X



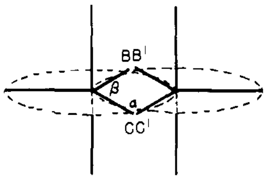
X′



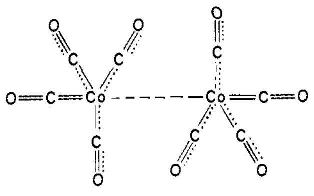
XI-a



XI-b



XII



XIII

Structure XII can be eliminated for the following reasons. The angles α and β in XII are 60 and 120°, respectively. Assuming that the metal to bridge-carbon distance in dicobalt octacarbonyl is the same as that determined in $Fe_2(CO)_9$,[23] *i.e.*, 1.80 Å., then the Co–Co distance is 1.80 Å., which is considerably smaller than 2.50, 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 would also reduce the angle β to 90° and thereby destroy the trigonal bipyramid configuration around the cobalt. Thus, only structures XIa and XIb need be considered. In either structure the trigonal bipyramid 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 $Fe_2(CO)_9$.[21,23]

A group theory analysis showed that XIa (C_{2v}

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[22] J. S. Anderson, *Quart. Rev.*, 1, 355 (1948).

[23] H. M. Powell and R. V. G. Ewens, *J. Chem. Soc.*, 286 (1939).

[24] H. W. Sternberg, H. Greenfield, R. A. Friedel, J. Wotiz, R. Markby and I. Wender, THIS JOURNAL, **76**, 1457 (1954).

[25] In a note added in proof, Cable, Nyholm and Sheline suggested structure XIb as a possible alternative to XII.

TABLE IV

VIBRATIONS OF $Co_2(CO)_8$

Structure																			
XIa *cis* trigonal bipyramid					XIb, *trans* trigonal bipyramid					XIII, trigonal bipyramids eclipse form					XIII, trigonal bipyramids staggered form				
C_{2v}					C_{2h}					D_{3h}					D_{3d}				
Class	R	IR	Modes	Desig.	Class	R	IR	Modes	Desig.	Class	R	IR	Modes	Desig.	Class	R	IR	Modes	Desig.
A_1	+	+	15	ν_1-ν_{15}	A_g	+	−	15	ν_1-ν_{15}	A_1'	+	−	7	ν_1-ν_7	A_{1g}	+	−	7	ν_1-ν_7
A_2	+	−	8	ν_{16}-ν_{23}	A_u	−	+	10	ν_{16}-ν_{25}	A_1''	−	−	2	ν_8-ν_9	A_{1u}	−	−	2	ν_8-ν_9
B_1	+	+	14	ν_{24}-ν_{37}	B_g	+	−	9	ν_{26}-ν_{34}	A_2'	−	−	1	ν_{10}	A_{2g}	−	−	1	ν_{10}
B_2	+	+	11	ν_{38}-ν_{48}	B_u	−	+	14	ν_{35}-ν_{48}	A_2''	−	+	6	ν_{11}-ν_{16}	A_{2u}	−	+	6	ν_{11}-ν_{16}
										E'	+	+	8	ν_{17}-ν_{24}	E_g	+	−	8	ν_{17}-ν_{24}
										E''	+	−	8	ν_{25}-ν_{32}	E_u	−	+	8	ν_{25}-ν_{32}

IR active modes:		IR active modes:		IR active modes:		IR active modes:	
Bridge CO stretch	2	Bridge CO stretch	1	Apical CO stretch	1	Apical CO stretch	1
Terminal CO stretch	5	Terminal CO stretch	3	Equatorial CO stretch	2	Equatorial CO stretch	2
Co–C stretch	8	Co–C stretch	5	Co–C stretch	3	Co–C stretch	3
Co–C–O bend	25	Co–C–O bend	15	Co–C–O bend	8	Co–C–O bend	8

symmetry) produces five terminal and two bridge carbonyl stretching frequencies while XIb (C_{2h} symmetry) produces three terminal and one bridge carbonyl stretching vibrations (Table IV). 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 XIb is strongly supported.

The symmetry of model XIa prescribes 8 Co–C stretching and 25 bending frequencies which are infrared-active, whereas model XIb prescribes only 5 Co–C stretching and 15 bending, infrared-active frequencies. The long wave length spectrum of dicobalt octacarbonyl exhibits only three bands and two band shoulders. By analogy with $Fe(CO)_5$[21] and $Ni(CO)_4$,[10] the strong bands at 641 and 531 cm.$^{-1}$ are probably Co–C stretching and Co–C–O bending, respectively.

The high bridge carbonyl frequency (1876 cm.$^{-1}$) in dicobalt octacarbonyl may be explained in terms of ring strain.[5,21] An alternate explanation may be the presence of a type of hyperconjugation similar to that operative in phosgene.[6c] In phosgene, the carbonyl stretching frequency is increased and the bond length decreased in comparison with formaldehyde, a fact that cannot be explained by ring strain.[26]

Intensities.—To further characterize the presumed bridge carbonyl structure, intensity measurements have been made on the assigned absorption bands. The absolute intensity[27] for the $Co_2(CO)_8$ bridge carbonyl band at 1860 cm.$^{-1}$ (cyclohexane solution) is 4.0×10^4 per carbonyl and the extinction coefficient is 680 per carbonyl, assuming two bridge carbonyls to be present. These values compare reasonably well with intensities of strongly absorbing organic carbonyl groups,[27] particularly those in conjugated systems.

Structure without Bridge Carbonyls.—Although it appears reasonably certain that the band at 1876 cm.$^{-1}$ is due to a bridge carbonyl stretching vibration, a structure such as XIII, where the dimerization is achieved by means of a cobalt–cobalt bond, cannot be ruled out.[28] A group theory analysis showed that both the staggered (D_{3d} symmetry) and the eclipsed form (D_{3h} symmetry) of model XIII predict three bands (Table IV) in the carbonyl region. One of these is due to the apical carbonyls and could be assigned as the 1876 cm.$^{-1}$ "bridge carbonyl" band. Therefore, structure XIII should not be excluded solely on the basis of infrared data. In this connection, it is of interest to note that the spectra of the two dimeric carbonyls, dimanganese and dirhenium decacarbonyl, do not contain any bands assignable to bridge carbonyl,[29] an indication that dimerization does not require the existence of bridge carbonyls.

Ultraviolet Spectrum of $Co_2(CO)_8$.—The ultraviolet spectrum of a cyclohexane solution of $Co_2(CO)_8$, Fig. 3, shows two absorption bands at 3500 and at 2800 Å., which have been reported by Hieber[11] and by Cable, Nyholm and Sheline.[5] The spectrum of the gaseous state, Fig. 3, is similar, except that the band maxima are shifted to shorter wave length. In spite of the instability of dicobalt octacarbonyl to ultraviolet light and to oxygen dissolved in solvents, the molar extinctions of the present determinations compare favorably with those measured by Hieber. For example, at 3500 Å. in cyclohexane our value is 4300 and Hieber's value in *n*-heptane is 4900.

The broad band at 2800 Å. is the band attributed by Cable, Nyholm and Sheline[5] to bridge carbonyl. This assignment is plausible; cobalt hydrocarbonyl does not have the same band. However, tetracobalt dodecacarbonyl, which exhibits the bridge carbonyl band in infrared, does not have a 2800 Å. band (Fig. 3). Conversely, the reaction product of acetylene and dicobalt octacarbonyl has a broad ultraviolet band near 2800 Å., although the structure has no bridge carbonyls. Thus, the assignment of the 2800 Å. band to bridge

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(26) A. F. Wells, "Structural Inorganic Chemistry," Oxford at the Clarendon Press, New York, 1950, p. 518; Jules Duchesne, *J. Chem. Phys.*, **22**, 1464 (1954).

(27) R. N. Jones, D. A. Ramsay, D. S. Keir and K. Dobriner, THIS JOURNAL, **74**, 80 (1952).

(28) E. O. Brimm and M. A. Lynch, private communication. In a dsp^3 trigonal bipyramid, two π bonds are permitted. If one of these π bonds serves the three equatorial bonds and the other the two apical bonds, then the occurrence of two band regions in dicobalt octacarbonyl would be explained. The two sets of three equatorial bonds would have carbonyl bands near 2000 cm.$^{-1}$ and the single apical carbonyl in each bipyramid would be completely double-bonded. The latter is based on the reasonable assumption that no cobalt–cobalt double bond would form.

(29) E. O. Brimm, M. A. Lynch, Jr., and W. J. Sesny, THIS JOURNAL, **76**, 3831 (1954).

carbonyl in the ultraviolet spectrum of dicobalt octacarbonyl is in doubt.

Tetracobalt Dodecacarbonyl, $Co_4(CO)_{12}$

A structure has been suggested for $Co_4(CO)_{12}$.[30] The chemical behavior of $Co_4(CO)_{12}$ does not permit one to draw many conclusions concerning its structure. The reaction with sodium in liqud ammonia[31]

$$[Co(CO)_3]_4 + 3Na \longrightarrow Co + 3Na[Co(CO)_4] \quad (7)$$

is compatible with a salt-like structure such as $Co[Co(CO)_4]_3$. The infrared spectrum of $Co_4(CO)_{12}$ (Fig. 2), however, is not saltlike and shows bands for both terminal and bridge carbonyl groups. The ratio of areas under the bands, compared with the same ratio in $Co_2(CO)_8$, indicates for $Co_4(CO)_{12}$ a ratio of 2:1 for terminal to bridge carbonyls.

The ultraviolet spectrum of tetracobalt dodecacarbonyl is shown in Fig. 3.

Experimental

Spectral Determinations.—Infrared spectra were determined on a Perkin-Elmer Model 21 double-beam spectrophotometer. The spectra of solutions, Fig. 2, were obtained both in conventional cells (0.63 and 0.20 mm.) and in special recessed cells (0.034 and 0.0061 mm.) described previously.[32] The recessed cells are demountable and the thicknesses are quite reproducible. They are very convenient for working with volatile solvents and with unstable materials which produce insoluble residues.

Ultraviolet spectra were run on a Cary Model 11 spectrophotometer.

Samples were prepared for spectral investigation as follows

1. **Cobalt Hydrocarbonyl and Cobalt Deuterocarbonyl.**—The hydro- and deuterocarbonyl were prepared in currents of helium and argon, respectively.[8] The gas samples contained approximately 0.5 millimole per liter of the respective carbonyls, when freshly prepared. A mass spectrometric analysis of the gas from decomposition of the deuterocarbonyl showed that the original sample consisted of 65% deutero- and 35% hydrocarbonyl.

For ultraviolet measurements, cobalt hydrocarbonyl was freshly prepared and dissolved in cyclohexane. The solution was kept at the temperature of liquid N_2 until it was transferred to an ultraviolet cell. Because of the instability of hydrocarbonyl to radiation and to oxygen dissolved in solvents, measurements were made at very high scanning speeds (50 Å. per second) and no accurate values for the concentrations of the hydrocarbonyl either in the gas phase or in the solution phase were obtained. Approximate values for concentrations in the solution phase are given in Fig. 3. For infrared measurements the approximate concentration in *n*-heptane is given in Fig. 2.

2. **Cobalt Carbonyl Anion.**—Cobalt carbonyl anion was prepared according to equation 2 by treating 3 g. of dicobalt octacarbonyl with 10 ml. of pyridine in the absence of air.

3. **Dicobalt Octacarbonyl.**—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 fitted with a rubber stopper containing an inlet and outlet tube provided with stopcocks, and purged with synthesis gas (CO and H_2, 1:1) from which any trace of $Fe(CO)_5$ had been removed by passage through cold sulfuric acid and two liquid nitrogen traps. Without interrupting the gas current, the stopper was removed, 3.0 g. of dicobalt octacarbonyl placed in the flask, the stopper inserted, and purging continued for 2 hours. The inlet and outlet tubes were now closed, and the flask was shaken in order to disperse the dicobalt octacarbonyl. After two days, a gas sample was withdrawn, which according to published vapor pressure data,[33] contained 0.72 mg. (0.002 mmole) of dicobalt octacarbonyl per liter.

In the absence of sufficient pressure of carbon monoxide, dicobalt octacarbonyl decomposes into the tetramer and carbon monoxide. A gas sample of dicobalt octacarbonyl could therefore not be obtained by simply evaporating into an evacuated gas cell.

4. **Tetracobalt Dodecacarbonyl.**—In an erlenmeyer flask provided with a side arm and a ground joint were placed 3 g. of dicobalt octacarbonyl, 75 ml. of cyclopentane, and some boiling chips. A slow current of nitrogen was passed through the side arm and the flask was attached to a reflux condenser provided with a mercury seal and heated for 24 hours in a glycerol bath at 48 to 52°. Without interruption of the nitrogen stream, the flask was detached from the condenser, the cyclopentane solution decanted, and the residue washed several times with *n*-heptane by decantation. Finally, 75 ml. of *n*-heptane was added, the flask stoppered, and the contents of the flask allowed to stand in an atmosphere of nitrogen for 48 hours while the flask was occasionally shaken to ensure saturation of the solution. Ten ml. of the saturated *n*-heptane solution contained 0.0764 g. (0.1335 mmole) of tetracobalt dodecacarbonyl, as determined by a gasometric method described previously for the determination of dicobalt octacarbonyl.[34]

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PITTSBURGH, PA.

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[31] H. Behrens, *Naturforschung*, **7b**, 321 (1952).

[32] R. A. Friedel and M. G. Pelipetz, *J. Opt. Soc. Am.*, **43**, 1051 (1953).

[33] L. Mond, H. Hirtz and M. D. Cowap, *J. Chem. Soc.*, **97**, 798 (1910).

[34] H. W. Sternberg, I. Wender and M. Orchin, *Anal. Chem.*, **24**, 174 (1952).