larger. Effects of a pronounced ion–electron interaction of some sort seem to be indicated by our experiments with mixed metal–salt solutions which will be reported shortly. Present theoretical calculations indicate that perhaps the use of equation 4 is not justified. No alternative is yet at hand however so detailed consideration of the data in the dilute range of concentration will be postponed until a more adequate theory is available.

MURRAY HILL, N. J.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF FLORIDA STATE UNIVERSITY AND THE SCHOOL OF APPLIED CHEMISTRY OF THE NEW SOUTH WALES UNIVERSITY OF TECHNOLOGY]

The Spectra and Structure of Dicobaltoctacarbonyl[1]

BY JOE W. CABLE,[2] RONALD S. NYHOLM AND RAYMOND K. SHELINE

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The infrared spectrum from 2.5–15 μ and the visible and ultraviolet spectra from 2100–7000 Å. were obtained for dicobaltoctacarbonyl. The presence of a carbonyl frequency at 1858 cm.$^{-1}$ in the infrared spectrum and the peak at 2800 Å. in the ultraviolet spectrum indicate the presence of bridged carbonyls in the molecule. Four feasible structures with bridging carbonyl groups were proposed and critically examined. It was concluded that the most probable structure was that of two trigonal bipyramids joined at an edge.

Introduction

In recent years there has been a great amount of work done concerning the structures of the metal carbonyls. This class of compounds is particularly interesting to the structural chemist because of the wide variety of structure types which these compounds may assume. It was found[3] that in the case of $Fe_2(CO)_9$ the infrared spectrum revealed the presence of a bridged, ketone-type carbonyl, thus confirming the bridged structure previously proposed. A similar approach was taken in this study of dicobaltoctacarbonyl.

Experimental

(a) **Preparation of Sample.**—The $Co_2(CO)_8$ used in taking these spectra was received from Dr. Irving Wender of the Synthetic Liquid Fuels Division of the Bureau of Mines. Since the compound is unstable and oxidized by air, the samples were purified by vacuum sublimation immediately before use. The vacuum system was the usual high vacuum pump used in conjunction with a mercury diffusion pump. The sublimation was carried out at room temperature. It was found that the sample in this finely divided condition was oxidized very readily, and the solutions had to be made very quickly.

The *n*-hexane used as a solvent was obtained from Phillips Petroleum Company and was purified by the following procedure: 300 ml. of *n*-hexane was washed with 100 ml. of pyrosulfuric acid, then with six successive 100-ml. portions of water. The *n*-hexane was then dried over magnesium perchlorate, and distilled through a column of activated silica gel.

(b) **Infrared Spectrum.**—The absorption spectrum was taken on a Perkin–Elmer model-21 spectrophotometer using NaCl optics. The sample was run at room temperature in *n*-hexane solution with a cell thickness of 0.5 mm. The spectrophotometer was calibrated by obtaining the spectrum of water vapor in the air and checking the peaks recorded against standard values. These corrections have been applied to the reported values where necessary. The absorption curve is given in Fig. 1. This spectrum has been previously reported[4] and used as an analytical tool in a study of cobalt hydrocarbonyl. The values reported agree very well with those obtained in this study.

(c) **Visible and Ultraviolet Spectra.**—The visible and ultraviolet spectra were taken from 2100 to 7000 Å. on the Beckman DU spectrometer. Solutions of concentration 1.6 × 10^{-5}, 1.6 × 10^{-4}, 2.86 × 10^{-5} and 2.86 × 10^{-4} *M* in *n*-hexane were used.

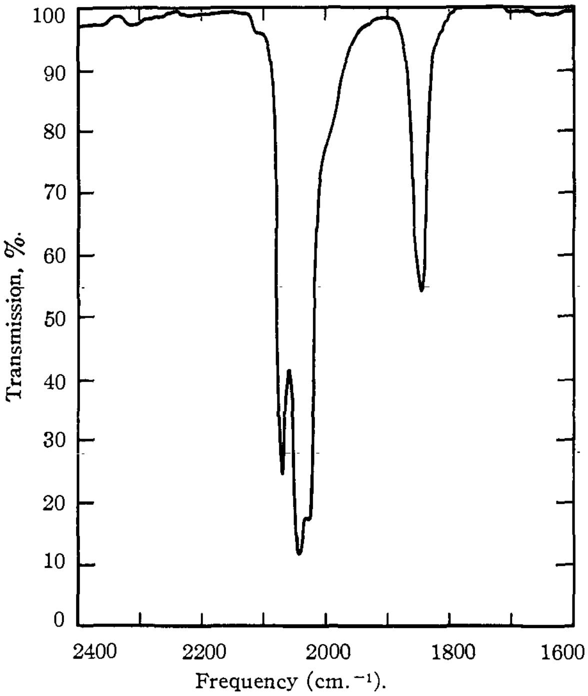

Fig. 1.—The infrared spectrum of $Co_2(CO)_8$. Those portions omitted showed negligible absorption in the rocksalt region.

Discussion

The infrared spectrum exhibits three strong carbon monoxide type carbonyl bands at 2070, 2043 and 2025 cm.$^{-1}$. In addition there is a strong band at 1858 cm.$^{-1}$ which indicates the presence of a ketone type carbonyl. The ultraviolet spectrum exhibits a curve sloping downward smoothly from an intense peak at a shorter wave length. There are two slight peaks; one at 2800 Å. with a molar extinction coefficient of 372 ± 64, and the other at 3520 Å. with a molar extinction coefficient of 315 ± 100. The peak at 2800 Å. is attributed to a forbidden $n \rightarrow \pi^*$ transition found in all saturated alde-

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[2] From portions of a thesis submitted by J. W. C. to the Graduate School of the Florida State University in partial fulfillment of the requirements for the degree of Doctor of Philosophy.

[3] R. K. Sheline and K. S. Pitzer, THIS JOURNAL, **72**, 1107 (1950).

[4] H. W. Sternberg, *et al.*, *ibid.*, **75**, 2717 (1953).

hydes and ketones. This transition involves a non-bonding p-electron of the oxygen atom being excited to an antibonding molecular orbital and is localized on the C=O part of the molecule. It would therefore be expected for metal carbonyls containing bridged carbonyls but not for those with only carbon monoxide type carbonyls. In this case the transition, though forbidden, is enhanced by perturbation effects due to the field of the cobalt atom.

Since both the infrared and the ultraviolet spectra indicate the presence of a bridged carbonyl, as well as carbon monoxide type carbonyls, any structure must explain: (1) molecular weight; (2) presence of bridged carbonyls; (3) presence of carbon monoxide type carbonyls: (4) diamagnetism.

There have been two structures proposed for dicobaltoctacarbonyl. These two structures are shown in Fig. 2 along with other possible structures.

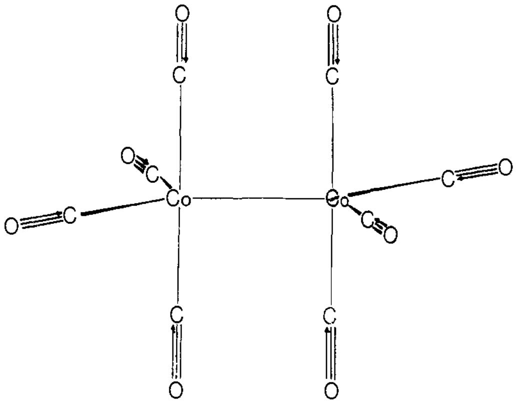

I

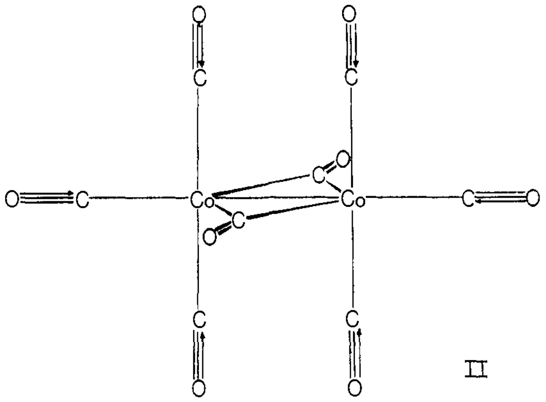
Fig. 2.—Possible structures of $Co_2(CO)_8$.

Structure I.[5]—Each cobalt atom receives two electrons from each carbonyl group and in addition one of the remaining 3d-electrons from each cobalt atom is shared in forming a single covalent σ-bond between the cobalt atoms. The hybridization is dsp^3 with a trigonal bipyramidal configuration. This structure does not satisfy condition (2) above and must be discarded.

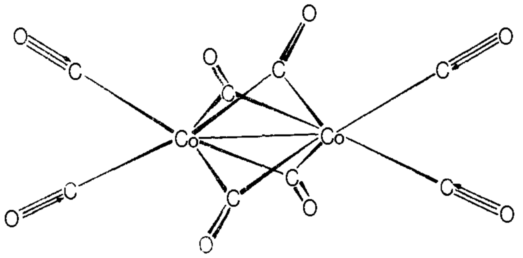
Structure II.[6]—Each cobalt atom receives two electrons from each of the terminal carbonyls and one from each of the bridged carbonyls. In order to explain the diamagnetism of the molecule it is necessary to assume that the remaining unpaired 3d electron from each atom is coupled in the formation of a single covalent bond.

This structure is most easily visualized by assuming each cobalt atom to form six bonds. Three of the bonding orbitals are planar sp^2 hybrids, two are dp hybrids perpendicular to this plane. The cobalt–cobalt bond is formed from an unhybridized d-orbital. The configuration around each cobalt atom is trigonal bipyramidal, with the two bipyramids joined at an edge in the complete molecule.

It is seen that this structure satisfies all **of** the above stated conditions.


II

Structure III.—If one assumes that the cobalt atom forms six equivalent d^2sp^3 hybrid bonding orbitals, then according to the accepted hybridization rules the most stable configuration of the bonds is an octahedral arrangement. It is obvious that such a structure would involve terrific strain if forced into the geometry required for a molecule which would satisfy the four necessary conditions above. Duffey[7] has shown that six equivalent d^2sp^3 hybrid orbitals may form stronger bonds in a trigonal prismatic configuration than in an octahedral arrangement if a little more d-character and less p-character be included in the hybridization.


III

One disadvantage to this assumption is that the presence of the two pairs of non-bonding d-electrons strongly favors an octahedral structure. However, since the geometry of the molecule would allow more efficient overlapping of the bonding orbitals in the trigonal prismatic configuration, the possibility of this structure still remains. Of course, the diamagnetism has to be explained by the formation of a cobalt–cobalt bond by coupling of the remaining unpaired 3d electrons. The configuration around each cobalt is trigonal prismatic, with the two prisms being joined at a face in the complete molecule.

Structure IV.—If one assumes that the cobalt atom forms five equivalent dsp^3 hybrid bonding orbitals, then, according to the accepted hybridization rules, a trigonal bipyramidal structure is obtained. This is essentially structure II, except that non-equivalent bonding orbitals have been assumed. According to Daudel and Bucher,[8] five equivalent dsp^3 hybrid orbitals yield a trigonal bipyramidal structure only if the d-orbital is higher in energy than the s- and p-orbitals. If the

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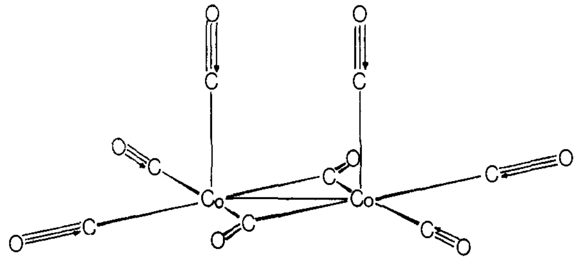
[5] Y. K. Syrkin and M. E. Dyatkina, "The Structure of Molecules," Butterworth, London, 1950, p. 365.

[6] J. S. Anderson, *Quart. Rev.*, **1**, 331 (1947).

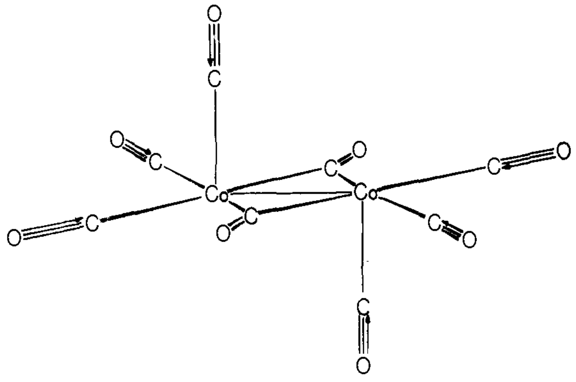
[7] G. H. Duffey, *J. Chem. Phys.*, **17**, 1328 (1949); **18**, 128 (1950).

[8] R. Daudel and A. Bucher, *J. chim. phys.*, **42**, 6 (1945).

d-orbital is lower in energy a square pyramidal configuration is the most stable. In the case of cobalt the 3d-orbital is higher than the 4s but lower than the 4p. The possibility of a square pyramidal structure must consequently be considered. This configuration would, in fact, involve less strain than either the trigonal bipyramid II or trigonal prism III structures. Assuming this configuration there are two possible structures for the complete molecule: *cis* IVa and *trans* IVb. In this case also a cobalt–cobalt bond must be assumed to account for the observed diamagnetism.



IV A



IV B

Of the five structures which have been considered four satisfy the necessary conditions. The vibrational analyses of these four structures as obtained from symmetry properties and group theory have been tabulated in Tables I–IV.

These analyses were carried further so as to obtain a qualitative picture of the normal vibrations. Briefly, the method used consists in breaking the molecule down into smaller units, by neglecting force constants between some of the atoms. The breakdown is carried far enough so that every normal mode for the unit can be depicted: the total symmetry of the molecule is retained in making these calculations, even though the symmetry of the unit may be different. The normal modes of the units are then combined into the complete molecule. In this way a rather complex molecule can be completely analyzed.

In the trigonal bipyramidal structure II, which has D_{2h} symmetry, there are 22 infrared active normal frequencies. These consist of 6 Co–C bendings, 5 Co–C stretchings, 7 C–O bendings and 4 C–O stretchings. Of the 4 C–O stretchings, three involve mainly the terminal carbonyls ($-C \equiv O$) and one involves mainly the bridged carbonyls ($>C=O$).

TABLE I

VIBRATIONS OF $Co_2(CO)_8$ (TRIGONAL BIPYRAMID, D_{2h})

Type	Activity	Skeletal vibrations	Designation	Non-skeletal vibrations	Designation
A_g	R	5	$\nu_1-\nu_5$	4	$\nu_6-\nu_9$
A_u	Ia	1	ν_{10}	1	ν_{11}
B_{1g}	R	3	$\nu_{12}-\nu_{14}$	3	$\nu_{15}-\nu_{17}$
B_{1u}	IR	3	$\nu_{18}-\nu_{20}$	3	$\nu_{21}-\nu_{23}$
B_{2g}	R	3	$\nu_{24}-\nu_{26}$	3	$\nu_{27}-\nu_{29}$
B_{2u}	IR	4	$\nu_{30}-\nu_{33}$	4	$\nu_{34}-\nu_{37}$
B_{3g}	R	1	ν_{38}	2	$\nu_{39}-\nu_{40}$
B_{3u}	IR	4	$\nu_{41}-\nu_{44}$	4	$\nu_{45}-\nu_{48}$

TABLE II

VIBRATIONS OF $Co_2(CO)_8$ (TRIGONAL PRISM, D_{2h})

Type	Activity	Skeletal vibrations	Designation	Non-skeletal vibrations	Designation
A_g	R	5	$\nu_1-\nu_5$	4	$\nu_6-\nu_9$
A_u	Ia	2	$\nu_{10}-\nu_{11}$	2	$\nu_{12}-\nu_{13}$
B_{1g}	R	3	$\nu_{14}-\nu_{16}$	3	$\nu_{17}-\nu_{19}$
B_{1u}	IR	3	$\nu_{20}-\nu_{22}$	3	$\nu_{23}-\nu_{25}$
B_{2g}	R	2	$\nu_{26}-\nu_{27}$	2	$\nu_{28}-\nu_{29}$
B_{2u}	IR	4	$\nu_{30}-\nu_{33}$	4	$\nu_{34}-\nu_{37}$
B_{3g}	R	2	$\nu_{38}-\nu_{39}$	3	$\nu_{40}-\nu_{42}$
B_{3u}	IR	3	$\nu_{43}-\nu_{45}$	3	$\nu_{46}-\nu_{48}$

TABLE III

VIBRATIONS OF $Co_2(CO)_8$ (*trans*-SQUARE PYRAMID C_{2h})

Type	Activity	Skeletal	Designation	Non-skeletal	Designation
A_g	R	7	$\nu_1-\nu_7$	6	$\nu_8-\nu_{13}$
A_u	IR	5	$\nu_{14}-\nu_{18}$	5	$\nu_{19}-\nu_{23}$
B_g	R	5	$\nu_{24}-\nu_{28}$	6	$\nu_{29}-\nu_{34}$
B_u	IR	7	$\nu_{35}-\nu_{41}$	7	$\nu_{42}-\nu_{48}$

TABLE IV

VIBRATIONS OF $Co_2(CO)_8$ (*cis*-SQUARE PYRAMID C_{2V})

Type	Activity	Skeletal	Designation	Non-skeletal	Designation
A_1	R, IR	8	$\nu_1-\nu_8$	7	$\nu_9-\nu_{15}$
A_2	R	5	$\nu_{16}-\nu_{20}$	5	$\nu_{21}-\nu_{25}$
B_1	R, IR	6	$\nu_{26}-\nu_{31}$	6	$\nu_{32}-\nu_{37}$
B_2	R, IR	5	$\nu_{38}-\nu_{42}$	6	$\nu_{43}-\nu_{48}$

In the trigonal prism structure III, which also has D_{2h} symmetry, there are twenty infrared active vibrational modes. These consist of 7 Co–C bendings, 3 Co–C stretchings, 6 C–O bendings and 4 C–O stretchings. Of the 4 C–O stretchings, two involve mainly the terminal carbonyls and two involve mainly the bridged carbonyls.

In the *cis*-square pyramid structure IVa which has C_{2V} symmetry, there are 38 infrared active fundamentals. These consist of 1 Co–Co stretching, 11 Co–C bendings, 7 Co–C stretchings, 12 C–O bendings and 7 C–O stretchings. Of the 7 C–O stretchings, five involve mainly the terminal carbonyls and two involve mainly the bridged carbonyls.

In the *trans*-square pyramid structure IVb, which has C_{2h} symmetry there are 24 infrared active fundamentals. These consist of 7 Co–C bendings, 5 Co–C stretchings, 8 C–O bendings and 4 C–O stretchings. Of the 4 C–O stretchings, three involve mainly the terminal carbonyls and one involves mainly the bridged carbonyls.

Of all the infrared active fundamentals the only ones expected to occur in the rocksalt region are the C–O stretchings. Both structures II and IVb predict the occurrence of three $C \equiv O$ stretching frequencies in the range 2000–2150 cm.$^{-1}$ and one $C{=}O$ stretching frequency in the range 1750–1850 cm.$^{-1}$. The predicted spectra for these two models agree perfectly with the observed spectrum. Structures III and IVa may be discarded because the spectra predicted from these models do not agree with the observed spectrum.

It is doubtful as to whether the infrared spectrum in the KBr and CsBr regions would help in deciding between the trigonal bipyramid and the *trans*-square pyramid, since these two structures predict very similar spectra in these regions. Furthermore, these two structures predict identical Raman spectra.

It seems then that the only basis for decision is that of precedent. The structures of $Fe(CO)_5$ ($3d,4s,4p^3$), $TaBr_5$, $TaCl_5$, $NbCl_5$ and $NbBr_5$ ($4d,5s,5p^3$) have all been determined to be trigonal bipyramidal. These examples are similar to the case in question and seem to throw some doubt upon the validity of Daudel and Bucher's argument.

At present, there seems to be only one example supporting the square pyramid argument. Jensen and Nygaard[9] have concluded from dipole moment measurements that the molecule $NiBr_3{\cdot}2Et_3P$ ($3d,4s,4p^3$) appears to have a square pyramidal structure. It should, however, be noted that the atom polarization in this case is such that their interpretation cannot be regarded as conclusive. In a strikingly similar case, the dipole moment measurements of $Fe(CO)_5$ were interpreted[10] to indicate a square pyramidal structure for the molecule. This has since been disproved by an electron diffraction study.[11] It may be concluded that the most probable structure of dicobaltoctacarbonyl is structure II, the trigonal bipyramid.[12] There has, however, been no experimental evidence which disagrees with the *trans*-square pyramid structure. The need for an X-ray diffraction study of this compound is obvious.

Nature of Bonding

It is very likely that the bridged carbonyls in this compound are similar to those in strained cyclic ketones. It has been observed by many investigators that the carbonyl frequency in cyclic ketones and lactones is a complex function of the ring strain. The frequency increases with an increase of ring strain. This is probably due to the increasing amount of s character in the bonding orbital to the oxygen as the carbonyl angle decreases from 120 to 90°. This increase in the proportion of s character results in an increase in bond strength. Thus the carbonyl frequency of cyclohexanone and aliphatic ketones is 1714 cm.$^{-1}$, of cyclopentanone 1744 cm.$^{-1}$ and cyclobutanone 1774 cm.$^{-1}$. From this observation and the experimentally determined factors for $Fe_2(CO)_9$ it is possible to approximate the carbonyl angle in $Co_2(CO)_8$. The ketone carbonyl frequency in $Fe_2(CO)_9$ has been reported[3] to be 1828 cm.$^{-1}$ and the carbonyl angle has been found[13] to be 87°. The unusually high frequency (1858 cm.$^{-1}$) of the ketone carbonyl in $Co_2(CO)_8$ indicates that the carbonyl angle is less than 87°. Assuming the same type of effect in the metal carbonyls as in the cyclic ketones, the carbonyl angle in $Co_2(CO)_8$ is approximately 80°.

If a cobalt carbon distance of $\sim$2.0 Å. is assumed then this value for the carbonyl angle yields a cobalt–cobalt distance of $\sim$2.57 Å. These distances are in good agreement with covalent radii data.

In Fig. 2 the carbon oxygen bonds in the terminal carbonyls have been depicted as triple bonds and the corresponding cobalt–carbon bonds as single bonds. It should be realized that the bonds are probably not of integral order and cannot be properly depicted by a single structure. In structure II (Fig. 2) the symmetry of the orbitals permit the formation of two strong π-bonds between the cobalt atom and the three terminal carbon atoms. Thus the maximum bond order for the cobalt–carbon bond is $1^2/_3$ and for the carbon–oxygen bond the corresponding bond order is $2^1/_3$.

As was to be expected the carbonyl frequencies observed for this compound are very close to those observed for the other iron group carbonyls. It must be concluded that the bond character is also very similar. In general, the bond lengths and vibration frequencies support the contention that the carbon–oxygen bond in the terminal carbonyls has slightly less than triple bond character and the metal–carbon bond slightly more than single bond character. The carbon–oxygen bond in the bridged carbonyl is of double bond character just as in organic ketones.

Acknowledgments.—The authors wish to thank Dr. Irving Wender for the samples used in this investigation. They also are grateful to Professors M. Kasha, D. P. Craig and I. G. Ross for their helpful discussions of the subject.

TALLAHASSEE, FLORIDA

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[9] K. A. Jensen and B. Nygaard, *Acta Chem. Scand.*, **3**, 474 (1949).

[10] E. Bergman and L. Engel, *Z. physik. Chem.*, **B13**, 232 (1931).

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

[12] NOTE ADDED IN PROOF.—Since the submission of this paper the authors have discovered another structure which agrees with the data. This structure has C_{2h} symmetry and is a modification of structure II. The two bipyramids are joined at an edge formed by the line between the end points of an equatorial and a polar axis.

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