Magnetic Susceptibility Measurements.—For the experiments involving solids each compound was carefully packed in the conventional glass tube and measured using the Gouy technique. At temperatures other than room temperature the sample tube was suspended inside an aluminum block surrounded by a glass Dewar. Heating and cooling coils in the aluminum block were actuated by a thermocouple control, and any temperature from −170 to 100° could be maintained automatically by the control system.

LOS ANGELES, CALIFORNIA

[CONTRIBUTION OF CENTRAL EXPERIMENT STATION U. S. BUREAU OF MINES]

Infrared Spectrum and Structure of Chromium Hexacarbonyl, $Cr(CO)_6$

BY S. LEONARD SHUFLER, HEINZ W. STERNBERG AND R. A. FRIEDEL

RECEIVED SEPTEMBER 30, 1955

The infrared spectrum of chromium hexacarbonyl, $Cr(CO)_6$, previously reported[1] in connection with a study of $Fe(CO)_6^{++}$, indicates only one intense C≡O stretching frequency in the vapor phase. This constitutes strong evidence for the equivalence of all C≡O bonds and a regular octahedral structure for chromium hexacarbonyl and other metal hexacarbonyls. These results provide an experimental means for detecting the presence of a metal hexacarbonyl in metal carbonyl reactions.

In the study[1] of $Fe(CO)_6^{++}$, an infrared spectrum of a metal hexacarbonyl was desired. The spectrum of $Cr(CO)_6$ was reported to indicate an octahedral structure.[1] An infrared spectrum of solid $W(CO)_6$, previously reported,[2] was inadequate due to scattering by solid particles. To avoid the uncertainty of a structural assignment from a solid state spectrum, the spectrum of $Cr(CO)_6$ has been determined in the gas phase. One sharp, strong band at 2000 cm.$^{-1}$ was observed (Fig. 1) in the C≡O stretching region, a fact which, according to group theory, supports the structure of a regular octahedron (structure I, Fig. 2). The band at 668 cm.$^{-1}$, near the location of a similar band in cobalt hydrocarbonyl,[3] is either a CO bending or a Cr–C stretching vibration.

A weak band was found at 1965 cm.$^{-1}$ at about the usual interval for metal carbonyls,[3] 35 cm.$^{-1}$, away from the fundamental on the low-frequency side. This band occurs in the spectra of many metal carbonyls and was originally labeled as a combination band.[3] But it is more likely attributable to a vibration involving C^{13},[4] the carbon isotope which occurs in nature in concentrations of about 1.1%. Intensity measurements on the 1965 cm.$^{-1}$ band for $Cr(CO)_6$ and for the corresponding band in other metal carbonyls (Table III of ref. 3) show that with one exception the intensity of this band is about 1–2% of the intensity of the nearest strong band. For cobalt hydrocarbonyl, the intensity of the band at 2010 cm.$^{-1}$ is over 4% of the intensity of the nearest strong band; Edgell has assigned this band as a fundamental.[4]

According to electron-diffraction data,[5] the most probable structure of the metal hexacarbonyls $Cr(CO)_6$, $Mo(CO)_6$ and $W(CO)_6$ is that of a regular octahedron of O_h symmetry (structure I). If a distinction could be made between polar and equatorial bonds in metal hexacarbonyls, as assumed by Sheline in the case of $W(CO)_6$,[2] the structure would be a tetragonal bipyramid of D_{4h} symmetry (structure II or III), and two infrared-active C≡O stretchings would be expected. But the geometry of a regular octahedron precludes any differentiation between polar and equatorial bonds. The fact that only one intense infrared band is observed in the 2,000 cm.$^{-1}$ region is definite evidence that all C≡O bonds in $Cr(CO)_6$ are equivalent (structure I).

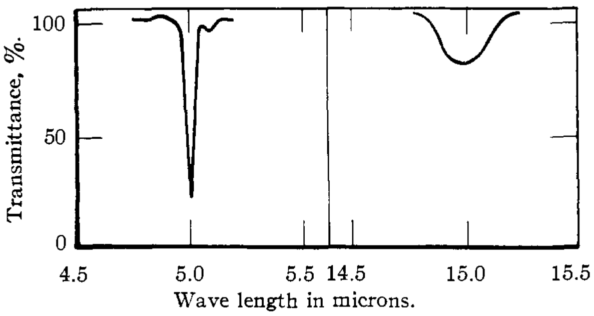

Fig. 1.—Infrared spectrum of $Cr(CO)_6$ vapor.

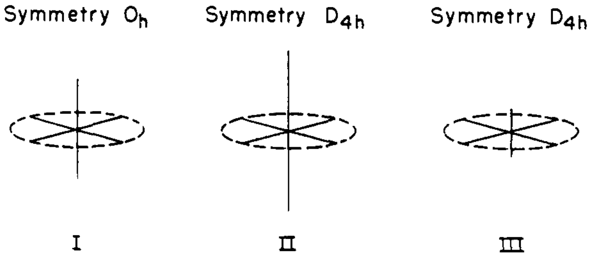

Fig. 2.—Possible structures of metal hexacarbonyls: I = regular octahedron, II and III = bipyramid.

Experimental

A few crystals of $Cr(CO)_6$ were placed in a round-bottom flask provided with a ground joint.[6] A stopcock fitted with a ground joint was attached to the flask, the flask evacuated, the stopcock closed, and the flask immersed in a steam-bath. An evacuated, 10-cm., KBr cell was then connected to the flask, the stopcock opened and the pressure allowed to equilibrate between the flask and the cell. To obtain the relative transmission of the vapor in the 2–15 mu region, an evacuated KBr cell was used as a reference. The instrument was a Perkin-Elmer Model 21, double-beam spectrophotometer.

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(1) H. W. Sternberg, R. A. Friedel, S. L. Shufler and I. Wender, THIS JOURNAL, **77**, 2675 (1955).

(2) R. K. Sheline, *ibid.*, **72**, 5761 (1950).

(3) R. A. Friedel, I. Wender, S. L. Shufler and Heinz W. Sternberg, *ibid.*, **77**, 3951 (1955).

(4) W. F. Edgell, private communication.

(5) L. O. Brockway, R. V. G. Ewens and M. W. Lister, *Trans. Faraday Soc.*, **34**, 1350 (1938).

(6) We wish to thank Drs. E. O. Brimm and M. A. Lynch, Jr., of Linde Air Products Co., Tonawanda, N. Y., for supplying a sample of $Cr(CO)_6$.

NOTE ADDED IN PROOF.—L. H. Jones (*J. Chem. Phys.*, **23**, 2448 (1955)), has given the correct assignment for the $C^{13}\equiv O$ isotope band in the spectrum of $Ni(CO)_4$. But he erroneously implies that the intensity of the C^{13} band, (2022 cm.$^{-1}$), should be 4% of the intensity of the $Ni(C^{12}O)_4$ fundamental (2060 cm.$^{-1}$). The intensity of the fundamental is lessened by about 4.4% because of the natural abundance of $Ni(C^{13}O)(C^{12}O)_3$. But this C_{3v} molecule has three infrared-active CO stretching vibrations among which the intensity is distributed. Only 1 or 2% of the absorption intensity is expected to appear at the C^{13} band position, (2022 cm.$^{-1}$).

N. J. Hawkins, *et al.* (*J. Chem. Phys.*, **23**, 2422 (1955)), recently reported a detailed infrared and Raman spectral study of $Cr(CO)_6$. They incorrectly assigned the $C^{13}\equiv O$ isotope frequency at 1965 cm.$^{-1}$ as the second overtone of the 668 cm.$^{-1}$ vibration.

BRUCETON, PENNA.

[CONTRIBUTION FROM THE COATES CHEMICAL LABORATORY OF LOUISIANA STATE UNIVERSITY]

The Stabilization of the Salicylaldehyde–Glycine Schiff Base through Metal Complex Formation[1,2]

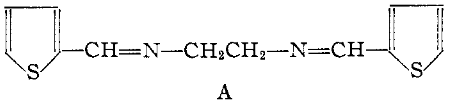
BY GUNTHER L. EICHHORN AND N. DOUGLAS MARCHAND

RECEIVED JANUARY 26, 1956

The coördination of copper(II) ion with the Schiff base produced from salicylaldehyde and glycine results in a stabilization of the double bond under conditions that would promote its rupture in the absence of the metal. The structural factors that determine whether metal coördination will stabilize or labilize Schiff bases are discussed. The composition of the complexes may be deduced from an extension of the method of continuous variation to a three-component complex system.

The participation of metal ions in many of the bond-forming and bond-breaking enzymatic processes of biochemistry makes it clear that individual chemical bonds in organic molecules are sometimes strengthened, and at other times weakened, through coördination of the molecules with metal ions. It is therefore of some interest to examine simple model systems to determine under what conditions metal complex formation affects molecules in these antithetical ways.

The Schiff bases constitute a series of molecules that appear well suited to serve in such model systems, since their carbon–nitrogen double bonds are susceptible both to hydrolytic cleavage and to coördination with metal ions. It has been demonstrated[3] that the double bond in 2-thiophenal-ethylenediamine is weakened by metal coördination;



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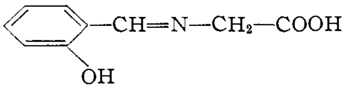
the present investigation reveals that the stability of the double bond in salicylal–glycine



B

is enhanced by complex formation. The method of investigation consisted of a comparison of the spectra of Schiff base complexes of copper(II) with those of the copper complexes of glycine and of salicylaldehyde, and of a continuous variation study of the system copper(II) : salicylaldehyde : glycine.

Experimental

Solution Conditions.—In order to effect the solution of all components of the various mixtures to be studied, a 50% water–dioxane solvent was used throughout. The upper *p*H limit, beyond which precipitation of copper(II) hydroxide occurs, proved to be *p*H 5; spectrophotometric and continuous variation studies were therefore conducted at *p*H 5 and *p*H 3. Adjustment of *p*H was accomplished by means of a Beckman Model H-2 *p*H meter through addition of dilute sodium hydroxide or nitric acid. (The Beckman readings give very nearly the correct *p*H in 50% dioxane solutions.[4]) The ionic strength of the solutions was held constant by the addition of sufficient sodium nitrate for a 1.2 *M* concentration (greater than hundredfold excess over the concentrations of the active components).

Reagents.—The 1,4-dioxane was purified according to the procedure described by Weissberger and Proskauer.[5] Eastman salicylaldehyde was distilled under nitrogen and a heart-cut taken at 196.5°; the product was stored under nitrogen to prevent the formation of oxidation products. Glycine (Merck) was dried for several hours at 110°, and reagent grade copper(II) nitrate (Merck), sodium nitrate (Merck), sodium hydroxide (Baker) and nitric acid (du Pont) were used without purification.

Spectra of the Complexes.—The solutions for the determination of absorption spectra all contained 0.0104 *M* copper(II) nitrate and the calculated quantity of glycine and salicylaldehyde to give the desired concentration ratio in each solution. Plots of the spectra at *p*H 3 and at *p*H 5 are shown in Fig. 1, and in Figs. 2–4, respectively.

Continuous Variation.—The solutions used in the two-component continuous variation experiments all contained copper(II) and glycine or salicylaldehyde at a total concentration of 0.0104 *M*; the ratio of the concentrations of metal ion and organic component, however, varied from solution to solution. The plot of *Y* (observed optical density *vs.* optical density calculated for a system in which no reaction occurs[5a]) *vs.* composition at selected wave lengths is contained in Fig. 5 for copper(II)–salicylaldehyde at *p*H 5 and for copper(II)–glycine at *p*H 3 and 5. Measurements were actually carried out for all solutions at 600, 625, 700, 750 and 768 mμ.

The solutions used for the three-component continuous variation study were made up so that the sum of the concentrations of all three components was 0.0104 *M*. Optical density measurements were made at all of the above wave lengths; *Y*-values at 625 mμ have been plotted for *p*H 3 and *p*H 5 in Figs. 6 and 7, respectively.

Results and Discussion

Spectra at *p*H 3.—Inspection of Fig. 1 reveals that the solution containing two moles of salicylal-

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[1] Presented at the 126th meeting of the American Chemical Society, New York, 1954.

[2] Taken in part from the M.S. thesis of N. Douglas Marchand, Louisiana State University, 1953.

[3] G. L. Eichhorn and J. C. Bailar, Jr., THIS JOURNAL, **75**, 2905 (1953); G. L. Eichhorn and I. M. Trachtenberg, *ibid.*, **76**, 5183 (1954).

[4] M. Calvin and K. W. Wilson, *ibid.*, **67**, 2003 (1945).

[5] A. Weissberger and E. Proskauer, "Organic Solvents," Oxford, Clarendon Press, 1935.

[5a] W. C. Vosburgh and S. R. Cooper, THIS JOURNAL, **63**, 437 (1941).