

bands to diminish in intensity and shift to longer wave length, but in acidified water-dioxane the spectrum is essentially that of the substituted aldehyde.

Since the solutions used for the spectrophotometric studies were necessarily much more dilute than those used for potentiometric titrations, it was necessary to consider the concentration effect. Solutions which were 0.02 *M* in Schiff bases I and III were prepared in 50% v./v. water-dioxane and solutions which were 0.04 *M* in I and III were prepared in 50% v./v. 0.005 *M* HClO<sub>4</sub>-dioxane. At time intervals aliquots of these solutions were removed and diluted with dioxane to give 10<sup>-5</sup> *M* solutions. The spectra of these solutions revealed that hydrolysis proceeded in the more concentrated water-dioxane solutions so that it was nearly complete within about 1 hr. Hydrolysis in the more concentrated acid-dioxane solutions was complete within the few seconds required for mixing. The hydrolysis was quenched by dilution with a large volume of dioxane.

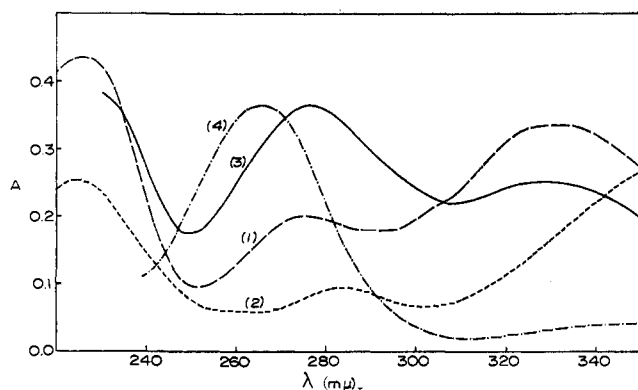


Fig. 5.—Absorption spectra of N-(2-hydroxy-3-methoxybenzylidene)-*p*-anisidine (V): (1)  $2 \times 10^{-5}$  *M* Schiff base in absolute ethanol and (2) in a 0.02 *M* solution of HCl (dissolved in gaseous HCl) in absolute ethanol; (3)  $2.14 \times 10^{-5}$  *M* Schiff base in dioxane and (4) in 50% v./v. dioxane-0.005 *M* HClO<sub>4</sub> (aqueous).

Although no attempt was made to follow the kinetics of the hydrolytic cleavage of the Schiff bases, the times recorded for the spectral changes permit crude comparisons. The hydrolysis of I or II was almost complete within 5 min. in the water-dioxane solutions of the same concentrations as used for the spectral studies of the other compounds (ca.  $2 \times 10^{-5}$  *M*). The curves shown (Fig. 1 and 2) are for solutions 2–2.5 times as

concentrated as the others in order to be able to follow the hydrolysis. The approximate half-lives for the other compounds were: III, 6 min.; IV, 10 min.; V, 9 min.; and VI, 9 min. The unsubstituted *o*-hydroxy Schiff bases hydrolyze more rapidly than those with methoxy substituents. The faster hydrolysis of the Schiff bases of *o*-aminophenol as compared to those of types B and C was apparent from the difficulty in preparing the copper chelates of type A Schiff bases.

The spectrophotometric studies followed the hydrolysis of the Schiff bases in the presence of water and acid. It is worth considering the effect of the metal ions also. Eichhorn and Marchand<sup>5</sup> reported that coordination with a metal ion stabilized the Schiff bases of salicylaldehyde types B and C toward hydrolytic cleavage, while those Schiff bases which do not involve the C=N linkage as part of the chelate ring are made more susceptible to hydrolytic cleavage by coordination. In the copper(II) complexes of Schiff bases derived from *o*-aminophenol, the C=N bond is not a part of the chelate ring. The acquisition of a formal positive charge on the nitrogen as a result of coordination or protonation probably makes the C of the C=N bond more susceptible to attack by water to bring about the hydrolytic cleavage of the C=N bond. The copper complex of *o*-aminophenol should be considerably more stable than that of the corresponding Schiff bases because of the greater basicity of the NH<sub>2</sub> group compared to the C=N group. The complexes of the Schiff bases of types B and C give a stable chelate ring only as long as the C=N bond remains unbroken. These complexes of the Schiff bases should be more stable than those of either the aldehyde or amine alone.

Although all of the Schiff bases studied cleave very rapidly in the presence of both water and acid, cleavage causes difficulty in the preparation of the copper chelates in the presence of water only for the Schiff bases of type A. Since the Schiff bases can be prepared in or recrystallized from aqueous ethanol, equilibrium must be established between the Schiff base and the aldehyde and amine. In the presence of excess amine or in the basic solution produced from partial hydrolysis in concentrated solutions, the Schiff base is fairly stable. In dilute solutions the hydrolysis is nearly complete. During potentiometric titrations the initial acidic solution should cause almost complete cleavage of the Schiff bases, but some reformation might occur as the solutions become more basic during the titrations. The interpretation of the results of such titrations would be difficult because of the complex equilibria involved.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, COLUMBIA UNIVERSITY, NEW YORK 27, N. Y.]

## The Electronic Structures of Octahedral Metal Complexes. I. Metal Hexacarbonyls and Hexacyanides

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The bonding in metal hexacarbonyls and hexacyanides is described in terms of molecular orbitals. Vapor phase electronic spectra for the metal hexacarbonyls are reported in the range 3500–1700 Å. A molecular orbital energy level scheme is presented which is able to account for the observed d-d and charge-transfer absorption bands in the d<sup>6</sup> metal complexes. The charge-transfer transitions all are assigned as metal (d) to ligand ( $\pi^*$ ).

### Introduction

Transition metal carbonyls and cyanides are among the simplest complexes in which both metal-to-ligand

and ligand-to-metal types of  $\pi$ -bonding are of importance. Thus a knowledge of the electronic energy levels for typical metal carbonyls and cyanides is very desirable.

Recently progress has been made in assigning the electronic spectra of several metal cyanide complexes: Perumareddi, Liehr, and Adamson have treated the  $d^1$ ,  $d^2$ ,  $d^8$ ,  $d^9$ , and  $d^{10}$  metal complexes<sup>1</sup>; the spectrum of  $\text{Fe}(\text{CN})_6^{3-}$  has received considerable attention<sup>2</sup>; Robin has provided a theoretical interpretation of the charge-transfer processes in Prussian blue<sup>3</sup>; an interpretation of the spectra of  $\text{M}(\text{CN})_6^{n-}$  complexes has been given<sup>4</sup>; and the d-d spectrum of the  $\text{Cr}(\text{CN})_6^{3-}$  complex is well understood.<sup>5</sup>

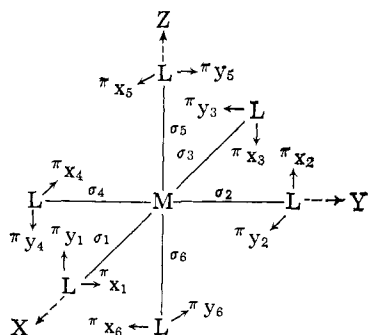


Fig. 1.—Coordinate system for the  $\sigma$ - and  $\pi$ -molecular orbitals of an  $\text{ML}_6$  complex.

One of the present authors and colleagues have dealt with the square-planar metal cyanides<sup>6</sup> and the metal pentacyanonitrosyl complexes.<sup>7-9</sup> Of the metal carbonyls, complete spectral assignments have been given only for the  $\text{Mn}(\text{CO})_5\text{X}$  type complexes.<sup>10</sup>

It is important to establish the main similarities and differences in the electronic spectra of isoelectronic metal carbonyls and cyanides and to relate these spectral comparisons to the nature of the M-CN and M-CO bonds. In this paper the electronic spectra of  $d^6$  metal carbonyls and cyanides are assigned on the basis of a derived molecular orbital energy level scheme. The differences in the energies of the single electron molecular orbitals for representative metal hexacarbonyls and hexacyanides are obtained and a general discussion of electronic structure is presented.

**Molecular Orbitals for Octahedral Metal Carbonyls and Cyanides.**—The coordinate system adopted for the case of full  $\sigma$ - and  $\pi$ -bonding in the  $O_h$  symmetry is given in Fig. 1. The metal valence orbitals are  $nd$ ,  $(n+1)s$ , and  $(n+1)p$ . The carbon 2s and 2p<sub>z</sub> orbitals will be used for  $\sigma$ -bonding; for  $\pi$ -bonding, both the ligand  $\pi$ -bonding ( $\pi^b$ ) and  $\pi$ -antibonding ( $\pi^*$ ) molecular orbitals will be combined with the  $d_\pi$  and  $p_\pi$  metal orbitals to form the  $\pi$ -molecular orbital system for the complex. The single electron molecular orbitals all are assumed to have the form

$$\psi(\text{m.o.}) = C_M\Phi(\text{M}) + C_L\Phi(\text{L}) \quad (1)$$

(1) J. R. Perumareddi, A. D. Liehr, and A. W. Adamson, *J. Am. Chem. Soc.*, **85**, 249 (1963).

(2) (a) C. S. Naiman, *J. Chem. Phys.*, **35**, 323 (1961); (b) G. Basu and R. L. Belford, *ibid.*, **37**, 1933 (1962); (c) C. S. Naiman, *ibid.*, in press; (d) the spectrum of  $\text{Cr}(\text{CN})_6\text{NO}^{2-}$  has been related to the  $d^5$  metal hexacyanide level diagram by C. S. Naiman, *ibid.*, **35**, 1503 (1961).

(3) M. B. Robin, *Inorg. Chem.*, **1**, 337 (1962).

(4) (a) G. Gliemann, *Theoret. chim. Acta*, **1**, 14 (1962); (b) E. König, *ibid.*, **1**, 23 (1962).

(5) (a) C. E. Schäffer, private communication; (b) also quoted in C. K. Jørgensen, "Absorption Spectra and Chemical Bonding in Complexes," Pergamon Press, New York, N. Y., 1962, p. 291.

(6) H. B. Gray and C. J. Ballhausen, *J. Am. Chem. Soc.*, **85**, 260 (1963).

(7) C. J. Ballhausen and H. B. Gray, *Inorg. Chem.*, **2**, 426 (1963).

(8) H. B. Gray and C. J. Ballhausen, *J. Chem. Phys.*, **36**, 1151 (1962).

(9) H. B. Gray, I. Bernal, and E. Billig, *J. Am. Chem. Soc.*, **84**, 3404 (1962).

(10) H. B. Gray, E. Billig, A. Wojcicki, and M. Farona, *Can. J. Chem.*, **41**, 1281 (1963).

where the  $C$ 's are subject to conditions of normalization and orthogonality and the  $\Phi$ 's are proper metal and ligand orbital combinations for the molecular orbital in question. These proper combinations for  $\Phi(\text{M})$  and  $\Phi(\text{L})$  are given in Table I. Group overlap integrals are given for  $\text{Cr}(\text{CO})_6$ .

The  $\sigma$ -molecular orbital system utilizes the  $nd_{x^2-y^2}$  and  $nd_{z^2}$  ( $e_g$ ),  $(n+1)s$  ( $a_{1g}$ ), and  $(n+1)p_x$ ,  $(n+1)p_y$ , and  $(n+1)p_z$  ( $t_{1u}$ ) metal orbitals with the proper linear combinations of ligand  $\sigma$ -orbitals. Thus there are formed six bonding and six antibonding  $\sigma$ -molecular orbitals.

The pure  $\pi$ -molecular orbitals are composed of the  $nd_{xy}$ ,  $nd_{xz}$ , and  $nd_{yz}$  ( $t_{2g}$ ) metal orbitals and the  $t_{2g}$  combinations of  $\pi^b$  and  $\pi^*$  ligand molecular orbitals. The instability order of the combining  $\pi$ -orbitals is always  $\pi^b(\text{L}) < nd_\pi < \pi^*(\text{L})$ . Thus there are formed three (degenerate) strongly bonding  $\pi$ -molecular orbitals mainly localized on the CN<sup>-</sup>'s or CO's; three virtually nonbonding (which may be either weakly bonding or antibonding, depending on the stabilities of  $\pi^b(\text{L})$  and  $\pi^*(\text{L})$  relative to  $nd_\pi$ ) molecular orbitals mainly localized on the metal; and three strongly antibonding molecular orbitals mainly localized on the CN<sup>-</sup>'s or CO's.

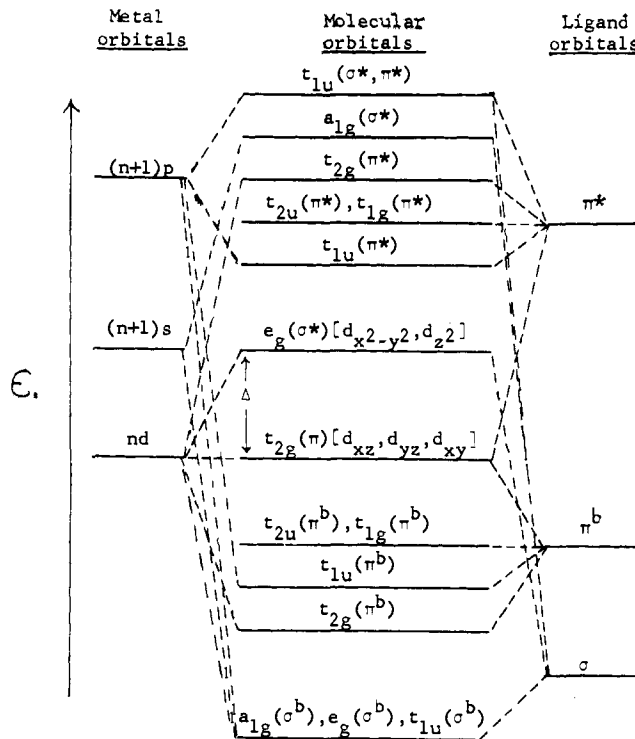


Fig. 2.—Molecular orbital energy level diagram for metal hexacyanides and hexacarbonyls.

Although the  $(n+1)p$  metal orbitals ( $t_{1u}$ ) are expected to be primarily involved in  $\sigma$ -bonding, they may interact with the  $t_{1u}$  ligand  $\pi^b$  and  $\pi^*$  orbital combinations to yield three bonding and three antibonding molecular orbitals mostly localized on the ligands and three strongly antibonding molecular orbitals, with both  $\sigma$ - (*vide supra*) and  $\pi$ -character, mainly localized on the metal. The instability order  $\pi^*(\text{L}) < (n+1)p$  is assumed.

Finally, there are  $t_{1g}$  and  $t_{2u}$   $\pi^b$  and  $\pi^*$  ligand orbital combinations which do not interact with metal orbitals. The molecular orbital energy level scheme expected for the bonding situation described above is shown in Fig. 2.

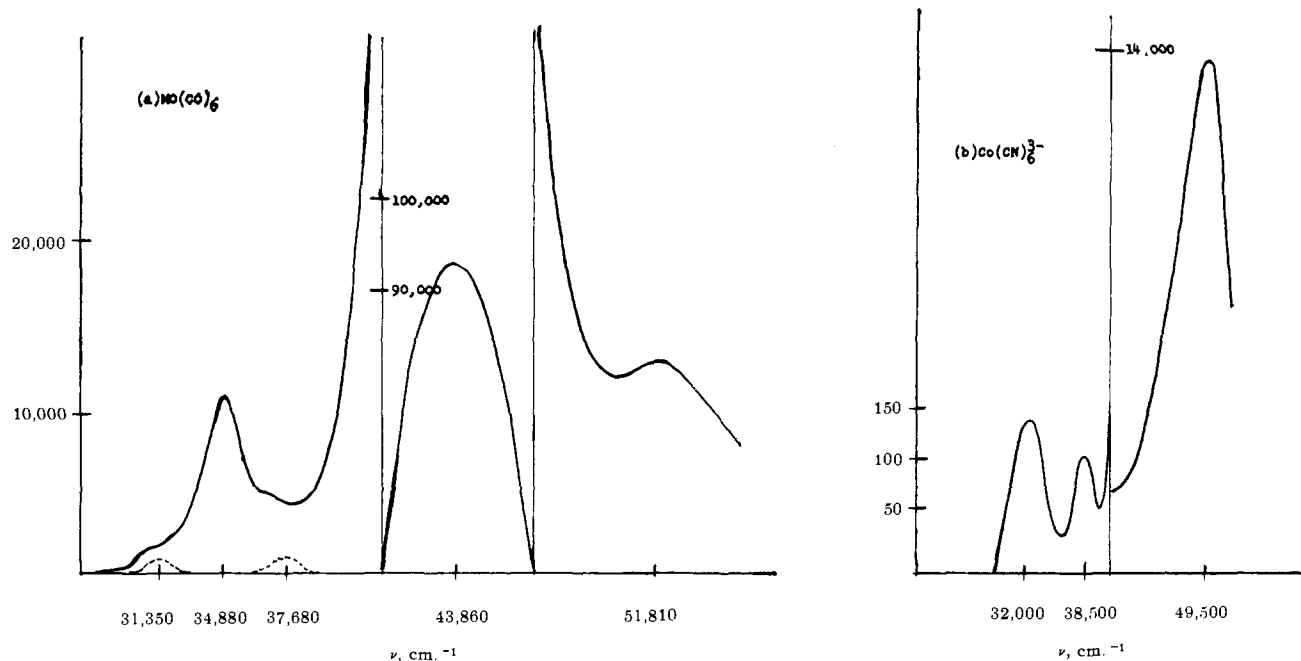


Fig. 3.—Electronic spectra of (a) Mo(CO)<sub>6</sub> (left curves) in the vapor phase and (b) Co(CN)<sub>6</sub><sup>3-</sup> (right curves) in water solution.

There will always be 36 electrons (6 from each ligand) to place in the molecular orbitals for the complex. In addition, the metal may furnish as many as 6 valence electrons for an octahedral metal carbonyl or cyanide complex. The ground state for a d<sup>6</sup> metal hexacarbonyl or hexacyanide is therefore

$$[t_{1u}(\sigma^b)]^6 [a_{1g}(\sigma^b)]^2 [e_g(\sigma^b)]^4 [t_{2g}(\pi^b)]^6 [t_{1u}(\pi^b)]^6 [t_{2u}(\pi^b)]^6 [t_{1g}(\pi^b)]^6 [t_{2g}(\pi)]^6 = {}^1A_{1g}$$

The most stable excited states for the d<sup>6</sup> complexes re-

and  $16F_2 - 115F_4$ , respectively, referred to the ground state  ${}^1A_{1g}$  as zero. Electronic absorption bands for the transitions  ${}^1A_{1g} \rightarrow {}^1T_{1g}$  and  ${}^1A_{1g} \rightarrow {}^1T_{2g}$  are expected to be weak, since these transitions are forbidden for electric dipole radiation. (2) Charge transfer from metal to ligand—the lowest energy transitions of this type are  $t_{2g}(\pi) \rightarrow t_{1u}(\pi^*)$ ,  $t_{2g}(\pi) \rightarrow t_{2u}(\pi^*)$ ,  $t_{1g}(\pi^*)$ , and  $t_{2g}(\pi) \rightarrow t_{2g}(\pi^*)$ . The  $t_{2u}(\pi^*)$  and  $t_{1g}(\pi^*)$  energies may be estimated at about  $-35,000 \text{ cm}^{-1}$  from ionization potential<sup>11</sup> and spectroscopic<sup>12</sup> data for CO and HCN. The  $t_{1u}(\pi^*)$  level should be more stable, and the  $t_{2g}(\pi^*)$

TABLE I

GROUP OVERLAP INTEGRALS FOR Cr(CO)<sub>6</sub> AND LIGAND-LIGAND INTERACTIONS FOR OCTAHEDRAL METAL COMPLEXES

Molecular orbital	Metal orbital	Ligand orbitals	$G_{ij}^a$	Ligand-ligand interaction <sup>b</sup>
$\Psi [a_{1g}(\sigma)]$	$[(n+1)s]$	$[(1/\sqrt{6})(\sigma_1 + \sigma_2 + \sigma_3 + \sigma_4 + \sigma_5 + \sigma_6)]$	0.990	..
$\Psi_1 [e_g(\sigma)]$	$[nd_{z^2}]$	$[(1/2\sqrt{3})(2\sigma_5 + 2\sigma_6 - \sigma_1 - \sigma_2 - \sigma_3 - \sigma_4)]$	.493	..
$\Psi_{11} [e_g(\sigma)]$	$[nd_{x^2-y^2}]$	$[(1/2)(\sigma_1 - \sigma_2 + \sigma_3 - \sigma_4)]$	.493	..
$\Psi_1 [t_{1u}(\sigma, \pi)]$	$[(n+1)p_x]$	$[(1/\sqrt{2})(\sigma_1 - \sigma_3)]$	.710	..
	$[(n+1)p_x]$	$[(1/2)(\pi_{y1} + \pi_{x5} - \pi_{x4} - \pi_{y6})]$	.480	+2β <sub>  </sub>
$\Psi_{11} [t_{1u}(\sigma, \pi)]$	$[(n+1)p_y]$	$[(1/\sqrt{2})(\sigma_2 - \sigma_4)]$	.710	..
	$[(n+1)p_y]$	$[(1/2)(\pi_{x1} + \pi_{y5} - \pi_{y4} - \pi_{x6})]$	.480	+2β <sub>  </sub>
$\Psi_{111} [t_{1u}(\sigma, \pi)]$	$[(n+1)p_z]$	$[(1/\sqrt{2})(\sigma_5 - \sigma_6)]$	.710	..
	$[(n+1)p_z]$	$[(1/2)(\pi_{y1} + \pi_{x5} - \pi_{x4} - \pi_{y6})]$	.480	+2β <sub>  </sub>
$\Psi_1 [t_{2g}(\pi)]$	$[nd_{xz}]$	$[(1/2)(\pi_{y1} + \pi_{x5} + \pi_{x2} + \pi_{y6})]$	.352	+2β <sub>⊥</sub>
$\Psi_{11} [t_{2g}(\pi)]$	$[nd_{yz}]$	$[(1/2)(\pi_{x2} + \pi_{y5} + \pi_{y4} + \pi_{x6})]$	.352	+2β <sub>⊥</sub>
$\Psi_{111} [t_{2g}(\pi)]$	$[nd_{xy}]$	$[(1/2)(\pi_{x1} + \pi_{y2} + \pi_{y3} + \pi_{x4})]$	.352	+2β <sub>⊥</sub>
$\psi_1 [t_{2u}(\pi)]$	..	$[(1/2)(\pi_{y2} - \pi_{x5} - \pi_{x4} + \pi_{y6})]$	..	-2β <sub>  </sub>
$\psi_{11} [t_{2u}(\pi)]$	..	$[(1/2)(\pi_{x1} - \pi_{y5} - \pi_{y4} + \pi_{x6})]$	..	-2β <sub>  </sub>
$\psi_{111} [t_{2u}(\pi)]$	..	$[(1/2)(\pi_{y1} - \pi_{x2} - \pi_{x3} + \pi_{y4})]$	..	-2β <sub>  </sub>
$\psi_1 [t_{1g}(\pi)]$	..	$[(1/2)(\pi_{y1} - \pi_{x5} + \pi_{x2} - \pi_{y6})]$	..	-2β <sub>⊥</sub>
$\psi_{11} [t_{1g}(\pi)]$	..	$[(1/2)(\pi_{x2} - \pi_{y5} + \pi_{y4} - \pi_{x6})]$	..	-2β <sub>⊥</sub>
$\psi_{111} [t_{1g}(\pi)]$	..	$[(1/2)(\pi_{x1} - \pi_{y2} + \pi_{y3} - \pi_{x4})]$	..	-2β <sub>⊥</sub>

<sup>a</sup> The group overlap integrals ( $G_{ij}$ 's) are for Cr(CO)<sub>6</sub>. The radial wave functions are: 3d and 4s for chromium from ref. 13; 2s for carbon from ref. 14; 2p for carbon from ref. 15; the 4p chromium radial function is taken to be  $\Phi(4p) = R_{sp}(1.20)$  where  $R_{sp}(1.20)$  is an STO with exponent 1.20. The Cr-C distance in Cr(CO)<sub>6</sub> is 1.92 Å, from ref. 16. The  $\sigma$ -valence orbital of CO and CN<sup>-</sup> is assumed to be an sp-hybrid. <sup>b</sup> For the  $\pi$ -molecular orbitals only, where, for example:  $\beta_{||} = \int (\pi_{y1})\mathcal{C}(\pi_{x2})d\tau$ ;  $\beta_{\perp} = \int (\pi_{y1})\mathcal{C}(\pi_{x4})d\tau$ .

sult from the following electronic transitions: (1) d-d transitions—these are the transitions that involve the molecular orbitals which are mainly composed of the central metal d-orbitals. The  $t_{2g}(\pi) \rightarrow e_g(\sigma^*)$  promotion gives spin-allowed excited states  ${}^1T_{1g}$  and  ${}^1T_{2g}$ . The Slater-Condon energies of  ${}^1T_{1g}$  and  ${}^1T_{2g}$  are  $-35F_4$

(11) F. H. Field and J. L. Franklin, "Electron Impact Phenomena," Academic Press, Inc., New York, N. Y., 1957, pp. 273 and 280.

(12) G. Herzberg, "Spectra of Diatomic Molecules," D. Van Nostrand and Co., Inc., New York, N. Y., 1950, p. 452; for HCN see K. Iguchi, *J. Chem. Phys.*, **23**, 1983 (1955).

(13) J. W. Richardson, W. C. Nieuwpoort, R. R. Powell, and W. F. Edgell, *J. Chem. Phys.*, **36**, 1057 (1962).

TABLE II

ELECTRONIC SPECTRA OF d<sup>6</sup> METAL HEXACARBONYLS AND HEXACYANIDES

Complex (sample)	$\lambda_{\text{max}}$ , Å	$\gamma_{\text{max}}$ , cm. <sup>-1</sup>	$f \times 10^3$	Assignment
Cr(CO) <sub>6</sub> (vapor)	3190	31,350	0.69	<sup>1</sup> A <sub>1g</sub> → <sup>1</sup> T <sub>1g</sub>
	2795	35,780	19.1	<sup>1</sup> A <sub>1g</sub> → <sup>1</sup> T <sub>1u</sub> <sup>(1)</sup>
	2248	44,480	145	<sup>1</sup> A <sub>1g</sub> → <sup>1</sup> T <sub>1u</sub> <sup>(2)</sup>
Mo(CO) <sub>6</sub> (vapor)	1950	51,280	2.5	t <sub>2g</sub> (π) → t <sub>2g</sub> (π*)
	3190	31,350	0.53	<sup>1</sup> A <sub>1g</sub> → <sup>1</sup> T <sub>1g</sub>
	2867	34,880	13.9	<sup>1</sup> A <sub>1g</sub> → <sup>1</sup> T <sub>1u</sub> <sup>(1)</sup>
	2654	37,680	0.41	<sup>1</sup> A <sub>1g</sub> → <sup>1</sup> T <sub>2g</sub>
	2280	43,860	178	<sup>1</sup> A <sub>1g</sub> → <sup>1</sup> T <sub>1u</sub> <sup>(2)</sup>
W(CO) <sub>6</sub> (vapor)	1930	51,810	22.4	t <sub>2g</sub> (π) → t <sub>2g</sub> (π*)
	3070	32,570	0.36	<sup>1</sup> A <sub>1g</sub> → <sup>1</sup> T <sub>1g</sub>
	2865	34,900	12.6	<sup>1</sup> A <sub>1g</sub> → <sup>1</sup> T <sub>1u</sub> <sup>(1)</sup>
	2690	37,170	0.30	<sup>1</sup> A <sub>1g</sub> → <sup>1</sup> T <sub>2g</sub>
	2240	44,640	208	<sup>1</sup> A <sub>1g</sub> → <sup>1</sup> T <sub>1u</sub> <sup>(2)</sup>
Fe(CN) <sub>6</sub> <sup>4-</sup> (aq. soln.)	1980	50,510	4.6	t <sub>2g</sub> (π) → t <sub>2g</sub> (π*)
	1900	52,630	4.0	t <sub>2g</sub> (π) → t <sub>2g</sub> (π*)
	4220	23,700	0.002	<sup>1</sup> A <sub>1g</sub> → <sup>3</sup> T <sub>1g</sub>
	3225	31,000	0.84	<sup>1</sup> A <sub>1g</sub> → <sup>1</sup> T <sub>1g</sub>
	2700	37,040	0.47	<sup>1</sup> A <sub>1g</sub> → <sup>1</sup> T <sub>2g</sub>
Ru(CN) <sub>6</sub> <sup>4-</sup> (aq. soln.) <sup>a</sup>	2180	45,870	53.5	<sup>1</sup> A <sub>1g</sub> → <sup>1</sup> T <sub>1u</sub> <sup>(1)</sup>
	2000	50,000	2.3	<sup>1</sup> A <sub>1g</sub> → <sup>1</sup> T <sub>1u</sub> <sup>(2)</sup>
	3225	31,000	...	<sup>1</sup> A <sub>1g</sub> → <sup>1</sup> T <sub>1g</sub>
	2060	48,500	85	<sup>1</sup> A <sub>1g</sub> → <sup>1</sup> T <sub>1u</sub> <sup>(1)</sup>
Os(CN) <sub>6</sub> <sup>4-</sup> (aq. soln.) <sup>a</sup>	1920	52,000	45	<sup>1</sup> A <sub>1g</sub> → <sup>1</sup> T <sub>1u</sub> <sup>(2)</sup>
	2130	47,000	110	<sup>1</sup> A <sub>1g</sub> → <sup>1</sup> T <sub>1u</sub> <sup>(1)</sup>
Co(CN) <sub>6</sub> <sup>3-</sup> (aq. soln.)	1950	51,300	95	<sup>1</sup> A <sub>1g</sub> → <sup>1</sup> T <sub>1u</sub> <sup>(2)</sup>
	3120	32,050	0.30	<sup>1</sup> A <sub>1g</sub> → <sup>1</sup> T <sub>1g</sub>
	2600	38,460	0.28	<sup>1</sup> A <sub>1g</sub> → <sup>1</sup> T <sub>2g</sub>
	2020	49,500	31.8	<sup>1</sup> A <sub>1g</sub> → <sup>1</sup> T <sub>1u</sub> <sup>(1)</sup>

<sup>a</sup> Estimated from Fig. 2 in ref. 3.

less stable than the -35,000 cm.<sup>-1</sup>. The t<sub>2g</sub>(π) orbital energy depends strongly on the metal under consideration, but is likely to be in the -70,000 to -85,000 cm.<sup>-1</sup> range. Thus the metal-to-ligand charge transfer transitions should appear in the 30,000-55,000 cm.<sup>-1</sup> region of the spectrum.

Only <sup>1</sup>A<sub>1g</sub> → <sup>1</sup>T<sub>1u</sub> transitions are allowed for d<sup>6</sup> metal hexacarbonyls and hexacyanides. Since both t<sub>2g</sub>(π) → t<sub>1u</sub>(π\*) and t<sub>2g</sub>(π) → t<sub>2u</sub>(π\*) promotions give <sup>1</sup>T<sub>1u</sub> excited states, there should be two intense charge-transfer bands of the metal-to-ligand type in the 30,000-50,000 cm.<sup>-1</sup> range: (3) Charge transfer from ligand to metal—the lowest energy allowed transition of this type is t<sub>2u</sub>(π<sup>b</sup>) → e<sub>g</sub>(π\*), <sup>1</sup>A<sub>1g</sub> → <sup>1</sup>T<sub>1u</sub>. The energy of the t<sub>2u</sub>(π<sup>b</sup>) orbital can be estimated at about -110,000 cm.<sup>-1</sup> from the ionization potentials of CO and HCN.<sup>10,17</sup> The e<sub>g</sub>(σ\*) energy is obtained from the previous estimate of the t<sub>2g</sub>(π) orbital energy and adding 35,000 cm.<sup>-1</sup> for Δ (*vide infra*). Thus the ligand-to-metal charge transfer for the d<sup>6</sup> complexes is not anticipated below 60,000 cm.<sup>-1</sup>.

**Electronic Spectra of d<sup>6</sup> Metal Hexacarbonyls and Hexacyanides. A. Metal Hexacarbonyls.**—The electronic spectrum of Cr(CO)<sub>6</sub> in the vapor phase shows two intense absorption bands at 35,780 and 44,480

(14) D. R. Hartree, "The Calculation of Atomic Structures," John Wiley and Sons, Inc., New York, N. Y., 1957, pp. 169-171.

(15) C. Zener, *Phys. Rev.*, **36**, 51 (1930).

(16) "Interatomic Distances," The Chemical Society, London, 1958, p. M188.

(17) The π<sup>b</sup>-level cannot be less stable than -110,000 cm.<sup>-1</sup> in either CO or HCN. The ionization potentials of CO and HCN are both approximately 14 e.v. The CO π<sup>b</sup>-level is very likely to be considerably more stable than -110,000 cm.<sup>-1</sup>, since in this case there is evidence<sup>18</sup> that the ionization potential refers to the removal of one of the carbon 2s electrons.

(18) H. H. Jaffé and M. Orchin, *Tetrahedron*, **10**, 212 (1960).

cm.<sup>-1</sup>, which are assigned as the allowed metal-to-ligand charge transfer transitions, <sup>1</sup>A<sub>1g</sub> → <sup>1</sup>T<sub>1u</sub><sup>(1)</sup> and <sup>1</sup>A<sub>1g</sub> → <sup>1</sup>T<sub>1u</sub><sup>(2)</sup>, respectively. In addition, shoulders indicating maxima at 31,350 and 51,280 cm.<sup>-1</sup> are in evidence. The low energy weak band is assigned as the first d-d transition, <sup>1</sup>A<sub>1g</sub> → <sup>1</sup>T<sub>1g</sub>. The weak band at 51,280 cm.<sup>-1</sup> probably results from the t<sub>2g</sub>(π) → t<sub>2g</sub>(π\*) transition.

The spectra of Mo(CO)<sub>6</sub> and W(CO)<sub>6</sub> are very similar to the spectrum of Cr(CO)<sub>6</sub>. Figure 3 shows the spectrum of Mo(CO)<sub>6</sub>. The intense bands at about 35,000 and about 43,000 cm.<sup>-1</sup> are present. Both the <sup>1</sup>A<sub>1g</sub> → <sup>1</sup>T<sub>1g</sub> and the <sup>1</sup>A<sub>1g</sub> → <sup>1</sup>T<sub>2g</sub> d-d bands apparently are resolved, the former on the low energy side, the latter on the high energy side of the first intense band. The separation of the two d-d bands is 6330 cm.<sup>-1</sup> for Mo(CO)<sub>6</sub>; it is only 4600 cm.<sup>-1</sup> for W(CO)<sub>6</sub>. The predicted difference between <sup>1</sup>T<sub>1g</sub> and <sup>1</sup>T<sub>2g</sub> is 16F<sub>2</sub> - 80F<sub>4</sub>. Thus we obtain the reasonable values F<sub>2</sub> = 10F<sub>4</sub> = 790 cm.<sup>-1</sup> for Mo(CO)<sub>6</sub> and F<sub>2</sub> = 10F<sub>4</sub> = 575 cm.<sup>-1</sup> for W(CO)<sub>6</sub>. The bands observed at higher energy than <sup>1</sup>A<sub>1g</sub> → <sup>1</sup>T<sub>1u</sub><sup>(2)</sup> are assigned to states arising from the transition t<sub>2g</sub>(π) → t<sub>2g</sub>(π\*). Complete spectral assignments for the M(CO)<sub>6</sub> complexes are summarized in Table II.

**B. Metal Hexacyanides.**—The electronic spectrum of Fe(CN)<sub>6</sub><sup>4-</sup> shows relatively weak bands at 31,000 and 37,040 cm.<sup>-1</sup>. These bands are assigned as the expected d-d transitions, <sup>1</sup>A<sub>1g</sub> → <sup>1</sup>T<sub>1g</sub> and <sup>1</sup>A<sub>1g</sub> → <sup>1</sup>T<sub>2g</sub>, respectively. There is a very weak band at 23,700 cm.<sup>-1</sup>, which is assigned as the first spin-forbidden transition, <sup>1</sup>A<sub>1g</sub> → <sup>3</sup>T<sub>1g</sub>. This assignment agrees with the -70F<sub>4</sub> Slater-Condon energy of <sup>3</sup>T<sub>1g</sub> relative to <sup>1</sup>T<sub>1g</sub>. The two charge-transfer bands are at 45,870 (<sup>1</sup>A<sub>1g</sub> → <sup>1</sup>T<sub>1u</sub><sup>(1)</sup>) and 50,000 cm.<sup>-1</sup> (<sup>1</sup>A<sub>1g</sub> → <sup>1</sup>T<sub>1u</sub><sup>(2)</sup>). The spectra of Ru(CN)<sub>6</sub><sup>4-</sup> and Os(CN)<sub>6</sub><sup>4-</sup> are similar, except the weaker bands for Os(CN)<sub>6</sub><sup>4-</sup> apparently are obscured by the more intense charge transfer.

The absorption spectrum of K<sub>3</sub>Co(CN)<sub>6</sub> in aqueous solution is shown in Fig. 3. The two d-d bands, <sup>1</sup>A<sub>1g</sub> → <sup>1</sup>T<sub>1g</sub> and <sup>1</sup>A<sub>1g</sub> → <sup>1</sup>T<sub>2g</sub>, are displayed as sharp maxima at 32,050 and 38,460 cm.<sup>-1</sup>. The first charge-transfer band is located at 49,500 cm.<sup>-1</sup> (<sup>1</sup>A<sub>1g</sub> → <sup>1</sup>T<sub>1u</sub><sup>(1)</sup>). The <sup>1</sup>A<sub>1g</sub> → <sup>1</sup>T<sub>1u</sub><sup>(2)</sup> transition should appear at about 53,000 cm.<sup>-1</sup>. However, since it is difficult to obtain high resolution solution spectra in this region, the exact position of the <sup>1</sup>A<sub>1g</sub> → <sup>1</sup>T<sub>1u</sub><sup>(2)</sup> band was not located. The spectral assignments for the M(CN)<sub>6</sub><sup>n-</sup> complexes are given in Table II.

## Discussion

The d-d transitions in most of the d<sup>6</sup> metal carbonyls and cyanides are hard to locate with certainty, since the large Δ-values mean that metal-to-ligand charge transfer may occur at about the same energy as the two bands due to the t<sub>2g</sub>(π) → e<sub>g</sub>(σ\*) transition. For the complexes in which the metal furnishes fewer than 6 valence electrons (such as the d<sup>5</sup> Fe(CN)<sub>6</sub><sup>3-</sup>), additional charge-transfer bands due to ligand-to-metal transitions further obscure the weak d-d bands.<sup>2</sup> Nevertheless, in many cases reliable values for Δ are available for M(CO)<sub>6</sub> and M(CN)<sub>6</sub><sup>n-</sup> complexes. These Δ-values are summarized in Table III.

With the exception of the d<sup>1</sup>-d<sup>3</sup> complexes, the Δ-values in Table III all are approximately 35,000 cm.<sup>-1</sup>. It is somewhat surprising to find similar Δ-values for complexes with widely varying charges on the central metal. One of the good examples for comparison purposes is the negligible change in Δ in going from Fe(CN)<sub>6</sub><sup>4-</sup> to Fe(CN)<sub>6</sub><sup>3-</sup>. Recall that in halide, ammine, and aquo metal complexes, an increase in the

TABLE III

MAGNITUDE OF THE d-d SPLITTING PARAMETER  $\Delta$  FOR DIFFERENT METAL HEXACARBONYLS AND HEXACYANIDES

Complex	$\Delta$ , cm. <sup>-1</sup>	Complex	$\Delta$ , cm. <sup>-1</sup>
Cr(CO) <sub>6</sub>	34,150 <sup>a</sup>	Fe(CN) <sub>6</sub> <sup>3-</sup>	35,000 <sup>f</sup>
Mo(CO) <sub>6</sub>	34,150 <sup>a</sup>	Co(CN) <sub>6</sub> <sup>3-</sup>	34,800 <sup>a</sup>
W(CO) <sub>6</sub>	34,570 <sup>b</sup>	Fe(CN) <sub>6</sub> <sup>4-</sup>	33,800 <sup>a</sup>
Ti(CN) <sub>6</sub> <sup>3-</sup>	22,300 <sup>c</sup>	Ru(CN) <sub>6</sub> <sup>4-</sup>	33,800 <sup>a</sup>
V(CN) <sub>6</sub> <sup>3-</sup>	23,390 <sup>c</sup>	Os(CN) <sub>6</sub> <sup>4-</sup>	>34,000
Cr(CN) <sub>6</sub> <sup>3-</sup>	26,600 <sup>d</sup>		

<sup>a</sup> For 35F<sub>4</sub> = 2800 cm.<sup>-1</sup>. <sup>b</sup> For 35F<sub>4</sub> = 2000 cm.<sup>-1</sup>. <sup>c</sup> From ref. 1. <sup>d</sup> From ref. 5. <sup>e</sup> From ref. 2a.

positive charge on the central metal ion means a substantial increase in  $\Delta$ . For example, for Fe(H<sub>2</sub>O)<sub>6</sub><sup>2+</sup>,  $\Delta = 10,400$  cm.<sup>-1</sup>; for Fe(H<sub>2</sub>O)<sub>6</sub><sup>3+</sup>,  $\Delta = 14,300$  cm.<sup>-1</sup>.<sup>19</sup> However, halide, ammonia, and water ligands do not engage the metal in metal (d<sub>π</sub>)-to-ligand (π\*) π-bonding, and since  $\Delta$  is the difference in the orbital energies of e<sub>g</sub>(σ\*) and t<sub>2g</sub>(π), the expected increase in  $\Delta$  due to an increase in σ-bonding in going from Fe<sup>2+</sup> to Fe<sup>3+</sup> (in the hexacyanides) is canceled by the accompanying decrease in  $\Delta$  due to a decrease in d<sub>π</sub> → (CN<sup>-</sup>) back donation.<sup>20</sup> This observed constancy of  $\Delta$  with a change in the charge on the central metal ion may be expected in other octahedral complexes in which there is extensive back bonding,<sup>20</sup> provided systems with approximately the same number of valence electrons are compared. Indeed, the  $\Delta$ -values for the metal hexacyanides decrease rapidly as the number of d-electrons decreases in the M<sup>3+</sup> complexes. Thus we have the  $\Delta$ -order: Co(CN)<sub>6</sub><sup>3-</sup> ≈ Fe(CN)<sub>6</sub><sup>3-</sup> >> Cr(CN)<sub>6</sub><sup>3-</sup> > V(CN)<sub>6</sub><sup>3-</sup> > Ti(CN)<sub>6</sub><sup>3-</sup>. This of course indicates that ligand (π<sup>b</sup>)-to-metal π-bonding is relatively more important in the d<sup>1</sup>-d<sup>3</sup> cases, and metal-to-ligand (π\*) π-bonding is more important in the d<sup>5</sup>-d<sup>6</sup> cases.

Maximum back bonding in the cases here under investigation occurs in the metal hexacarbonyls, since the t<sub>2g</sub>(π) level must be assumed quite stable to account for the large  $\Delta$ -values observed. It is interesting that  $\Delta$  in the M(CO)<sub>6</sub> series increases only slightly in the order Cr(CO)<sub>6</sub>, Mo(CO)<sub>6</sub>, and W(CO)<sub>6</sub>. This follows the usual pattern of  $\Delta(3d) < \Delta(4d) < \Delta(5d)$  in a consistent series of complexes, but the effect here is very small, indicating that the σ- and π-changes almost cancel in the 3d, 4d, and 5d valence orbitals in this case. The constancy of the total M-CO bond order for M = Cr, Mo, or W in an analogous series of complexes is also indicated from vibrational spectral results.<sup>21</sup>

The metal hexacarbonyls and hexacyanides all appear to exhibit the two allowed charge transfer bands predicted for metal-to-ligand (π\*) type transitions. There is considerable evidence in favor of these assignments. First of all, the band positions are in agreement with the results of a simple calculation (*vide supra*). Also, recall that for the other type of charge transfer (ligand (π<sup>b</sup>) → metal), the predicted energies are far larger than the energies observed. The most convincing evidence, however, is the comparison of band positions in the series Cr(CO)<sub>6</sub>, Fe(CN)<sub>6</sub><sup>4-</sup>, and Co(CN)<sub>6</sub><sup>3-</sup>. The first band shifts to higher energies in this series in the order: Cr(CO)<sub>6</sub> < Fe(CN)<sub>6</sub><sup>4-</sup> < Co(CN)<sub>6</sub><sup>3-</sup>. This is the order expected

(19) See ref. 5b, p. 110.

(20) In molecular orbital language, back donation (or back bonding) means considerable participation of empty ligand orbitals (usually π\*) in the occupied π-molecular orbitals mostly localized on the metal. We are fortunate to have the simple words "back donation" to describe such a state of affairs.

(21) F. A. Cotton and C. S. Kraihanzel, *J. Am. Chem. Soc.*, **84**, 4432 (1962).

for metal-to-ligand (π\*) type charge transfer, since the ionization potential of electrons in metal d<sub>π</sub>-type orbitals must increase in the order Cr<sup>0</sup> < Fe<sup>2+</sup> < Co<sup>3+</sup>. This increase in the energy of a particular charge-transfer transition on increasing the positive charge of the central metal ion is characteristic of metal-to-ligand (π\*) transitions and has been used as evidence for this same transition type in square-planar cyanide complexes. The ligand-to-metal type charge transfer, which occurs in metal halide complexes, shifts to lower energy, as expected, on increasing the positive charge of the central metal ion. This is demonstrated nicely in the PtCl<sub>4</sub><sup>2-</sup> and AuCl<sub>4</sub><sup>-</sup> complexes.

The difference in the energies of the <sup>1</sup>A<sub>1g</sub> → <sup>1</sup>T<sub>1u</sub><sup>(1)</sup> and <sup>1</sup>A<sub>1g</sub> → <sup>1</sup>T<sub>1u</sub><sup>(2)</sup> transitions is due to two factors. First, ligand-ligand interactions result in a stabilization of the t<sub>1u</sub>(π\*) molecular orbitals; this stabilization is 4β<sub>||</sub> relative to the t<sub>2u</sub>(π\*) molecular orbitals. This part of the total energy difference is probably between 1000 and 2000 cm.<sup>-1</sup> for all the M(CO)<sub>6</sub> and M(CN)<sub>6</sub><sup>n-</sup> complexes. The remainder of the difference in the <sup>1</sup>A<sub>1g</sub> → <sup>1</sup>T<sub>1u</sub><sup>(1)</sup> and <sup>1</sup>A<sub>1g</sub> → <sup>1</sup>T<sub>1u</sub><sup>(2)</sup> transition energies is due to the stabilization of the t<sub>1u</sub>(π\*) ligand orbital combination by π-interaction with the metal (n + 1)p-orbitals. Thus the magnitude of the total splitting gives an indication of the degree of involvement of the (n + 1)-p-metal orbitals in π-bonding.

An examination of Table II reveals that the splitting of the two charge-transfer bands is 3500–4300 cm.<sup>-1</sup> for the M(CN)<sub>6</sub><sup>4-</sup> complexes and 8700–9740 cm.<sup>-1</sup> for M(CO)<sub>6</sub> complexes. Thus the involvement of the (n + 1)p-metal orbitals in π-interaction increases considerably in going from M<sup>2+</sup> hexacyanides to M<sup>0</sup> hexacarbonyls. This is reasonable since the (n + 1)p-orbitals are undoubtedly more expanded for the neutral metal atoms.

The intensity of the 45,000 cm.<sup>-1</sup> band in the M(CO)<sub>6</sub> complexes is unusually large. The allowed transition is t<sub>2g</sub>(π) → t<sub>2u</sub>(π\*)(<sup>1</sup>A<sub>1g</sub> → <sup>1</sup>T<sub>1u</sub><sup>(2)</sup>), which involves a molecular orbital (t<sub>2g</sub>(π)) substantially delocalized out to the CO's and a molecular orbital (t<sub>2u</sub>(π\*)) essentially localized on the CO's. Thus a large contribution to the intensity from ligand-ligand integrals is suggested. This particular contribution to the intensity would increase with an increase in back donation and, indeed, the *f*-value of the <sup>1</sup>A<sub>1g</sub> → <sup>1</sup>T<sub>1u</sub><sup>(2)</sup> band may be related to the amount of back donation. The order of increasing *f* of the <sup>1</sup>A<sub>1g</sub> → <sup>1</sup>T<sub>1u</sub><sup>(2)</sup> band is Co(CN)<sub>6</sub><sup>3-</sup> < Fe(CN)<sub>6</sub><sup>4-</sup> < Ru(CN)<sub>6</sub><sup>4-</sup> < Os(CN)<sub>6</sub><sup>4-</sup> < Cr(CO)<sub>6</sub> < Mo(CO)<sub>6</sub> < W(CO)<sub>6</sub>. The Co(CN)<sub>6</sub><sup>3-</sup> complex is assumed to have the smallest <sup>1</sup>A<sub>1g</sub> → <sup>1</sup>T<sub>1u</sub><sup>(2)</sup> band intensity, since no maximum or shoulder separate from the <sup>1</sup>A<sub>1g</sub> → <sup>1</sup>T<sub>1u</sub><sup>(1)</sup> band could be resolved. The above order is certainly a reasonable prediction of the order of increasing back donation in these complexes. We are now investigating this matter in some detail.

## Experimental

The K<sub>3</sub>[Co(CN)<sub>6</sub>] complex was prepared as described in the literature.<sup>22</sup> A sample of Cr(CO)<sub>6</sub> was donated by the Ethyl Corporation. Samples of Mo(CO)<sub>6</sub> and W(CO)<sub>6</sub> were provided by the Climax Molybdenum Co.

Spectra in the 3500–1900 Å. region were taken with a Cary 14 spectrophotometer purged with nitrogen. The vapor phase spectra were obtained using quartz gas cells, with path lengths from 1 to 10 cm. The vapor phase spectral measurements were extended to 1700 Å. using a nitrogen-purged Perkin-Elmer Model 350 spectrophotometer.

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(22) J. H. Bigelow and J. C. Bailar, *Inorg. Syntheses*, **2**, 225 (1946).

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[CONTRIBUTION FROM THE RICHARDSON CHEMISTRY LABORATORY, TULANE UNIVERSITY, NEW ORLEANS 18, LA.]

## Complexes of Iron(II) and Some 5-Substituted Tetrazoles<sup>1</sup>

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Three microcrystalline complexes of iron(II) have been prepared using the anions of 5-trifluoromethyltetrazole, 5-nitrotetrazole, and 5-chlorotetrazole. The complexes conform to the general formula  $\text{Fe}(\text{T})_2 \cdot 2\text{H}_2\text{O}$  where T represents the respective tetrazolate anion. Infrared and Mössbauer effect studies have made it possible to propose a structure for these compounds. The Mössbauer studies seem to indicate a partial localization of the  $\pi$ -cloud between two nitrogen atoms allowing bonding to occur at the corners of a tetrahedron. Quadrupole splitting is absent which indicates the electric field gradient tensor is zero at the iron atom lattice site. This arises in a field reducible to cubic symmetry (*i.e.*, either tetrahedral or octahedral). Infrared data substantiate this finding by showing a loss of resonance character of the tetrazole ring and an increase in N=N bond character. To substantiate the bonding postulated, chemical evidence of the oxidation state of iron was utilized. A tentative structure is given along with infrared and Mössbauer data.

The complexes and properties of some 5-substituted tetrazole complexes of copper(II) have been recently reported<sup>3,4</sup> wherein the substituent was phenyl, a substituted phenyl, or an amino group. These publications dealt with complexes of tetrazole where the substituent on the tetrazole ring was an electron-rich source and could donate electrons to the delocalized  $\pi$ -cloud of the ring. These complexes were reported to be very insoluble in most solvents.

The present work was initiated to prepare the tetrazole analog of ferrocene by using tetrazoles with strongly electronegative groups on the carbon. The result was unexpected in that an iron(II) complex with tetrahedral configuration was formed. These compounds—similar to those of the copper(II) ion—are almost totally insoluble in the usual solvents.

Resonance absorption of low energy  $\gamma$ -radiation (Mössbauer effect)<sup>5,6</sup> has proved to be a powerful tool in the elucidation of molecular architecture and charge states in suitable target materials. Among the compounds of iron which have been studied using this technique are  $\text{K}_2\text{FeO}_4$ ,<sup>7</sup>  $\text{Fe}(\text{acac})_3$ ,<sup>8</sup> ferrocene<sup>9</sup> and ferrocene related compounds,<sup>10</sup> iron carbonyls<sup>11</sup> and related compounds,<sup>12</sup> alloys and intermetallic systems, and a large number of metal-organic compounds. In the present investigation, three iron(II) tetrazole compounds have been studied in an attempt to relate the observable Mössbauer parameters to the structures of these novel substances. In addition, the infrared spectra for these compounds are here reported and interpreted in terms of a suggested bonding scheme.

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(2) To whom inquiries should be addressed.

(3) N. A. Daugherty and C. H. Brubaker, Jr., *J. Am. Chem. Soc.*, **83**, 3779 (1961).

(4) C. H. Brubaker, Jr., *ibid.*, **82**, 82 (1960).

(5) For recent reviews, see "The Mössbauer Effect," H. Frauenfelder, W. A. Benjamin, Inc., New York, N. Y., 1962.

(6) (a) A. J. F. Boyle and H. E. Hall, *Rept. Progr. Phys.*, **25**, 441 (1962);

(b) R. L. Mössbauer, *Ann. Rev. Nucl. Sci.*, **12**, 123 (1962).

(7) G. K. Wertheim and R. H. Herber, *J. Chem. Phys.*, **36**, 2497 (1962).

(8) G. K. Wertheim, W. R. Kingston, and R. H. Herber, *ibid.*, **37**, 687 (1962).

(9) L. M. Epstein, *ibid.*, **36**, 2731 (1962).

(10) R. H. Herber and G. K. Wertheim, 140th National Meeting of the American Chemical Society, Chicago, Ill., Sept., 1961; to be submitted to *J. Chem. Phys.*

(11) M. Kalvius, U. Zahn, P. Kienle, and H. Eicher, *Z. Naturforschung*, **17a**, 494 (1962); R. H. Herber, W. R. Kingston, and G. K. Wertheim, *Inorg. Chem.*, **2**, 153 (1963).

(12) G. K. Wertheim and R. H. Herber, *J. Phys. Chem.*, in press.

## Experimental

The chemicals used in this investigation were reagent grade. The tetrazoles used were obtained from Dr. Ronald Henry,<sup>13</sup> whose generosity in supplying these is gratefully acknowledged.

**Analytical Methods.**—The percentage iron was determined gravimetrically by igniting the hydroxide to  $\text{Fe}_2\text{O}_3$ . The samples for analyses were decomposed by heating gently with 6 N  $\text{NH}_4\text{OH}$ , digesting the precipitated iron oxides on a steam bath for 3 hr., redissolving in 2 N HCl, adding  $\text{H}_2\text{O}_2$ , and reprecipitating with base.

The tetrazole content of the complexes was determined gravimetrically by precipitating the tetrazoles as their silver salts.<sup>14</sup> The silver salts of the tetrazoles used in this investigation must be handled with care since they detonate easily when dry.<sup>15</sup> Samples for analysis were decomposed by treating with 1 N aqueous NaOH. The hydrous iron oxides were filtered off and washed with distilled water. The filtrate and washings were combined and acidified with 0.1 N  $\text{HNO}_3$  to a pH of 6.5. A 10% excess based on a calculated value of  $\text{AgNO}_3$  was added to precipitate the tetrazole. The precipitates were dried in a vacuum oven at 65° to constant weight.

Determination of C, H, and N in the complexes was made by Alfred Bernhardt.<sup>16</sup> The waters of hydration were determined by initial loss of weight on thermal decomposition analysis.

**A. Complex with 5-Trifluoromethyltetrazole,  $\text{Fe}(\text{C}_2\text{N}_4\text{F}_3)_2 \cdot 2\text{H}_2\text{O}$ .**—To a solution prepared by diluting 2.5 ml. of 12 N HCl 1:1 with distilled water was added 1.0 g. of  $\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$ . A second solution was prepared by dissolving 1.8 g. of sodium 5-trifluoromethyltetrazole in 5.0 ml. of distilled water. The solution of the ferrous chloride was added slowly to the solution of the tetrazole and a pink microcrystalline precipitate formed which was collected on a fine grade fritted glass crucible and dried *in vacuo* over  $\text{P}_2\text{O}_5$ .

*Anal.* Calcd. for  $\text{Fe}(\text{C}_2\text{N}_4\text{F}_3)_2 \cdot 2\text{H}_2\text{O}$ : Fe, 15.3; C, 13.1; N, 30.6; H, 1.1. Found: Fe, 15.0; C, 13.3; N, 31.2; H, 1.3.

When neutral aqueous solutions of  $\text{FeSO}_4$  and  $\text{NaC}_2\text{N}_4\text{F}_3$  were mixed in a 1:2 ratio, an intensely colored gel formed which thickened to a rubbery mass. No attempt was made to analyze the gel.

**B. Complex with 5-Nitrotetrazole,  $\text{Fe}(\text{CN}_5\text{O}_2)_2 \cdot 2\text{H}_2\text{O}$ .**—To a solution of 2.5 ml. of 12 N HCl diluted 1:1 with distilled water was added 1.0 g. of  $\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$ . This solution was added slowly to one containing 2.5 g. of sodium 5-nitrotetrazole in 5.0 ml. of distilled water. A yellow microcrystalline precipitate formed which was collected on a fine grade fritted glass crucible and dried *in vacuo* over  $\text{P}_2\text{O}_5$ .

*Anal.* Calcd. for  $\text{Fe}(\text{CN}_5\text{O}_2)_2 \cdot 2\text{H}_2\text{O}$ : Fe, 17.5; C, 7.5; N, 43.8; H, 1.3. Found: Fe, 17.5; C, 6.9; N, 41.4; H, 1.8.

**C. Complex with 5-Chlorotetrazole,  $\text{Fe}(\text{CN}_4\text{Cl})_2 \cdot 2\text{H}_2\text{O}$ .**—To a solution of 2.5 ml. of 12 N HCl diluted 1:1 with distilled water was added 1.0 g. of  $\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$ . This was added slowly to one containing 1.8 g. of sodium 5-chlorotetrazole in distilled

(13) U. S. Naval Ordnance Test Station, China Lake, Calif.

(14) R. Herbst and J. Mihina, *J. Org. Chem.*, **15**, 1082 (1950).

(15) E. von Herz, U. S. Patent 2,066,954, Jan. 5, 1937.

(16) Micronalytisches Laboratorium im Max Planck Institute für Kohlenforschung, Mülheim, Germany.