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Preparation and Structures of Metal Cyanide-Lewis Acid Bridge Compounds

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Interaction of BF_3 with cyanide complexes leads to formation of a new class of compounds containing cyanide bridges between the transition metal and BF_3 (e.g., $-\text{Ni}-\text{C}\equiv\text{N}-\text{BF}_3$). Representative compounds include

$\text{K}_2\text{Ni}(\text{CN})_4 \cdot 4\text{BF}_3$, $\text{K}_4\text{Fe}(\text{CN})_6 \cdot 6\text{BF}_3$, $\text{K}_4\text{Mo}(\text{CN})_8 \cdot 8\text{BF}_3$, and $\text{Fe}(\text{phen})_2(\text{CN})_2 \cdot 2\text{BF}_3$ (phen = 1,10-phenanthroline). A similar BH_3 adduct was also prepared— $\text{Fe}(\text{phen})_2(\text{CN})_2 \cdot 2\text{BH}_3$. The bridge structure of these compounds is supported by chemical evidence and infrared spectra. This structure was further corroborated by magnetic measurements and electronic spectra which indicate retention of metal-carbon bonding. Consideration of d-d-transitions and stability of bridge adducts leads to the conclusion that, where these phenomena are concerned, the cyanide group does not "transmit" large inductive effects. By contrast, charge transfer spectra of $\text{Fe}(\text{phen})_2(\text{CN})_2$ are greatly affected by Lewis acid addition.

Introduction

A variety of chemical and physical evidence indicates that simple transition metal cyanide complexes such as potassium ferrocyanide involve metal-carbon bonds ($-\text{Fe}-\text{C}\equiv\text{N}$).¹ In addition to these simple complexes many compounds are known in which both ends of $\text{C}\equiv\text{N}^-$ are coordinated to metal atoms.^{2,3} Analogy with the latter class of compounds and with nitrile- BF_3 adducts, such as $\text{CH}_3-\text{C}\equiv\text{N}-\text{BF}_3$, prompted this study of the Lewis basicity of cyanide complexes.

Initial experiments were carried out with $\text{K}_2\text{Ni}(\text{CN})_4$ and BF_3 .⁴ The investigation was extended to include BF_3 addition compounds of $\text{K}_4\text{Fe}(\text{CN})_6$ and $\text{K}_4\text{Mo}(\text{CN})_8$. These particular compounds were chosen for study because their variety in coordination number and stereochemistry and their range of oxidation states provided a test of the generality of bridge adduct formation. Furthermore, they afforded systems in which the lack of CN^- rearrangement upon addition of BF_3 could be demonstrated by magnetic measurements (in the case of $\text{K}_4\text{Fe}(\text{CN})_6$) and visible spectral measurements (particularly in the case of $\text{K}_4\text{Mo}(\text{CN})_8$).

Addition of BF_3 to the complex cyanides was slow. This observation was originally attributed to the high lattice energies of the complexes. Therefore, interaction of Lewis acids with uncharged complexes, dicyanoethylenediaminepalladium(II) and dicyano-bis-1,10-phenanthrolineiron(II), also was investigated.

Experimental

Manipulation of BF_3 and B_2H_6 as well as dehydration of the cyanide complexes was performed on a preparative high vacuum line,⁵ and solid bridge adducts were handled in a nitrogen-filled dry-box. Reaction of BF_3 with stopcock grease was avoided by the use of Kel-F 90.⁶ Prolonged reactions were carried out in sealed tubes or grease-free O-ring systems. Design of these reaction vessels was such that stoichiometry of reaction could be followed by P, V, T measurement of initial and unused BF_3 and also by weight gain of the solid. The agreement between these two methods was good.

Boron trifluoride was Matheson 99% pure material which was further purified through formation and subsequent decomposition of the benzonitrile adduct (vapor pressure at -111.6° , 301 mm.).⁷ Diborane was prepared by the reaction of KBH_4 with cold concentrated sulfuric acid.⁸ After several fractionations

(1) See for example, N. A. Curry and W. A. Ranciman, *Acta Cryst.*, **12**, 674 (1959); T. Moeller, "Inorganic Chemistry," John Wiley and Sons, Inc., New York, N. Y., 1952, p. 719.

(2) D. A. Dows, A. Haim and W. K. Wilmarth, *J. Inorg. Nucl. Chem.*, **21**, 33 (1961).

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

(4) D. F. Shriver, *J. Am. Chem. Soc.*, **84**, 4610 (1962).

(5) R. T. Sanderson, "Vacuum Manipulation of Volatile Compounds," John Wiley and Sons, Inc., New York, N. Y., 1948.

(6) A chloro-fluoro-carbon grease produced by Minnesota Mining and Manufacturing Co.

(7) H. C. Brown and R. B. Johansson, *J. Am. Chem. Soc.*, **72**, 2937 (1950).

(8) H. G. Weiss and I. Shapiro, *ibid.*, **81**, 6167 (1959); W. Jolly, "Synthetic Inorganic Chemistry," Prentice-Hall, Inc., Englewood Cliffs, N. J., 1960, p. 159.

from a -150° bath, the infrared spectrum and vapor pressure (225.8 mm. at -111.6°) agreed with literature values.^{9,10}

Cyanide complexes were prepared by published methods and dehydrated by prolonged heating under high vacuum ($<10^{-4}$ mm.). $\text{K}_2\text{Ni}(\text{CN})_4$ ¹¹ was recrystallized five times from water as a hydrate and subsequently dehydrated. *Anal. Calcd.*: C, 19.94; H, 0.00; N, 23.25. *Found*: C, 19.97; H, 0.00; N, 23.56. $\text{K}_4\text{Mo}(\text{CN})_8$ ¹² was recrystallized three times from water as the hydrate and dehydrated under vacuum at 50° . *Anal. Calcd.*: C, 20.87; H, 0.00; N, 24.33. *Found*: C, 20.62; H, 0.00; N, 24.05. Reagent grade $\text{K}_4\text{Fe}(\text{CN})_6$ was recrystallized from water and dehydrated under vacuum in the dark. $\text{Fe}(\text{CN})_2(\text{phen})_2$ ¹³ was recrystallized from sulfuric acid. *Anal. Calcd.*: N, 16.67. *Found*: N, 16.68. Reproducible C and H analyses could not be obtained on this complex but nitrogen analyses, which were reproducible, and spectra indicated a pure compound. $\text{Pd}(\text{CN})_2(\text{en})_2$ (en = ethylenediamine) was recrystallized from water. The structure and analysis of this material will be reported elsewhere.¹⁴

Infrared spectra were obtained from mulls of the various compounds in Fluorolube and Nujol using a Baird AB-2 and a Beckman IR 5. Both of these instruments were equipped with sodium chloride prisms and wave length calibration was performed using either a polystyrene film or indene. The CN stretching region was investigated with a Perkin-Elmer 112 equipped with a CaF_2 prism. This instrument was calibrated in the 4.5 to 4.8 μ region using carbon monoxide.

Due to moisture sensitivity of the bridge adducts, most electronic spectra were taken on solids using mull reflectance and mull transmittance. The former method is a simple variant of standard reflectance techniques. A thick opaque mull of the complex was prepared in a dry-box using a minimum amount of mineral oil and was sandwiched between quartz windows. Reflectance from the sample was compared with that of a similar magnesium carbonate mull using a Beckman DU equipped with a standard reflectance attachment. The mull method was advantageous from these standpoints: (1) Exposure of the moisture-sensitive compounds to the atmosphere was avoided. (2) Improvement in reproducibility was obtained since the sample did not shift around. (3) An increase in reflectance was obtained.

The method was checked with praseodymium chloride heptahydrate and found to be comparable with the standard reflectance technique in regard to resolution and position of reflectance minima.¹⁵

Mull transmittance¹⁶ was particularly useful in the 450 to 300 $m\mu$ region which was inaccessible with our reflectance apparatus. Again mulls were prepared in a dry-box and sandwiched between quartz plates, and spectra were obtained on a Beckman DK2 using oil-soaked filter paper as a scattering agent in both reference and sample beams. This method was neither as sensitive or reproducible as the reflectance technique. Wave length calibration of the spectrophotometer was checked with didymium glass.

Magnetic measurements were performed at room temperature. To minimize errors due to the large and somewhat uncertain diamagnetic corrections, $\text{K}_4\text{Fe}(\text{CN})_6$ was used as a standard for

(9) W. J. Lehman, C. O. Wilson, J. F. Ditter and I. Shapiro, *Advances in Chemistry Series No. 32*, American Chemical Society, Washington, D. C., 1961, p. 139.

(10) H. E. Wirth and E. D. Palmer, *J. Phys. Chem.*, **60**, 911 (1956).

(11) W. C. Fernelius and J. J. Burbage, *Inorg. Syntheses*, **2**, 227 (1946).

(12) N. H. Furman and C. O. Miller, *ibid.*, **3**, 160 (1950).

(13) A. A. Schilt, *J. Am. Chem. Soc.*, **82**, 3000 (1960).

(14) D. F. Shriver, P. Smith and R. Christian, to be submitted.

(15) The author is indebted to Mr. Allen Luntz for performing this check.

(16) F. A. Cotton, D. M. L. Goodgame, M. Goodgame and A. Sacco, *J. Am. Chem. Soc.*, **83**, 4157 (1961).

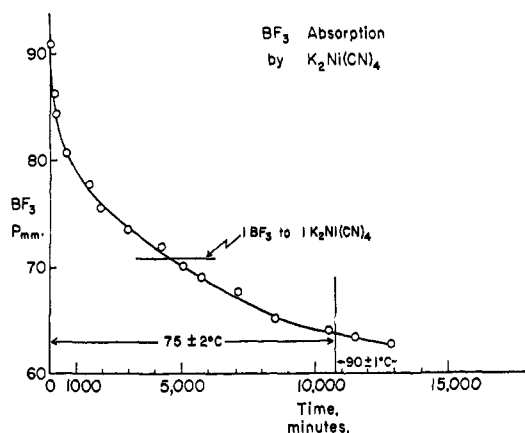
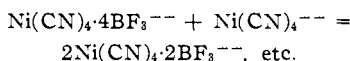


Fig. 1.—BF₃ absorption by K₂Ni(CN)₄.

comparison with K₄Fe(CN)₆·6BF₃ and K₂Ni(CN)₄ was used as a standard for K₂Ni(CN)₄·BF₃. In both systems, addition of BF₃ resulted in a diamagnetic contribution to the molar susceptibility which was accountable in terms of the diamagnetism of BF₃.¹⁷

Results and Discussion

Preparation.—Anhydrous K₂Ni(CN)₄ absorbs BF₃ at 85° and less than 300 mm. to form a 1:1 adduct after about three hours reaction time, but the composition appears to be a consequence of the particular conditions. Figure 1 shows that there is no definite break in the absorption of BF₃ at 1:1 stoichiometry. Apparently, rate of formation of the bridge adduct is limited by diffusion of BF₃ through the solid. Infrared spectra of an approximately 1:1 adduct display this feature since the freshly prepared material yields two broadened CN stretch bands at 2127 and 2235 cm.⁻¹. Upon warming the complex to about 80° for several weeks, a definite shoulder appeared on each of the two bands (at *ca.* 2295 cm.⁻¹ on the high frequency band and *ca.* 2075 cm.⁻¹ on the lower frequency band). The interpretation is that BF₃ first coordinates Ni(CN)₄⁻² ions close to the surface. Thus, the initial product is composed primarily of Ni(CN)₄·4BF₃⁻² on the exterior of each particle and Ni(CN)₄⁻² anions on the interior. These ions have high symmetry and each should display one degenerate band. Prolonged warming allows BF₃ diffusion to occur



The resulting products are of lower symmetry and accordingly a splitting of CN stretch frequencies results. When K₂Ni(CN)₄ and BF₃ were allowed to stand in a sealed tube at room temperature for about two months the product was K₂Ni(CN)₄·4BF₃. In a typical reaction, 0.611 millimole of K₂Ni(CN)₄ and 3.310 millimoles of BF₃ were sealed in a Pyrex glass tube equipped with a break seal, which was allowed to stand at room temperature for seven weeks. The ratio of BF₃ absorbed to original K₂Ni(CN)₄ was 4.01 as determined by *P, V, T* measurement of BF₃ and 3.97 as determined by weight gain. No impurities were detected in an infrared spectrum of the recovered BF₃.

Procedures similar to those outlined above were employed in the synthesis of the other bridge adducts. Small scale high pressure reactions were generally carried out in sealed tubes and large scale low pressure reactions in a grease-free demountable apparatus. This apparatus consisted of a one-liter bulb connected to the vacuum line with an O-ring needle valve stopcock. The solid complex was contained in a 15-mm.

(17) Magnetic susceptibilities of B⁻² = -7 × 10⁻⁶ and F⁻ = -6.3 × 10⁻⁶ were taken from P. W. Selwood, "Magnetochemistry," Interscience Publishers, Inc., New York, N. Y., 1956, p. 91ff.

diameter tube attached to the bulb by means of an O-joint. Reaction conditions and results of some representative syntheses are summarized in Table I. Most of the boron trifluoride addition compounds appeared to absorb slightly more than the stoichiometric quantity of BF₃, but the small additional amount of BF₃ was easily removed under vacuum. Resulting stoichiometric compounds did not appear to evolve BF₃ under prolonged exposure to high vacuum. For comparison with the bridge adducts, interaction of BF₃ and KCN was investigated.

TABLE I
CONDITIONS AND STOICHIOMETRIES OF FORMATION

Original cyanide complex	Conditions for synthesis ^a	Ratio moles BX ₃ absorbed to moles original complex	
		By wt. gain	By <i>PVT</i> meas.
K ₂ Ni(CN) ₄	BF ₃ <i>P</i> > 1 atm., room temp. 7 wk.	3.97	4.01
K ₄ Fe(CN) ₆	BF ₃ <i>P</i> > 1 atm., room temp. 3 wk., <i>ca.</i> 80° 3 wk.	6.06	6.01
K ₄ Fe(CN) ₆	BF ₃ <i>P</i> < 1 atm., ^b 75° 10 wk.	5.97	6.00
K ₄ Mo(CN) ₆	BF ₃ <i>P</i> > 1 atm., room temp. 3 wk., 45° 1 wk.	..	7.98
K ₄ Mo(CN) ₆	BF ₃ <i>P</i> > 1 atm., 45° 4 wk.	7.98	8.08
Fe(phen) ₂ (CN) ₂	BF ₃ <i>P</i> < 1 atm., ^c 0° init., <i>ca.</i> 40° for 1 hr.	1.98	2.03
Fe(phen) ₂ (CN) ₂	BF ₃ <i>P</i> < 1 atm., ^c 1 day room temp.	..	1.97
Fe(phen) ₂ (CN) ₂	B ₂ H ₆ <i>P</i> < 1 atm., ^c 5 to 9 days room temp.	..	1.97 to 2.06 ^d

^a Reactions conducted at greater than 1 atmosphere pressure were performed in sealed Pyrex reaction tubes. ^b Conducted in the grease-free O-joint apparatus using *ca.* 6 g. of K₄Fe(CN)₆. ^c All reactions of Fe(phen)₂(CN)₂ were conducted in a tube directly on the vacuum line. ^d This reaction was complicated by decomposition of B₂H₆, as shown by the presence of slight amounts of H₂. However, a definite break in disappearance of B₂H₆ was observed at the 2:1 ratio.

The System KCN-BF₃.—Reagent grade KCN and a large excess of BF₃ were sealed in a reaction tube and later opened after standing at room temperature. In two such experiments a simple stoichiometric ratio was not obtained (ratios of moles BF₃ to moles KCN of 0.14 and 0.43 were obtained). The product of this reaction was brown-yellow and displayed a featureless rise in absorption above 400 mμ. Similarly, KCN and BF₃ in the presence of diethyl ether produced an initially colorless, soluble product which turned to a brown tar as the solvent was slowly removed under vacuum.

The stoichiometries presented in Table I establish the following new compounds: K₂Ni(CN)₄·4BF₃, K₄Fe(CN)₆·6BF₃, K₄Mo(CN)₆·8BF₃, Fe(phen)₂(CN)₂·2BF₃ and Fe(phen)₂(CN)₂·2BH₃. It is noteworthy that in all of these cases the parent cyanide was initially prepared as a hydrate and then dehydrated prior to reaction with BF₃. The process of dehydration appears to leave the complex in a reactive form for subsequent absorption of BF₃. Addition of BF₃ to compounds which crystallize without water of hydration (K₃Fe(CN)₆, K₃Cr(CN)₆ and Pd en(CN)₂) was quite sluggish and was never brought to completion.

The BF₃ bridge adducts were all highly moisture-sensitive and except for Fe(phen)₂(CN)₂·2BF₃ they were insoluble or reactive with common solvents. When K₂Ni(CN)₄·BF₃ was treated with water, nickel cyanide was identified as a hydrolysis product by infrared spectra and analysis. Calcd. for Ni(CN)₂·4H₂O: C, 13.14; H, 4.40; N, 15.32. Found: C, 13.08; H, 3.96; N, 15.55.

Structures.—While the stoichiometry of formation is highly suggestive of metal—C≡N—BF₃ bridge structures other possibilities exist. One is the abstraction of CN⁻ by BF₃; another is a simple flip of the CN⁻ giving rise to metal-nitrogen and carbon-boron bonds. A

less plausible reaction, in view of the stoichiometry, is a $CN^- - F^-$ metathesis. As outlined below, a variety of physical evidence indicates the correct structure involves metal $-C\equiv N-BF_3$ linkages.

Infrared spectra in the $C\equiv N$ stretch region are interpretable in terms of the bridge structure. As may be seen from Table II, addition of BF_3 gives rise to new $C\equiv N$ stretch frequencies which are higher than those of the respective parent compounds. Nitrile-boron halide complexes and transition metal-cyanide bridged complexes also display higher $C\equiv N$ stretching frequencies than simple nitriles or simple metal cyanide complexes.^{2,18} By analogy, the increase in $C\equiv N$ stretching frequency found here is evidence for $C\equiv N$ bridges.¹⁹

TABLE II
INFRARED SPECTRA IN THE $C\equiv N$ STRETCH REGION

Compound	Absorption frequencies (cm. ⁻¹) and relative intensities ^a
$K_2Ni(CN)_4$	2130(s) ^b
$K_2Ni(CN)_4 \cdot 4BF_3$	2245(s) ^b
$K_4Fe(CN)_6$	2047(s) ^c
$K_4Fe(CN)_6 \cdot 6BF_3$	Broad ca. 2155(s) ^b
$K_4Mo(CN)_8 \cdot 3H_2O$	2136(m), 2126(s), 2123(s), 2100(vs)
$K_4Mo(CN)_8 \cdot 8BF_3$	Broad ca. 2235(s) ^b
$Fe(phen)_2(CN)_2$	2079(s), 2067(ms)
$Fe(phen)_2(CN)_2 \cdot 2BF_3$	2173(ms), 2153(s)
$Fe(phen)_2(CN)_2 \cdot 2BH_3$	ca. 2165(ms), 2154(s)

s = strong, m = medium, v = very. ^a Estimated accuracies are ± 3 cm.⁻¹ for spectra recorded on the CaF_2 prism instrument and ± 9 cm.⁻¹ for spectra obtained on the $NaCl$ prism instruments. ^b No definite structure could be found in this band when a CaF_2 prism instrument was used. The value recorded here was obtained on a $NaCl$ prism instrument. ^c Ref. 2.

The effect of BF_3 addition on the infrared stretching region of $K_2Ni(CN)_4$ is illustrated by the following observations. Planar tetracyanonickelate displays one infrared absorption at 2130 cm.⁻¹. Addition of one BF_3 per tetracyanonickelate leads to an additional higher frequency absorption at 2235 cm.⁻¹ and finally $K_2Ni(CN)_4 \cdot 4BF_3$ has a single $C\equiv N$ stretch in the higher frequency region (2250 cm.⁻¹). If the local C_{3v} symmetry of coordinated BF_3 is ignored,²⁰ this single absorption peak is consistent with, but does not prove, a square planar array of cyanides coordinated to nickel.

A similar situation occurs for the octahedral $Fe(CN)_6^{-4}$ ion where selection rules lead to one infrared active $C\equiv N$ stretching fundamental for the parent and hexaboron trifluoride adduct. As may be seen in Table II, only one $C\equiv N$ stretch is observed for $K_4Fe(CN)_6 \cdot 6BF_3$. However, this band is broad for both the parent complex and the BF_3 adduct.

Perhaps more informative are the infrared spectra of less symmetrical bridge adducts. Dicyano-bis-1,10-phenanthrolineiron(II) displays two bands in the $C\equiv N$ stretch region indicating a *cis* configuration.²¹ Upon addition of BF_3 , the two bands appear at higher frequencies (Table II); thus the *cis* configuration probably remains intact upon bridge formation. Similarly, addition of B_2H_6 to $Fe(phen)_2(CN)_2$ results in two new $C\equiv N$ stretching frequencies (Table II).

(18) H. J. Coerver and C. Curran, *J. Am. Chem. Soc.*, **80**, 3522 (1958).

(19) The increase in stretching frequency upon bridge formation may be rationalized in terms of a simple vibrational model (ref. 2) or in terms of electronic effects (e.g., G. W. Chantry and R. A. Plane, *J. Chem. Phys.*, **35**, 1027 (1961); also W. Gerrard, M. F. Lappert, H. Pyzora and J. W. Wallis, *J. Chem. Soc.*, 2182 (1960)).

(20) Neglect of the low symmetry of coordinated BF_3 is reasonable and is made throughout the discussion. Another prominent assumption is neglect of site symmetry of the complex ion in its crystal lattice. This assumption is reasonable in view of the very small crystal field effects observed by L. H. Jones, *J. Chem. Phys.*, **36**, 1209 (1962), for $K_3Co(CN)_6$.

(21) N. K. Hammer and L. E. Orgel, *Nature*, **190**, 439 (1961).

$K_4Mo(CN)_8$ displays four infrared active $C\equiv N$ stretch frequencies, a result consistent with the near D_{2d} symmetry of the ion.²² However, the BF_3 adduct displays a broad asymmetric $C\equiv N$ stretch. In view of the asymmetry of this band and the moderate intensity of three of the $C\equiv N$ stretch absorptions in the parent $Mo(CN)_8^{-4}$ a firm case cannot be made for the $C\equiv N$ configuration in $Mo(CN)_8 \cdot 8BF_3^{-4}$.

Cyanide ($C\equiv N$) stretch frequencies were the most useful, for structural arguments, because of the certainty of their assignment, but lower frequency infrared bands were consistent with the proposed bridge structure. Among the lower frequency absorptions a band was always observed at ca. 1,100 cm.⁻¹ for BF_3 adducts. This band is assigned to the asymmetric BF_3 stretch, in keeping with the spectra of BF_4^- and amine- BF_3 adducts.^{23,24} Correspondingly, $Fe(phen)_2(CN)_2 \cdot 2BH_3$ displays three bands around 2,310 cm.⁻¹ which agrees with the previously assigned region for the BH stretching frequencies of coordinated BH_3 .²⁵ Clearly, the infrared data indicate the presence of CN bridges and in most cases lack of gross new geometries in fully substituted bridge adducts. However, these data do not rule out the possibility of metal-nitrogen bonding in the bridge complex. For evidence concerning this possibility, electronic spectra and magnetic properties were investigated.

The observed diamagnetism of $K_4Fe(CN)_6 \cdot 6BF_3$ offers evidence for metal-carbon bonding in this adduct. The basis for this conclusion is that cyanide (C-coordinated) and relatively few other ligands lie high enough on the spectrochemical series to cause spin pairing in Fe(II) complexes. In particular, fluoride ion (which might arise from $CN^- - F^-$ metathesis) is quite low in the series and leads to spin-free iron(II) complexes. As to the possibility of Fe-N bonding, the data of Robin indicate that Fe(III) in the Prussian blues is coordinated to the nitrogen end of cyanide but exists in a spin-free state.³ While this observation proves that the nitrogen end of cyanide lies lower on the spectrochemical series than the carbon end, it does not prove that nitrogen-coordinated CN^- would leave Fe(II) spin free (as a consequence of differences in d-electron repulsion it is easier to spin pair Fe(II) than Fe(III)). Somewhat more useful model systems are $-NCS^-$ and $-NCO^-$. Nitrogen-coordinated thiocyanate lies below ligands such as ammonia which are not capable of spin pairing divalent iron.^{26,27} Similarly, $-NCO^-$ should not bring about spin pairing of Fe^{+2} , since data of Cotton and Goodgame indicate this ligand is slightly below $-NCS^-$ on the spectrochemical series.²⁸

A sample corresponding to the composition $K_2Ni(CN)_4 \cdot BF_3$ was found to be diamagnetic. From this observation, $K_2Ni(CN)_4 \cdot BF_3$, like the parent complex $K_2Ni(CN)_4$, appears to involve square planar coordination of the nickel ion.

Visible and near-ultraviolet spectra ($>305 m\mu$) of $K_2Ni(CN)_4 \cdot 4BF_3$, $K_4Fe(CN)_6 \cdot 6BF_3$, $K_4Mo(CN)_8 \cdot 8BF_3$

(22) J. L. Hoard and H. H. Nordsieck, *J. Am. Chem. Soc.*, **61**, 2853 (1939).

(23) G. L. Cote and H. W. Thompson, *Proc. Roy. Soc. (London)*, **A210**, 217 (1951).

(24) A. R. Katritzky, *J. Chem. Soc.*, 2049 (1959).

(25) B. Rice, R. J. Galiano and W. J. Lehman, *J. Phys. Chem.*, **61**, 1222 (1957); also R. C. Taylor and C. Cluff, WADD Technical Report 60-262, Univ. Michigan, April, 1960, p. 91ff. Three bands are observed rather than the expected two B-H stretch frequencies because of Fermi resonance with a BH_2 deformation overtone.

(26) C. K. Jørgensen, "Absorption Spectra and Chemical Bonding in Complexes," Addison-Wesley, Reading, Mass., 1962, p. 109.

(27) W. Klem, H. Jacobi and W. Tilk, *Z. anorg. allgem. Chem.*, **201**, 1 (1931).

(28) F. A. Cotton and M. Goodgame, *J. Am. Chem. Soc.*, **83**, 1777 (1961), find $\Delta = 4150$ cm.⁻¹ for $Co(NCO)_4^{-2}$ whereas Jørgensen (ref. 26, p. 111) lists $\Delta = 4900$ cm.⁻¹ for $Co(NCS)_4^{-2}$.

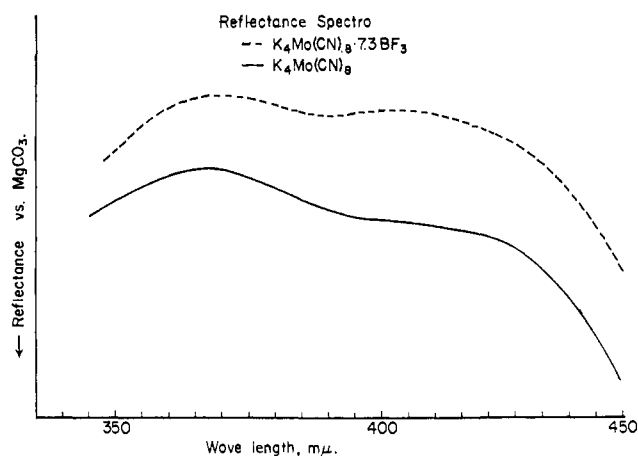


Fig. 2.—Reflectance spectra of $K_4Mo(CN)_8 \cdot 7.3BF_3$, ---, and $K_4Mo(CN)_8$, —.

and intermediate bridge adducts show no gross shifts in absorption bands relative to the parent complexes. The case of $K_4Mo(CN)_8BF_3$ addition compounds is particularly revealing. The parent octacyanomolybdate(IV) ion displays two fairly intense absorption bands in the visible spectrum. These have been assigned to d-d-transitions.²⁹ As may be seen in Fig. 2, addition of BF_3 has a negligible effect on absorption maxima; consequently, bridge addition does not destroy Mo-C bonding or greatly change the geometry of the first coordination sphere of Mo. In the case of $K_4Fe(CN)_6$ an absorption maximum was observed at $30,700\text{ cm}^{-1}$ in a mull transmittance spectrum while the complex $K_4Fe(CN)_6 \cdot 6BF_3$ has an absorption maximum in the same region. This absorption has been assigned to the ${}^1A_{1g} \rightarrow {}^1T_{2g}$ d-d-transition (ref. 26, p. 293). Again lack of gross rearrangement is indicated.

In contrast to the small spectral shifts found for d-d transitions of the above complexes, solid $Fe(phen)_2(CN)_2$ changes from dark violet (charge transfer maximum $16,200\text{ cm}^{-1}$, shoulder $19,600\text{ cm}^{-1}$) to orange-yellow (maximum $21,500\text{ cm}^{-1}$, shoulder $24,400\text{ cm}^{-1}$) upon addition of two BF_3 molecules. A large blue shift was also observed upon B_2H_6 addition. Schilt^{13,30} has shown that the visible absorption maximum of $Fe(phen)_2(CN)_2$ undergoes a large blue shift upon protonation, and evidence has been presented which indicates protonation of the nitrogen end of cyano-

(29) R. M. Golding and A. Carrington, *Mol. Phys.*, **5**, 377 (1962).

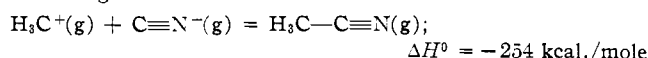
(30) A. A. Schilt, *J. Am. Chem. Soc.*, **82**, 5779 (1960).

nide.²¹ Thus large shifts in charge transfer spectra of $Fe(phen)_2(CN)_2$ derivatives are consistent with the bridge structure.

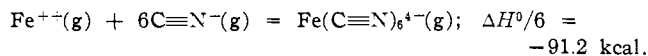
In summary, infrared data indicate the presence of a bridging CN^- , the presence of coordinated BF_3 (BH_3), and in some cases retention of geometry upon BF_3 addition. The electronic spectra and magnetic data also indicate retention of geometry and metal-carbon bonding in the bridge adducts. Chemical evidence for the bridge structures includes stoichiometry of formation and the observation that interaction of uncoordinated CN^- (KCN) with BF_3 leads to an intractable yellow-brown material which has different visible and infrared spectra from the compounds reported here.

Physical Consequences of Bridge Adduct Formation.

—In a previous communication it was mentioned that cyanide complexes have a much higher affinity for BF_3 than do organic nitriles (a factor of over 10^4 difference in K_p was indicated).⁴ The difference may be rationalized by considering nitriles as derivatives of carbonium ions: *e.g.*



This scheme then allows comparison with metal cyanide complex formation: *e.g.*



Comparison of the above heats of reaction shows that H_3C^+ ion is a much stronger Lewis acid than Fe^{+2} .³¹ Therefore, it is not surprising that significant differences exist in the electron availability of CN^- when attached to a carbonium ion as compared with CN^- attached to a metal ion.

Within the realm of "weak" acids (BX_3 , and metal ions), it appears, from small changes in d-d-transitions upon bridge formation and high stability of bridge adducts, that $C \equiv N^-$ is not highly effective in transmission of inductive effects.³²

(31) Data for these reactions were taken from the following sources: $\Delta H_f^0(CH_3^+)_g$ from F. H. Field and J. L. Franklin, "Electron Impact Phenomena," Academic Press, Inc., New York, N. Y., 1957, p. 249; $\Delta H_f^0(CN^-)_g$ from F. C. Ladd and W. H. Lee, *J. Inorg. Nucl. Chem.*, **14**, 14 (1960); other thermodynamic values were taken from the National Bureau of Standards Circular 500; absolute $\Delta H_f^0(H^+)_{aq}$ was taken equal to 111.1 kcal./mole. The heat of hydration of $Fe(CN)_6^{4-}$ was calculated using the Born equation with $r[Fe(CN)_6^{4-}] = 5.35 \text{ \AA.}$; see W. M. Latimer, "Oxidation Potentials," Prentice-Hall, Inc., New York, N. Y., 2nd ed., 1952, p. 20, and references therein.

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