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Single-Crystal Polarized Raman Scattering and Vibrational Assignments for Dicesium Lithium Metal Hexacyanides, $Cs_2LiM(CN)_6$ (M = Cr, Mn, Fe, Co, Rh, Ir)

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Single-crystal polarized Raman data for $Cs_2LiM(CN)_6$ (M = Cr, Fe, Co, Ir) and powder data for $Cs_2LiMn(CN)_6$ have been observed. The above, in conjunction with infrared data, form the basis for assignments of the optically active intra- and intermolecular vibrations for $Cs_2LiM(CN)_6$. The high symmetry of the $Cs_2LiM(CN)_6$ salts make the vibrational assignments unambiguous. Several interesting frequency shifts are observed in going from the $M(CN)_6{}^{3-}$ ions in aqueous solutions to the $Cs_2LiM(CN)_6$ crystalline lattices. The perturbations of $M(CN)_6{}^{3-}$ intramolecular vibrations are discussed in terms of mixing of internal and external molecular motion and lattice interactions. The rotatory mode, ν_{14}, has been observed at 91 cm^{-1} for the chromium salt.

Chemists have long been interested in bonding trends in transition metal cyanide complexes. One of the most useful probes for studying bonding in cyano complexes has been vibrational spectroscopy. For metal(III)–hexacyano complexes vibrational assignments and normal-mode calculations have provided invaluable information.[1] These simple binary cyanide complexes are useful models for describing bonding in more general cyano complexes. Unfortunately, the low space group symmetry and polytypism of the well-studied potassium salts $(K_3M(CN)_6)^2$ have obscured the vibrational assignments. The low-energy transitions have been particularly troublesome since lattice interactions and lattice modes have made assignments for internal modes difficult.

Recently, single-crystal polarized Raman scattering and infrared spectra have been observed for $Cs_2LiCo(CN)_6$.[3] The high space group and site symmetries for $Cs_2LiCo(CN)_6$ $(Fm3m, O_h)^4$ made it possible to obtain definitive assignments for all of the optically active modes for this salt. Several interesting shifts were observed for the $Co(CN)_6{}^{3-}$ moiety in going from aqueous solution to $Cs_2LiCo(CN)_6$. A normal-mode calculation including lattice modes[5] has shown that most of these frequency shifts can be reproduced without changing the intramolecular potential constants found for the isolated $Co(CN)_6{}^{3-}$ ion.[6]

Recent structural studies[7] have shown that $Cs_2LiM(CN)_6$ (M = Mn, Fe, Ir) are isostructural with $Cs_2LiCo(CN)_6$. Also, the structure of the chromium salt, though noncubic, shows only slight distortions from that of $Cs_2LiCo(CN)_6$.[8] The above indicates that it might be possible to obtain definitive vibrational assignments for this entire series of hexacyanides. Correlations of the $M(CN)_6{}^{3-}$ ion vibrations in aqueous solution with those obtained for the $Cs_2LiM(CN)_6$ salts are also of interest and will be given here.

Structure and Selection Rules

The Fe, Mn, Co, and Ir salts of $Cs_2LiM(CN)_6$ are isostructural and crystallize in the space group $Fm3m$ with four molecules per unit cell.[4,7] The results of a factor group analysis[3] show that there is one inactive rotatory mode (ν_{14}, F_{1g}) and three translatory modes (ν_{15} and ν_{16}, F_{1u} infrared active, and ν_{17}, F_{2g} Raman active). An approximate description of the expected normal modes and their selection rules are given in ref 5.

The symmetry species of the Raman-active modes can be distinguished using two different crystal orientations. (Actually one orientation would suffice if the electric vector of the incoming beam is rotated.) With the incident light along the (001) crystal direction and scattered radiation observed along (010), F_{2g} can be distinguished from A_{1g} and E_g. With the incident light along the (101) direction and scattered light observed along (010), E_g and A_{1g} can be distinguished.

The notation used here is that due to Swanson[9a] and is more general than the commonly used Porto notation.[9b] Scans with the incident radiation along the $(10\bar{1})$ direction, the polarization along (101), the analyzer oriented along (101), and scattered radiation observed along (010) are labeled $(10\bar{1})[(101)(101)^s](010)$. The superscript s refers to the polarization orientation of the analyzed scattered light with respect to the monochromator (h = horizontal, v = vertical, and s = scrambled). The full notation used here is useful for describing polarized scattering from single crystals since experiments which utilize general crystal directions cannot be labeled using Porto notation.

For the $Fm3m$ salts four scans were used (only three are required) to distinguish the A_{1g}, E_g, and F_{2g} symmetry species. For scan $(001)[(100)(100)^s](010)$ A_{1g} and E_g will be allowed, while for $(001)[(100)(001)^s](010)$ only F_{2g} will be allowed. For scan $(10\bar{1})[(101)(101)^s](010)$ A_{1g}, E_g, and F_{2g} will be allowed while for $(10\bar{1})[(101)(10\bar{1})^s](010)$ only E_g will be allowed.

Crystallographic results for the chromium salt[8] indicate the space group $P4_22_12$ (D_4), with two molecules per unit cell and the $Cr(CN)_6{}^{3-}$ moieties occupying sites of D_2 symmetry. A correlation diagram is presented in Figure 1. There are several important distinctions to be made between the selection rules for the $Cs_2LiCr(CN)_6$ salt and those of the isostructural series of $Fm3m$ salts. The A_{1g} and E_g modes in the O_h model remain Raman active and infrared inactive (A_1 and B_1 symmetry species of D_4). It is possible that factor group

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(1) L. H. Jones, "Inorganic Vibrational Spectroscopy," Marcel Dekker, New York, N. Y., 1971, Chapter 4.

(2) J. A. Kohn and W. D. Townes, *Acta Crystallogr.*, 14, 617 (1961).

(3) B. I. Swanson and L. H. Jones, *J. Chem. Phys.*, 53, 3761 (1970).

(4) A. Wolberg, *Acta Crystallogr., Sect. B*, 25, 161 (1969).

(5) B. I. Swanson and L. H. Jones, *J. Chem. Phys.*, 55, 4174 (1971).

(6) L. H. Jones, M. N. Memering, and B. I. Swanson, *J. Chem. Phys.*, 54, 4666 (1971).

(7) B. I. Swanson and R. R. Ryan, *Inorg. Chem.*, 12, 283 (1973); the iridium salt is not optically isotropic at room temperature but is observed to be $Fm3m$ at high temperatures.

(8) B. I. Swanson and R. R. Ryan, unpublished results.

(9) (a) B. I. Swanson, *Appl. Spectrosc.*, 27, 382 (1973); (b) T. C. Damen, S. P. S. Porto, and B. Tell, *Phys. Rev.*, 142, 570 (1966).

Figure 1. Correlation diagram for CsLiCr(CN)$_6$.

Figure 2. Raman spectra for Cs$_2$LiCo(CN)$_6$ in the C–N stretch, CMC deformation, and Cs–N stretch regions: (A) (001)[(100)-(100)^s](010); (B) (001)[(100)(001)^s](010); (C) (10$\bar{1}$)[(101)(101)^s]-(010); (D) (10$\bar{1}$)[(101)(10$\bar{1}$)^s](010).

splitting may be observed for A$_{1g}$ and E$_g$ modes in the *P*4$_2$2$_1$2 space group. All F modes become infrared and Raman active.

The polarizability tensor for the A$_1$ and B$_1$ symmetry modes contain only diagonal terms (A$_1$ ($x^2 + y^2$, z^2), B$_1$ ($x^2 - y^2$)). The polarizability tensor for the B$_2$ and E modes contain only off-diagonal terms (B$_2$ (xy), E (xz, yz)). Crystals of the Cr salt exhibit twinning with the unique c axis disordered along the (100), (010), and (001) crystal directions. In principle, because of this disorder, it should not be easy to distinguish between A$_1$ and B$_1$ modes. However, A$_1$ and B$_1$ modes can be readily distinguished from B$_2$ and E modes. In terms of the *Fm3m* model, A$_{1g}$ and E$_g$ cannot be readily distinguished from each other but they can be distinguished from F$_{2g}$. Polarized scattering for the F$_{1g}$ symmetry modes should be the same as that for F$_{2g}$ modes.

Experimental Section

The dicesium lithium salts Cs$_2$LiM(CN)$_6$ (M = Cr, Mn, Fe, Co, Rh, Ir) were prepared by combining aqueous solutions of the stoichiometric molar ratios of the individual salts Li$_3$M(CN)$_6$ and Cs$_3$M(CN)$_6$. The tricesium and trilithium salts were prepared from the potassium salts by ion exchange (hydrogen form resin Bio-Rad, AG 50W-X16 with ^{1}H replaced by Li or Cs). The potassium salts for Cr,[10] Mn,[11] and Co[12] were prepared using the usual literature methods while K$_3$Fe(CN)$_6$ was obtained from Baker and the Ir and Rh salts from Alfa. Single crystals of the Cr, Fe, Co, and Ir salts which were suitable for Raman studies were obtained by slow evaporation of aqueous solutions. The manganese salt decomposed in aqueous solutions since an excess of CN$^-$ could not easily be maintained.[11] Consequently, only powder Raman data could be obtained for the Mn salt.

We were unable to obtain a Raman spectrum of the Rh salt because of high background scattering. This may result in part from the small particle size of Cs$_2$LiRh(CN)$_6$. While the Rh salt is readily soluble in H$_2$O, a crystalline sample could not be obtained. The infrared results for the Rh salt are included for comparison.

Infrared data were obtained using a Perkin-Elmer 521 (4000-300 cm^{-1}). Nujol mulls were used for all of the samples and the instruments were calibrated using standard gases.[13] Raman spectra were obtained using a Spex 1401 double monochromator with pulse counting detection (RCA 31034 pm tube). A Spectra Physics Model 164 krypton ion laser was used for excitation (5682-A line). As the crystals studied were small (*ca.* 0.5-2.0 mm on an edge), a single-crystal cell for 90° scattering from small crystals was utilized.[14]

(10) J. H. Bigelow, *Inorg. Syn.*, 2, 203 (1946).
(11) J. A. Lower and N. C. Fernelius, *Inorg. Syn.*, 2, 213 (1946).
(12) G. G. Schlessinger, *Chemist-Analyst*, 56, 48 (1967).
(13) K. N. Rao, C. J. Humphreys, and D. H. Rank, "Wavelength Standards in the Infrared," Academic Press, New York, N. Y., 1966; "IUPAC Tables of Wavenumbers," Butterworths, London, 1961.
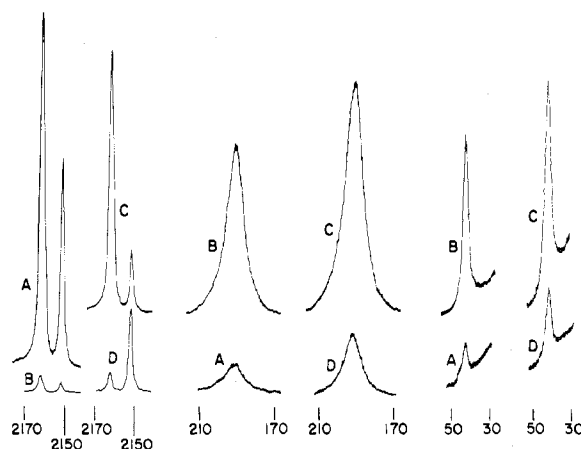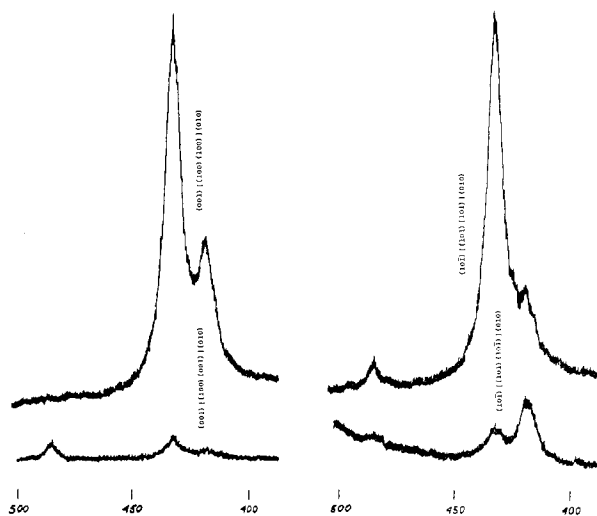(14) B. I. Swanson, *Appl. Spectrosc.*, 27, 235 (1973).

Figure 3. Raman spectra for Cs$_2$LiCo(CN)$_6$ in the M–C stretch and MCN deformation regions. See text for description of the notation.

The morphologies for the Cr, Fe, Co, and Ir are regular and the crystals can be aligned visually.

Assignments

In general, the vibrational assignments do not differ greatly from those obtained for the Co salt which has already been discussed.[3] A typical Raman spectrum is presented in Figures 2 and 3. While the assignments are straightforward, a few observations should be noted.

The F$_{2g}$ MCN deformation, ν_{10}, is weak for the Co salt and not observed at all for the Mn and Fe salts. In contrast, ν_{10} is quite strong for both Cr and Ir salts.

There are several interesting results for the Cr salt. First, the Raman-active modes exhibit polarized scattering identical with that of the *Fm3m* salts. For example, the E$_g$ and A$_{1g}$ C–N stretching vibrations can be distinguished with scans (10$\bar{1}$)[(101)(101)^s](010) and (10$\bar{1}$)[(101)(10$\bar{1}$)^s](010). The polarized single-crystal scattering is what would be expected from an *Fm3m* crystal rather than a crystal with space group *P*4$_2$2$_1$2. Twinning in the Cr salt apparently results in an averaged structure which scatters as would an *Fm3m* crystal except that the rotatory mode (F$_{1g}$) is active. None of the Raman-active modes exhibits factor group or site symmetry splittings.

A band which behaves like an F$_{2g}$ mode is observed at 91 cm^{-1} for the Cr salt. As there is no suitable combination or

overtone which could appear in this region, this band has been assigned to the F_{1g} rotatory mode, ν_{14}, for *Fm3m* symmetry. From the normal-mode treatment for the molecular vibrations in the $Cs_2LiCo(CN)_6$ lattice, a range of 80-130 cm^{-1} was estimated for ν_{14}. As the position of the rotatory mode is not expected to change greatly in proceeding from Co through Cr, the assigned value of 91 cm^{-1} is quite reasonable. The activity of this F_{1g} mode is the only observed deviation from *Fm3m* selection rules.

Finally, for $Cs_2LiCr(CN)_6$ the E_g C-N stretching mode is observed at higher frequency than the A_{1g} C-N stretch. For the other salts the reverse ordering is observed. This will be discussed later.

Discussion

The observed fundamentals for $Cs_2LiM(CN)_6$ salts are given in Table I. The difference between these frequencies and the fundamentals observed for $M(CN)_6{}^{3-}$ ions in aqueous solution[15] are given in Table II. General trends in the observed fundamentals of the $M(CN)_6{}^{3-}$ ions[15] as a function of the metal are repeated for the $Cs_2LiM(CN)_6$ salts. The most notable changes are for the M-C stretching frequencies (ν_2 and ν_4) which are seen to increase significantly in the series Cr → Co → Ir. A similar increase is observed for ν_7 and ν_8 in the series Cr → Co. (Both ν_7 and ν_8 involve considerable MC stretch.[5]) The decrease observed for ν_7 and ν_8 from Co to Ir is a result of the mass increase of the metal. These changes follow general trends in bonding which have been discussed earlier.[7,15,16]

Definitive assignments have been obtained for the troublesome low-energy CMC deformation modes. The CMC deformation and Cs-N stretching symmetry coordinates were found to be highly mixed in both F_{1u} and F_{2g} blocks for the Co salt.[5] It is probable that mixing of Cs-N and CMC motion is important for the remaining salts. All of the low-energy modes for $Cs_2LiM(CN)_6$ are insensitive to changing the metal atom.

As was the case for the Co salt, there are several interesting frequency shifts observed in going from the isolated $M(CN)_6{}^{3-}$ ions in aqueous solution to the $Cs_2LiM(CN)_6$ crystalline lattices. Large frequency increases (*ca.* 50-80 cm^{-1}) are indicated for the CMC deformation modes ν_9 and ν_{11} (see Table II and ref 5). However, it is misleading to attribute these large frequency shifts to changes in the CMC molecular motion. For isolated $M(CN)_6{}^{3-}$ both ν_9 and ν_{11} are primarily CMC deformations.[6] In $Cs_2LiM(CN)_6$ the Cs-N and CMC symmetry coordinates are highly mixed in ν_9 and ν_{11}.[5] The normal modes ν_9 and ν_{11} in crystalline $Cs_2LiM(CN)_6$ are not similar to nor can they be compared with ν_9 and ν_{11} for isolated $M(CN)_6{}^{3-}$ ions. These large "frequency shifts" provide a striking example of the danger of using solid-state vibrational data for a normal-mode calculation based on an isolated-ion model.

The C-N stretching modes for $Cs_2LiM(CN)_6$ (ν_1, ν_3, and ν_6) are all observed *ca.* 7-15 cm^{-1} higher than the corresponding modes for the isolated ions. Part of this frequency increase can be attributed to the requirement of compression of the Li-N bond each time the C-N bond is stretched. The Li-N stretching force constant enters into the expressions for C-N stretch symmetry force constants linearly.[5] In order to reproduce the C-N frequency shifts for the Co salt it was necessary to increase F_{CN}; such a change in the $M(CN)_6{}^{3-}$

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Table I. Observed Fundamentals for $Cs_2LiM(CN)_6$ (M = Cr, Mn, Fe, Co, Rh, Ir) (in cm^{-1})

| | M | | | | | |
	Cr	Mn	Fe	Co	Rh	Ir
ν_1	2139.8	2136.5	2141.8	2161.6		2180.9
ν_2	381.5	400.0	412.0	431.1		484.6
ν_3	2141.3	2136.5[a]	2136.8	2150.8		2157.4
ν_4	381.5[a]	400.0[a]	397.0	418.1		484.6[a]
ν_6	2138.5	2126.4	2118.0	2141.8	2147.7	2143.5
ν_7	468.5	492.0	522.0	566.0	518.2	516.7
ν_8	360.7	385.6	405.0	429.0	403.3	418.0
ν_9	164.0	165.8	171.7	162.2	173.1	152.6
ν_{10}	385			484.6		458.4
ν_{11}	175.7	178.7	178.8	189.9		181.1
ν_{15}	300	302.3	305.0	309.0	310.0	308.0
ν_{16}	56.5	57.5	58.0	57.8	55.0	54.7
ν_{17}	40.9	40.5	40.4	40.5		42.9

a Assumed values.

Table II. Differences between Observed Fundamentals for $Cs_2LiM(CN)_6$ and for Aqueous $M(CN)_6{}^{3-}$ (in cm^{-1}, $\nu_{crystal} - \nu_{aq}$)

| | M | | | | | |
	Cr	Mn	Fe	Co	Rh	Ir
ν_1	8[a]	8[a]	7[a]	10[c]		14[d]
ν_2	55[a]		20[a]	20[c]		22[d]
ν_3	9[a]	8[a]	8[a]	14[c]		14[d]
ν_4	55[a]			20[c]		35[d]
ν_6	11[b]	14[b]	10[b]	15[c]	15[b]	14[b]
ν_7	11[b]	9[b]	16[b]	2[c]	-4[b]	-4[b]
ν_8	22[b]	25[b]	16[b]	13[c]	16	17[b]
ν_{10}	5			1[c]		
ν_{11}				75[c]		

a ν_{aq} taken from ref 15. *b* ν_{aq} taken from L. H. Jones, *Inorg. Chem.*, 2, 777 (1963). *c* ν_{aq} taken from ref 6. *d* ν_{aq} taken from J. P. Mathieu and S. Cornevin, *J. Chim. Phys. Physiochim. Biol.*, 36, 271 (1959).

intramolecular potentials may also be required for the other complexes.

The reversal in A_{1g} and E_g C-N stretching modes for the chromium salt ($\nu_3 > \nu_1$) is intriguing. One possible explanation is that the cis-interaction constant, $F_{LiN,LiN}{}^c$, is more important for $Cs_2LiCr(CN)_6$ than for the other salts. For the Co salt $F_{LiN,LiN}{}^{Eg}$ ($F_{LiN} - 2F_{LiN,LiN}{}^c + F_{LiN,LiN}{}^t$) was expected to be about the same as $F_{LiN,LiN}{}^{A_{1g}}$ ($F_{LiN} + 4F_{LiN,LiN}{}^c + F_{LiN,LiN}{}^t$). A small negative value for $F_{LiN,LiN}{}^c$ in the Cr salt could result in a higher observed value for ν_3 than for ν_1.

For the M-C stretching modes a somewhat larger frequency increase is observed (up to 35 cm^{-1}). Since the CN moiety essentially moves as a unit for M-C stretch as shown by the normal-mode calculations, the Li-N bond also changes during a M-C stretch. For the Co salt the M-C frequency shifts could be reproduced by inclusion of the Li-N force constant without changing F_{MC}.[5] For the Cr salt the shifts observed for ν_2 and ν_4 are much higher than those observed for the other salts. This suggests a misassignment for ν_2 and ν_4 in aqueous solution.[15] Using the shifts observed for other $Cs_2LiM(CN)_6$ salts and the observed value for ν_2 in $Cs_2LiCr(CN)_6$ we estimate ν_2 and ν_4 to be *ca.* 350 cm^{-1} for $Cr(CN)_6{}^{3-}$.

Frequency shifts for those modes which primarily involve MCN deformation (ν_7 and ν_{10}) are not large. For Cr, Mn, and Fe salts ν_7 is observed to increase *ca.* 10 cm^{-1}, while for Co, Rh, and Ir no significant shifts are found.

The interesting frequency shifts observed for the internal modes of $M(CN)_6{}^{3-}$ in going from aqueous solution to the dicesium lithium salts indicate that one must be cautious in

using solid-state data in normal-mode calculations based on an isolated geometry. This is obvious for low-frequency internal modes where mixing of internal and external motion is important (such as CMC deformations in the present case). Surprisingly, significant errors can also be introduced by using solid-state data for high-energy vibrations where little or no mixing is expected. For the $Cs_2LiM(CN)_6$ salts there are no lattice modes of A_{1g} or E_g symmetry, yet C–N and M–C stretching modes of these symmetries are shifted as much as 30 cm^{-1}. Fortunately, for high-symmetry systems such as $Cs_2LiM(CN)_6$ mixing of internal and external modes and lattice interactions can be accounted for by basing the normal-coordinate calculation on a crystalline model. As more is learned about lattice perturbations of internal modes from simple systems like $Cs_2LiM(CN)_6$, it may become possible to carry out detailed vibrational analysis for more complex systems.

One interesting result of the present study is the assignment for the rotatory mode, ν_{14}, in $Cs_2LiCr(CN)_6$. It has not been possible to assign rotatory modes for hexacyanides in the past, since the low-energy regions for low-symmetry salts are complicated by other external modes. For high-symmetry $Fm3m$ salts the rotatory mode is inactive. Fortunately, for $Cs_2LiCr(CN)_6$ the slight distortion from cubic symmetry makes the rotatory mode active but does not result in additional bands in the low-energy region. The observed value of 91 cm^{-1} for ν_{14} will be quite useful in carrying out detailed calculations on $Cs_2LiM(CN)_6$ salts.

Stable Cyanide Complexes of Copper(II)[1]

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Although copper(II) is reduced by cyanide in aqueous solution, we have shown that cyanide can act as a donor to copper-(II) in the presence of ligands such as 1,10-phenanthroline and that stable mixed-ligand copper(II) cyanide complexes can be isolated. We have prepared and characterized the series of trigonal-bipyramidal monocyano complexes [Cu(phen)$_2$CN]-Y·nH$_2$O where Y$^-$ = Cl$^-$, Br$^-$, I$^-$, NO$_3{}^-$, ClO$_4{}^-$, and [Cu(phen)(CN)$_2$]$^-$. Also prepared was the square-planar Cu(phen)(CN)$_2$.

It is commonly known that in aqueous solution copper(II) is reduced to copper(I) by cyanide[2] and that simple cyano complexes of copper(II) are unstable at normal temperatures with respect to reduction and cannot be isolated.[3] It should be possible, however, by changing the environment around copper(II) from water to some other ligand, to alter the Cu-(II)–Cu(I) reduction potential so that stable mixed-ligand cyanide-containing complexes can be isolated. At present only two such complexes are definitely known:[4] [Cu(tet-a)-CN]ClO$_4$·H$_2$O and [(CuA)$_2$CN](ClO$_4$)$_3$ where tet-a and A represent respectively the cyclic tetradentate Schiff bases hexamethylazacyclotetradecane and hexamethyltetraaza-cyclotetradecadiene which both enforce square-planar environments about the copper(II). Undoubtedly the copper-(II)–cyanide linkage is not unique for these two complexes, and many other mixed-ligand copper(II) cyanide complexes which are stable to reduction should also be capable of synthesis. Of interest then are the types of ligands which will stabilize coordination of cyanide and the reasons for this stabilization.

Anticipating that good σ donors such as chelating nitrogen donors can deter transfer of an electron from cyanide to copper(II) by decreasing the actual positive charge on the copper, we have centered our investigations on copper(II) cyanide complexes containing ligands such as 1,10-phenan-

throline, 2,2′,2″-terpyridine, and ethylenediamine. We report herein our results with 1,10-phenanthroline (phen).

Experimental Section

Preparation of Complexes. 1,10-Phenanthroline monohydrate was purchased from Eastman Kodak Chemicals. All other chemicals were reagent grade and commercially available. Analyses were performed by Galbraith Laboratories, Knoxville, Tenn., and are presented in Table I.

Cyanobis(1,10-phenanthroline)copper(II) Nitrate Monohydrate. One gram (5.04 × 10^{-3} mol) of 1,10-phenanthroline monohydrate and 0.406 g (1.68 × 10^{-3} mol) of Cu(NO$_3$)$_2$·3H$_2$O were dissolved in 50 ml of water. A 25-ml aqueous solution of KCN (0.109 g, 1.68 × 10^{-3} mol) was then added dropwise to the hot stirring copper(II)–1,10-phenanthroline solution. During the addition of cyanide, a more intense dark blue solution formed and was allowed to cool slowly overnight to room temperature. Approximately 0.68 g of blue crystals was isolated after filtration, and the product, after being washed with distilled water, was dried over P$_2$O$_5$ for 24 hr.

Cyanobis(1,10-phenanthroline)copper(II) Dicyano-1,10-phenan-throlinecuprate(I) Hexahydrate. To 25 ml of a hot aqueous solution containing 0.350 g (1.77 × 10^{-3} mol) of 1,10-phenanthroline mono-hydrate and 0.143 g (0.592 × 10^{-3} mol) of Cu(NO$_3$)$_2$·3H$_2$O, an 8-ml aqueous solution of KCN (0.0771 g, 1.18 × 10^{-3} mol) was added dropwise. During the addition of cyanide a more intense blue color formed with the subsequent precipitation of a noncrystalline substance. The hot mixture was quickly filtered and the green filtrate was transferred to a beaker, placed on the warm hot plate, and allowed to cool to room temperature slowly overnight. Green needle-like crystals which are light sensitive were isolated. These were washed with water, air-dried, and stored in a vial covered with aluminum foil. The yield varies from 15 to 45 mg.

Cyanobis(1,10-phenanthroline)copper(II) Chloride Monohydrate. To 10 ml of a hot aqueous solution containing 0.0958 g (5.62 × 10^{-4} mol) of copper(II) chloride dihydrate and 0.334 g (1.74 × 10^{-3} mol) of 1,10-phenanthroline monohydrate, a 5-ml aqueous solution of KCN (0.0366 g, 5.62 × 10^{-4} mol) was added with stirring. Upon

(1) Presented in part at the 163rd National Meeting of the American Chemical Society, Boston, Mass., April 1972.

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