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.

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Registry No. $Cs_2LiCr(CN)_6$, 42055-48-1; $Cs_2LiMn(CN)_6$, 37164-28-6; $Cs_2LiFe(CN)_6$, 37164-29-7; $Cs_2LiCo(CN)_6$, 23591-91-5; $Cs_2LiRh(CN)_6$, 42055-51-6; $Cs_2LiIr(CN)_6$, 42055-52-7.

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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 $[Cu(phen)_2CN]Y \cdot nH_2O$ 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] $[Cu(tet\text{-}a)CN]ClO_4 \cdot H_2O$ and $[(CuA)_2CN](ClO_4)_3$ where tet-a and A represent respectively the cyclic tetradentate Schiff bases hexamethylazacyclotetradecane and hexamethyltetraazacyclotetradecadiene 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-phenanthroline, 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 $Cu(NO_3)_2 \cdot 3H_2O$ 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_2O_5 for 24 hr.

Cyanobis(1,10-phenanthroline)copper(II) Dicyano-1,10-phenanthrolinecuprate(I) Hexahydrate. To 25 ml of a hot aqueous solution containing 0.350 g (1.77×10^{-3} mol) of 1,10-phenanthroline monohydrate and 0.143 g (0.592×10^{-3} mol) of $Cu(NO_3)_2 \cdot 3H_2O$, 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 needlelike 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

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

[2] F. A. Cotton and G. Wilkinson, "Advanced Inorganic Chemistry," 3rd ed, Interscience, New York, N. Y., 1972, p 907.

[3] A. Longo and T. Buch, *Inorg. Chem.*, 6, 556 (1967).

[4] Y. M. Curtis and N. F. Curtis, *Aust. J. Chem.*, 19, 609 (1966).

Table I. Analytical Data for Copper(II) Cyanide Complexes

	% calcd				% found			
Compd	C	H	N	Cu	C	H	N	Cu
$[Cu(phen)_2CN]NO_3 \cdot H_2O$	56.65	3.42	15.86		57.05	3.54	15.66	
$[Cu(phen)_2CN]ClO_4 \cdot {}^1/_2H_2O$	53.76	3.07	12.53		53.42	3.13	12.50	
$[Cu(phen)_2CN]Cl \cdot H_2O$	59.64	3.60	13.92		59.60	3.36	13.98	
$[Cu(phen)_2CN]Br \cdot H_2O$	54.80	3.31	12.79		54.40	3.27	12.52	
$[Cu(phen)_2CN]I \cdot H_2O$	50.57	3.05	11.78		50.30	3.22	11.76	
$[Cu(phen)_2CN][Cu(phen)(CN)_2] \cdot 6H_2O$	54.86	4.25	14.75	14.88	55.07	4.02	14.70	14.78
$Cu(phen)(CN)_2$	56.86	2.73	18.95		56.30	2.65	18.71	

cooling to room temperature a small amount of green precipitate was filtered off, and the filtrate was allowed to cool in a refrigerator for 48 hr. The blue crystals which formed were washed with water and dried in a desiccator over P_2O_5 for 12 hr. Upon drying the crystals assumed a green color. The yield was 0.101 g.

Cyanobis(1,10-phenanthroline)copper(II) Bromide Monohydrate. Starting with $CuBr_2$, this was prepared by the same method as the above chloride complex.

Cyanobis(1,10-phenanthroline)copper(II) Iodide Monohydrate. To 30 ml of a hot aqueous solution containing 0.135 g (5.59×10^{-4} mol) of copper(II) nitrate trihydrate and 0.3327 g (1.68×10^{-3} mol) of 1,10-phenanthroline monohydrate, a 10-ml aqueous solution of potassium cyanide (0.0364 g, 5.59×10^{-4} mol) was added slowly with stirring followed by a solution of about 0.7 g of potassium iodide in 20 ml of water. Addition of the latter solution gave a copious green precipitate which was washed with water and dried in a desiccator over P_2O_5. The yield was 0.26 g.

Cyanobis(1,10-phenanthroline)copper(II) Perchlorate Hemihydrate. To the above hot aqueous solution of $[Cu(phen)_2CN]Cl$, a threefold excess of aqueous sodium perchlorate could be added, causing the precipitation of $[Cu(phen)_2CN]ClO_4 \cdot {}^1/_2H_2O$. The blue solid was filtered, washed with water, and dried in a desiccator over P_2O_5.

Dicyano(1,10-phenanthroline)copper(II). To 25 ml of a hot aqueous solution containing 0.327 g (1.65×10^{-3} mol) of 1,10-phenanthroline monohydrate and 0.199 g (8.24×10^{-4} mol) of $Cu(NO_3)_2 \cdot 3H_2O$, a solution of 0.107 g (1.65×10^{-3} mol) of KCN in 10 ml of water was slowly added with stirring. The gummy purple precipitate which formed was filtered, washed with water, and then dried over P_2O_5 in a desiccator. Approximately 0.19 g of the product was isolated.

Except for $[Cu(phen)_2CN]Cl \cdot H_2O$ and $Cu(phen)(CN)_2$ the above complexes were soluble in nitromethane, but they slowly decomposed upon standing. The complexes were soluble in no other common solvents.

Physical Measurements. Electronic spectra were measured using a Cary 14 spectrophotometer while infrared spectra were recorded on a Perkin-Elmer 521. Magnetic susceptibility measurements were done by both the Faraday and Gouy techniques. In both cases, the calibrant was $Hg[Co(NCS)_4]$.

Results and Discussion

All of the compounds reported in this paper contain cyanide coordinated to copper(II), and this can readily be verified by infrared spectroscopy. Ionic, noncoordinated cyanide, as in KCN, shows a single sharp absorption[5] (ν_{CN}) at 2080 cm^{-1}. Upon coordination to a metal ion, the CN stretching frequency invariably increases[6] with the magnitude of this increase dependent upon the strength of the σ and π metal-cyanide interaction.[7] For example, in Curtis' two compounds $[Cu(tet\text{-}a)CN]^+$ and $[(CuA)_2CN]^{3+}$ (*vide supra*), ν_{CN} is respectively (2109, 2103) and 2139 cm^{-1}.[4] With the compounds described herein as $[Cu(phen)_2CN]X$, where $X^- = Cl^-, Br^-, I^-, NO_3^-$, and ClO_4^-, the cyanide stretching frequency varies from 2149 to 2136 cm^{-1} and is characterized by a weak and broad absorption band. For $[Cu(phen)_2CN][Cu(phen)(CN)_2] \cdot 6H_2O$, ν_{CN} is 2140 cm^{-1} for the cyanide bonded to copper(II) while ν_{CN} is 2100 and 2082 cm^{-1} for cyanide bonded to copper(I). Finally for $Cu(phen)(CN)_2$, ν_{CN} is 2143 and 2137 cm^{-1} and both bands are very sharp compared to the monocyano complexes. The cyanide stretching frequencies for these compounds are listed in Table II.

Table II. Infrared Cyanide Stretching Frequencies of Copper(II) Cyanide Complexes[a]

Complex	ν_{CN}, cm^{-1}
$[Cu(phen)_2CN]NO_3 \cdot H_2O$	2136
$[Cu(phen)_2CN]Cl \cdot H_2O$	2140
$[Cu(phen)_2CN]Br \cdot H_2O$	2139
$[Cu(phen)_2CN]I \cdot H_2O$	2137
$[Cu(phen)_2CN]ClO_4 \cdot {}^1/_2H_2O$	2149
$[Cu(phen)_2CN][Cu(phen)(CN)_2] \cdot 6H_2O$	2140, 2100, 2082
$Cu(phen)(CN)_2$	2143, 2137

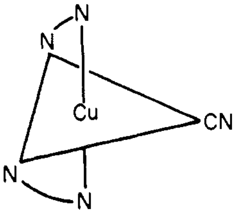
[a] All spectra were run as Nujol mulls.

Table III. Magnetic Susceptibilities of Copper(II) Cyanide Complexes at 296°K

Complex	μ, BM
$[Cu(phen)_2CN]NO_3 \cdot H_2O$	1.83
$[Cu(phen)_2CN]Cl \cdot H_2O$	1.88
$[Cu(phen)_2CN]Br \cdot H_2O$	1.90
$[Cu(phen)_2CN]I \cdot H_2O$	1.91
$[Cu(phen)_2CN][Cu(phen)(CN)_2] \cdot 6H_2O$	1.95
$[Cu(phen)_2CN]ClO_4 \cdot H_2O$	1.88
$[Cu(phen)(CN)_2]$	1.88

Support for the presence of Cu(II) is found from the magnetic susceptibilities of these compounds. All compounds show molar susceptibilities indicative of one copper(II) per formula unit as is shown in Table III. This magnetic data do not preclude the existence of dimers containing two weakly antiferromagnetically coupled copper(II) ions bridged by cyanide; however we find no infrared evidence for bridging cyanide in any of these complexes.

For all of the monocyano complexes synthesized, the electronic spectra showed a broad asymmetric absorption between 12.8 and 13.6 kK with a rudimentary shoulder at slightly lower energy. These data are listed in Table IV. Using the criteria of Hathaway,[8] the visible spectra seem most consistent with a five-coordinate trigonal-bipyramidal geometry in which the cyanide would be located in the equatorial plane as shown in I. This structure has been verified by X-ray crystallography for two analogous complexes



I

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(5) K. Nakamoto, "Infrared Spectra of Inorganic and Coordination Compounds," 2nd ed, Wiley-Interscience, New York, N. Y., 1970, p 80.

(6) K. Nakamoto, ref 5, p 178.

(7) See, for example, L. H. Jones, *Inorg. Chem.*, 2, 777 (1963).

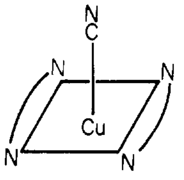
(8) B. J. Hathaway, *J. Chem. Soc., Dalton Trans.*, 1196 (1972).

Table IV. Electronic Spectra of Copper(II) Cyanide Complexes[a]

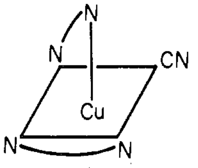
Complex	Absorptions, kK
$[Cu(phen)_2CN]NO_3 \cdot H_2O$	13.5 b
$[Cu(phen)_2CN]ClO_4 \cdot {}^1/_2H_2O$	13.3 b
$[Cu(phen)_2CN]Cl \cdot H_2O$	13.4 b
$[Cu(phen)_2CN]Br \cdot H_2O$	13.7 b
$[Cu(phen)_2CN]I \cdot H_2O$	13.8 b
$[Cu(phen)_2CN][Cu(phen)(CN)_2] \cdot 6H_2O$	21.7, 13.4 vb
$Cu(phen)(CN)_2$	18.2

[a] The spectra of these complexes were obtained as Nujol mulls.

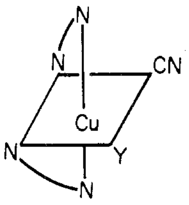
$[Cu(bipy)_2I]I$[9] and $[Cu(bipy)_2NH_3](BF_4)_2$[10] where bipy = 2,2′-bipyridine. Furthermore, Hathaway and coworkers have investigated a series of similar complexes $[Cu(bipy)_2X]Y$, where X and Y are various unidentate anionic ligands, and have also proposed a trigonal-bipyramidal structure on the basis of electronic and esr spectra. Other possibilities which do not seem as plausible would be a square-pyramidal structure (II, III) or a cis-octahedral structure (IV). In all three cases the electronic spectra observed for these monocyano adducts are inconsistent with the above formulations.[8,11] Also for II, there would be formidably unfavorable steric interactions arising from having two coplanar phenanthroline ligands.[12,13]



II



III



IV

It should be understood, however, that many copper(II) complexes possess irregular structures and that such irregularities cannot be deduced from the broad electronic spectra of these complexes. Undoubtedly some monocyano complexes may show significant deviations from trigonal-bipyramidal geometry, and in some cases the counterion could weakly interact with copper(II).

One possible case where a deviation from trigonal-bipyramidal geometry may occur is $[Cu(phen)_2CN]NO_3 \cdot H_2O$. Although the electronic spectrum is consistent with a trigonal-bipyramidal geometry, the infrared spectrum shows weak interaction of the nitrate ion and copper(II). For this complex, $\nu_3(NO_3^-)$ is split by 50 cm^{-1} at 1370 and 1320 cm^{-1}. This splitting is exceptionally small and is similar in magnitude to that found for $[Cu(en)_2](NO_3)_2$, 60 cm^{-1}, where "semicoordination" of nitrate has been proposed.[14] When nitrate is coordinated in a monodentate or bidentate fashion, splittings in ν_3 of approximately 100-200 cm^{-1} are found[15,16] and normal copper-oxygen bond lengths occur.[17] For weak interactions or semicoordination, the copper-oxygen bond distance is known to vary from 2.6 to 2.9 Å[17,18] with the weaker interaction giving the longer distance. Further support for the weak interaction of nitrate in the solid state is found upon examination of the splitting of the nitrate combination band $\nu_1 + \nu_4$ in the 1700-1800-cm^{-1} region. Lever[19] has proposed that this band can be used diagnostically to differentiate among ionic, monodentate, and bidentate nitrates with the expected splittings being as follows: ionic, none; monodentate,[20] 5-26 cm^{-1}; bidentate, 20-66 cm^{-1}. The splitting of $\nu_1 + \nu_4$ in $[Cu(phen)_2CN]NO_3 \cdot H_2O$ is 2 cm^{-1} which again substantiates the interpretation that the nitrate ion is very weakly interacting with copper(II). For the perchlorate complex $[Cu(phen)_2CN]ClO_4 \cdot {}^1/_2H_2O$, $\nu_3(ClO_4^-)$ is at 1080 cm^{-1} and is unsplit. This would signify noncoordination of perchlorate.

Various attempts were made to prepare complexes with two or more coordinated cyanides but only the complex $Cu(phen)(CN)_2$ was isolated. This complex is undoubtedly of square-planar symmetry. The high-energy band in the electronic spectrum at 18.2 kK is consistent with this assignment as is the presence of the two cyanide stretching bands in the infrared.

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Registry No. $[Cu(phen)_2CN]NO_3$, 42741-08-2; $[Cu(phen)_2CN]ClO_4$, 42741-09-3; $[Cu(phen)_2CN]Cl$, 42741-10-6; $[Cu(phen)_2CN]Br$, 42741-11-7; $[Cu(phen)_2CN]I$, 42741-12-8; $[Cu(phen)_2CN][Cu(phen)(CN)_2]$, 42741-13-9; $Cu(phen)(CN)_2$, 42741-14-0.

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(9) G. A. Barclay, B. F. Hoskins, and C. H. L. Kennard, *J. Chem. Soc.*, 5691 (1963).

(10) F. S. Stephens, *J. Chem. Soc., Dalton Trans.*, 1350 (1972).

(11) B. J. Hathaway, I. M. Proctor, R. C. Slade, and A. A. G. Tomlinson, *J. Chem. Soc. A*, 2219 (1969).

(12) L. H. Berka, W. T. Edwards, and P. A. Christian, *Inorg. Nucl. Chem. Lett.*, 7, 265 (1971).

(13) Only one exception is known to date. The complex $Cu(bipy)_2(ClO_4)_2$ is known to have a flattened tetrahedral (nearly square-planar) arrangement of the bipyridine ligands and a visible spectrum[11] quite distinct from those of those complexes believed to be trigonal bipyramidal: H. Nakai, *Bull. Chem. Soc. Jap.*, 44, 2412 (1971).

(14) I. J. Proctor, B. J. Hathaway, and P. Nicholls, *J. Chem. Soc. A*, 1678 (1968).

(15) N. F. Curtis and Y. M. Curtis, *Inorg. Chem.*, 4, 804 (1965).

(16) K. Nakamoto, "Infrared Spectra of Inorganic and Coordination Compounds," 2nd ed, Wiley-Interscience, New York, N. Y., 1970, pp 171-173.

(17) A. F. Cameron, K. P. Forrest, D. W. Taylor, and R. H. Nuttall, *J. Chem. Soc. A*, 2492 (1971).

(18) Y. Komiyama and E. C. Lingafelter, *Acta Crystallogr.*, 17, 1145 (1964).

(19) A. B. P. Lever, E. Mantovani, and B. S. Ramaswamy, *Can. J. Chem.*, 11, 1957 (1971).

(20) In Lever's classification, semicoordinated nitrate as in $[Cu(en)_2](NO_3)_2$ is included as monodentate.