References and Notes

(1) Presented before the 8th Midwest Regional American Chemical Society Meeting, Columbia, Mo., 1972, and the American Crystallographic Association summer meeting, Storrs, Conn., 1973.

(2) B. Morosin and J. R. Brathovde, *Acta Crystallogr.*, **17**, 705 (1964).

(3) M. Bartlett and G. J. Palenik, *Chem. Commun.*, 416 (1970).

(4) V. W. Day, B. R. Stults, E. L. Tasset, R. O. Day, and R. S. Marianelli, *J. Amer. Chem. Soc.*, **96**, 2650 (1974).

(5) (a) D. M. Collins, W. R. Scheidt, and J. L. Hoard, *J. Amer. Chem. Soc.*, **94**, 6689 (1972); (b) A. B. Hoffman, D. M. Collins, V. W. Day, E. B. Fleischer, T. S. Srivastava, and J. L. Hoard, *ibid.*, **94**, 3620 (1972).

(6) J. L. Hoard, *Science*, **174**, 1295 (1971), and references cited therein.

(7) B. R. Stults, V. W. Day, E. L. Tasset, and R. S. Marianelli, *Inorg. Nucl. Chem. Lett.*, **9**, 1259 (1973).

(8) W. J. Geary, *Coord. Chem. Rev.*, **7**, 84 (1971), and references cited therein.

(9) G. Schwarzenbach and H. Flaschka, "Complexometric Titrations," Methuen, London, Great Britain, 1969, p 230.

(10) R. B. Fischer and D. G. Peters, "Quantitative Chemical Analysis," W. B. Saunders Co., Philadelphia, Pa., 1969, p 253.

(11) A. Earnshaw, "Introduction to Magnetochemistry," Academic Press, New York, N. Y., 1968.

(12) R. G. Charles, *Inorg. Syn.*, 7, 183 (1963).

(13) (a) G. H. Cartledge, *J. Amer. Chem. Soc.*, **73**, 4416 (1951); (b) G. H. Cartledge, *ibid.*, **74**, 6015 (1952).

(14) The number in parentheses following each *m/e* value is the relative abundance of the corresponding ion with mass 154 taken as the base peak for all complexes.

(15) "International Tables for X-Ray Crystallography," Vol. I, Kynoch Press, Birmingham, England, 1969, pp 89, 101.

(16) "International Tables for X-Ray Crystallography," Vol. III, Kynoch Press, Birmingham, England, 1968, p 166.

(17) D. T. Cromer and J. L. Mann, *Acta Crystallogr., Sect. A*, **24**, 324 (1968).

(18) D. T. Cromer, *Acta Crystallogr.*, **18**, 17 (1965).

(19) See paragraph at end of paper regarding supplementary material.

(20) K. Nakamoto, "Infrared Spectra of Inorganic and Coordination Compounds," Wiley-Interscience, New York, N. Y., 1970.

(21) M. Mikami, I. Nakagawa, and T. Shimanouchi, *Spectrochim. Acta, Part A*, **23**, 1037 (1967).

(22) S. Pinchas, B. L. Silver, and I. Laulicht, *J. Chem. Phys.*, **46**, 1506 (1967).

(23) K. Nakamoto, C. Udovich, and J. Takemoto, *J. Amer. Chem. Soc.*, **92**, 3973 (1970).

(24) P. J. Staples and M. L. Tobe, *J. Chem. Soc.*, 4812 (1960).

(25) K. Bowman and Z. Dori, *Inorg. Chem.*, **9**, 395 (1970).

(26) R. Ziolo, J. Thick, and Z. Dori, *Inorg. Chem.*, **11**, 626 (1972).

(27) W. Beck, W. P. Fehlhammer, P. Pollmann, and R. S. Tobias, *Inorg. Chim. Acta*, **2**, 467 (1968).

(28) R. F. Ziolo and Z. Dori, *J. Amer. Chem. Soc.*, **90**, 6560 (1968).

(29) D. R. Herrington and L. J. Boucher, *Inorg. Nucl. Chem. Lett.*, 7, 1091 (1971).

(30) R. J. H. Clark and C. S. Williams, *Spectrochim. Acta*, **22**, 1081 (1966).

(31) A. R. Davis, C. J. Murphy, and R. A. Plane, *Inorg. Chem.*, **9**, 423 (1970).

(32) S. C. Jain and R. Rivest, *Inorg. Chim. Acta*, **4**, 291 (1970).

(33) N. S. Gill, R. H. Nuttall, D. E. Scaife, and D. W. A. Sharp, *J. Inorg. Nucl. Chem.*, **18**, 79 (1961).

(34) C. G. McDonald and J. S. Shannon, *Aust. J. Chem.*, **19**, 1545 (1966).

(35) J. E. Davis, B. M. Gatehouse, and K. S. Murray, *J. Chem. Soc., Dalton Trans.*, 2523 (1973).

(36) A. Earnshaw, E. A. King, and L. K. Larkworthy, *J. Chem. Soc. A*, 1048 (1968).

(37) R. L. Martin, "New Pathways in Inorganic Chemistry," University Press, Cambridge, 1968, p 175.

(38) A. P. Gineberg, *Inorg. Chim. Acta*, **5**, 45 (1971).

(39) The first number in parentheses following an averaged value is the rms value of the estimated standard deviation of a single value. The second and third numbers, when given, represent the mean and maximum deviation from the averaged value, respectively.

(40) J. P. Fackler, Jr., and A. Avdeef, *Inorg. Chem.*, **13**, 1864 (1974).

(41) S. Koda, *et al.*, *J. Chem. Soc. D.*, 1321 (1971).

(42) The crystal structure of $Mn(acac)_2(NCS)$, see ref 4, shows the seven-atom (excluding hydrogen atoms) acetylacetonate ligand to be nonplanar, having deviations from planarity as large as 0.09 Å.

(43) R. B. Von Dreele, J. J. Stezowski, and R. C. Fay, *J. Amer. Chem. Soc.*, **93**, 2887 (1971).

(44) J. V. Silverton and J. L. Hoard, *Inorg. Chem.*, **2**, 243 (1963).

(45) M. R. Caira, J. M. Haigh, and T. R. Nassimbeni, *Inorg. Nucl. Chem. Lett.*, **8**, 109 (1972).

(46) E. C. Lingafelter and R. L. Braun, *J. Amer. Chem. Soc.*, **88**, 2951 (1966).

(47) P. K. Hon and C. E. Pfluger, *J. Coord. Chem.*, **3**, 67 (1973).

(48) R. F. Ziolo, A. P. Gaughan, Z. Dori, C. G. Pierpont, and R. Eisenberg, *Inorg. Chem.*, **10**, 1289 (1971).

Contribution from the Department of Chemistry,
University of Michigan, Ann Arbor, Michigan 48104

Crystal and Molecular Structure of Cyanobis(1,10-phenanthroline)copper(II) Nitrate Monohydrate

OREN P. ANDERSON*

Received June 26, 1974 AIC40414F

The crystal and molecular structure of cyanobis(1,10-phenanthroline)copper(II) nitrate monohydrate, $[Cu(N_2C_{12}H_8)_2CN](NO_3)\cdot H_2O$, has been determined from three-dimensional single-crystal X-ray diffraction data, collected by counter techniques. The dark-blue crystals are triclinic, space group $P\bar{1}$ (No. 2), with two formula units in a unit cell of dimensions $a = 10.816$ (2) Å, $b = 12.098$ (2) Å, $c = 10.118$ (2) Å, $\alpha = 105.62$ (2)°, $\beta = 110.10$ (2)°, $\gamma = 66.68$ (2)°. The structure was refined by full-matrix least-squares methods to a weighted R of 0.076 for 2392 independent reflections with $I > 3\sigma(I)$. The coordination geometry of the monomeric complex ion is based on a distorted trigonal bipyramid with the cyanide ligand bonding to copper(II) in an equatorial position. Bond lengths are as follows: Cu–N(equatorial), 2.123 (6) and 2.102 (6) Å; Cu–N(axial), 2.001 (10) and 2.014 (10) Å; Cu–C, 1.935 (10) Å; C–N(cyanide), 1.16 (1) Å. The water molecule of hydration is found to be hydrogen bonded simultaneously to the nitrogen atom of the coordinated cyanide ion and to one of the nitrate oxygen atoms.

Introduction

The most interesting aspects of the coordination chemistry of copper(II) can be succinctly summarized: (1) the variety of coordination geometries available about Cu(II), (2) the influence of the $3d^9$ electronic distribution on the coordination geometry, and (3) the relative stability *vs.* the 1+ oxidation state as a function of coordinating ligand and coordination geometry. With regard to the last point, it has long been known that several ligands, among them the iodide and cyanide ions, do not generally form stable complexes with the cupric ion. In aqueous solution at ordinary temperatures, cyanide reduces copper(II) to cuprous cyanide, with simultaneous formation of cyanogen.[1] At low temperatures in nonaqueous solvents, the existence of complex ions such as the tetracyanocuprate(II) anion has been claimed, although the ion has not been isolated.[2]

Recently, it has been shown that by choosing ligands which strongly prefer to coordinate the cupric rather than the cuprous ion, it is possible to stabilize the copper(II) ion sufficiently to allow direct bonding between cyanide and the cupric ion in aqueous solution at ordinary temperatures. Such was the case for the stable complexes $[Cu(tet\text{-}a)CN]ClO_4\cdot H_2O$ (tet-a = 5,7,7,12,14,14-hexamethyl-1,4,8,11-tetraazacyclotetradecane) and $[Cu_2A_2(CN)](ClO_4)_3$ (A = 5,7,7,12,14,14-hexamethyl-1,4,8,11-tetraazacyclotetradeca-4,11-diene),[3] the

---

* Address correspondence to the Department of Chemistry, Colorado State University, Fort Collins, Colo. 80523.

structure of the latter having been recently established.[4] In these cases, cyanide was able to coordinate directly to copper(II), presumably due to the stabilization of the 2+ oxidation state provided by the macrocyclic tetradentate ligands. More recently, interesting cyanide complexes of copper(II) have been synthesized employing 1,10-phenanthroline (hereafter abbreviated phen) as the stabilizing ligand,[5] among which was the title compound, cyanobis(1,10-phenanthroline)copper(II) nitrate monohydrate. Since ligands such as 1,10-phenanthroline and 2,2'-bipyridine are not capable of square-planar coordination at copper(II) on steric grounds,[6] the basic coordination geometry for the [Cu(phen)$_2$CN]$^+$ cation was suggested to be similar to the trigonal-bipyramidal coordination found in iodobis(2,2'-bipyridine)copper(II) iodide.[7] It was also suggested, on the basis of infrared evidence, that a derivative six-coordinate structure might be found for the geometry about the cupric ion, due to counterion "semicoordination."[8] To ascertain the mode of bonding of the cyanide ion and the overall coordination geometry in this novel complex, an X-ray crystallographic study was undertaken on the title compound, cyanobis(1,10-phenanthroline)copper(II) nitrate monohydrate.

Experimental Section

Crystal Data. For [Cu(N$_2$C$_{12}$H$_8$)$_2$CN](NO$_3$)·H$_2$O (mol wt 530.0, triclinic) $a = 10.816$ (2) Å, $b = 12.098$ (2) Å, $c = 10.118$ (2) Å, $\alpha = 105.62$ (2)°, $\beta = 110.10$ (2)°, $\gamma = 66.68$ (2)°, $V = 1128.04$ Å^3, $\rho_{\text{obsd}} = 1.56$ g cm^{-3}, $\rho_{\text{calcd}} = 1.56$ g cm^{-3}, $Z = 2$, and $F(000) = 542$; space group $P\bar{1}$, Mo Kα radiation, λ_1 0.70926 Å, λ_2 0.71354 Å, and μ(Mo Kα) = 10.55 cm^{-1}.

Data Collection and Reduction. Dark blue crystals of the title compound were kindly supplied by Dr. M. Wicholas. Preliminary Weissenberg and precession photographs revealed no symmetry, and the centric triclinic space group C_i^1-$P\bar{1}$ was chosen for further work (later shown to be correct by successful solution and refinement of the structure).

The crystal chosen for data collection was mounted in a random orientation on the Syntex $P\bar{1}$ diffractometer. The crystal was accurately centered, and the orientation matrix was obtained from least-squares calculations on the automatically determined 2θ, ω, and χ settings of 15 high-order reflections.[9] Measurement of the setting angles for 72 high-order reflections at 20 (±1)° (including 19 with negative 2θ values) allowed calculation (by least-squares methods) of the unit cell parameters and standard deviations reported above. The cell reported above is related to a type I cell (positive reduced form)[23] by the transformation matrix [0$\bar{1}$0/00$\bar{1}$/100]. The dimensions of the reduced cell are $a = 10.118$ Å, $b = 10.816$ Å, and $c = 12.098$ Å, $\alpha = 66.68°$, $\beta = 74.38°$, and $\gamma = 69.90°$. The measured density reported was obtained by neutral buoyancy in chloroform–1,2-dibromoethane.

The intensities of 4218 unique reflections with $2\theta \leq 50°$ were measured by θ–2θ scans, employing Mo Kα radiation passed through a graphite monochromator. The scan range was 1° on either side of the Kα_1 and Kα_2 peaks, with a minimum scan rate of 2°/min automatically increased to a maximum of 24°/min for very strong reflections. Background was counted at either end of the scan, for a time equal to the duration of the scan. The intensities of three reference reflections (002, 35$\bar{1}$, and 011) were measured every 50 reflections and showed no significant changes during the data collection. Intensities were calculated as $I = D[A - (B/C)]$, and standard deviations were calculated from $\sigma(I) = D[A + (B/C)]^{1/2}$, where D is the scan rate, A is the total corrected count, B is the total background count, and C is the ratio of background to scan times. The intensity was corrected for coincidence losses on strong reflections by the formula $A = [1 - (1 - 4\tau I_o)^{1/2}]/2\tau$, where I_o is the observed intensity, τ is the counter dead time, and A is the corrected count. The intensities were also corrected for Lorentz and polarization effects. Reflections with $I > 3\sigma(I)$ were judged to be observed; the 2392 reflections which met this criterion were used in the solution and refinement of the structure. An absorption correction was applied to the observed reflections,[10] employing a gaussian grid technique. For the crystal used, roughly a thick six-sided plate with approximate dimensions 0.02 × 0.007 × 0.015 cm, extrema in the reciprocal transmission factor were 1.233 and 1.106.

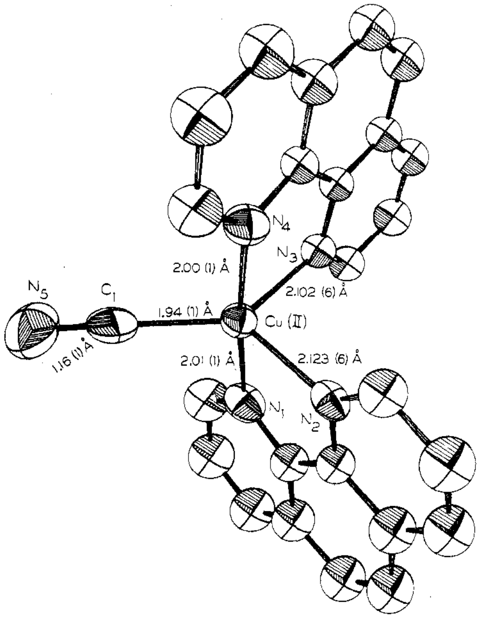

Figure 1. Coordination geometry of the monomeric cation [Cu(phen)$_2$CN]$^+$. Hydrogen atoms have been omitted for clarity.

Solution and Refinement of Structure. The position of the copper(II) ion was assigned from the highest nonorigin peak in the initial Patterson map. The positions of all nonhydrogen atoms were obtained from a series of Fourier syntheses phased by the atoms in known positions. Scattering factors for copper(II) were taken from ref 11, those for C, N, and O from ref 12, and those for H from ref 13, while correction terms $\Delta f'$ and $\Delta f''$ for anomalous dispersion due to copper were taken from ref 14.

Two cycles of full-matrix least-squares refinement with isotropic thermal parameters for all atoms except copper(II), the cyanide ion, and the coordinating nitrogen atoms, which were refined anisotropically, lowered R $(=[\sum \| F_o| - |F_c \|]/\sum |F_o|)$ from its initial value of 0.315 to 0.107 (unobserveds not included) and R_w $(=[\sum w(|F_o| - |F_c|)^2/\sum w|F_o|^2]^{1/2}$, $w = \sigma^{-2}(F_o))$ from its initial value of 0.351 to 0.109 (no unobserveds). The CLS refinement program minimizes $w(\Delta F)^2$. At this point a difference Fourier map clearly indicated the presence of the hydrogen atoms attached to the phenanthroline rings (electron density 0.3–0.5 e Å^{-3}). These hydrogen atoms were then included in fixed calculated positions 0.95 Å from ring carbon atoms, with fixed isotropic thermal parameters 1 Å^2 larger than those of the carbon atoms to which they were attached. Hydrogen atoms of the water of hydration were not as pronounced in the difference Fourier and were not included. Two final cycles of refinement on all atoms, with thermal parameters assigned as above, reduced R to 0.083 and R_w to 0.076. On this final cycle, no shifts in positional parameters were greater than 10% of the standard deviation, and the maximum shifts in thermal parameters were less than 30% of the standard deviation. An extinction correction was deemed unnecessary. A final difference Fourier map showed no peak higher than 0.7 e Å^{-3} and no depression lower than −0.3 e Å^{-3}.

Atomic positions and isotropic thermal parameters are listed in Table I, and anisotropic thermal parameters, in Table II.

Results and Discussion

The calculated bond lengths and angles involving the copper(II) ion are reported in Table III, while the bond lengths and angles within the phenanthroline ligands and the nitrate anion are found in Table IV (standard deviations reported include the contributions from the standard deviations in the unit cell parameters but not coordinate covariance). Figure 1 shows a view of the coordination geometry about the cupric ion. The monomeric complex ion is seen to exhibit approximately trigonal-bipyramidal coordination geometry about the copper(II) ion, with the cyanide ion occupying an equatorial position. The angles in the equatorial plane are considerably distorted from the ideal trigonal angle of 120°, with one small angle of 98.6° between the Cu–N(phen) bonds in the

Table I. Atomic Coordinates (Fractional) and Isotropic Thermal Parameters[a]

Atom	x	y	z	U, Å^2
Cu(II)	0.2674 (1)	0.2697 (1)	0.2809 (1)	
N(1)	0.3122 (7)	0.3712 (6)	0.1872 (8)	
N(2)	0.1240 (7)	0.2586 (6)	0.0767 (7)	
N(3)	0.4318 (7)	0.1085 (6)	0.2447 (7)	
N(4)	0.2229 (7)	0.1568 (6)	0.3560 (7)	
C(1)	0.2476 (11)	0.3956 (9)	0.4449 (11)	
N(5)	0.2360 (13)	0.4749 (9)	0.5397 (10)	
C(2)	0.4081 (11)	0.4258 (10)	0.2473 (11)	0.070 (3)
C(3)	0.4227 (12)	0.5030 (10)	0.1741 (12)	0.075 (3)
C(4)	0.3409 (12)	0.5179 (10)	0.0457 (12)	0.073 (3)
C(5)	0.2382 (10)	0.4654 (9)	−0.0247 (11)	0.062 (3)
C(6)	0.1450 (11)	0.4709 (10)	−0.1636 (12)	0.068 (3)
C(7)	0.0571 (11)	0.4173 (10)	−0.2224 (12)	0.072 (3)
C(8)	0.0396 (10)	0.3392 (9)	−0.1463 (10)	0.058 (3)
C(9)	−0.0513 (11)	0.2726 (9)	−0.1954 (11)	0.066 (3)
C(10)	−0.0553 (11)	0.2047 (10)	−0.1176 (12)	0.068 (3)
C(11)	0.0357 (10)	0.1974 (8)	0.0222 (10)	0.055 (3)
C(12)	0.1304 (9)	0.3276 (8)	−0.0043 (9)	0.042 (2)
C(13)	0.2282 (9)	0.3886 (8)	0.0552 (10)	0.045 (2)
C(14)	0.5341 (9)	0.0863 (8)	0.1876 (9)	0.045 (2)
C(15)	0.6319 (10)	−0.0307 (9)	0.1681 (10)	0.057 (3)
C(16)	0.6234 (10)	−0.1235 (8)	0.2109 (10)	0.055 (3)
C(17)	0.5192 (9)	−0.1031 (8)	0.2745 (9)	0.042 (2)
C(18)	0.5044 (10)	−0.1947 (8)	0.3268 (10)	0.054 (3)
C(19)	0.4038 (10)	−0.1707 (8)	0.3874 (10)	0.053 (2)
C(20)	0.3024 (9)	−0.0497 (8)	0.4017 (9)	0.046 (2)
C(21)	0.1923 (10)	−0.0166 (9)	0.4615 (10)	0.056 (3)
C(22)	0.1032 (10)	0.0974 (9)	0.4702 (11)	0.062 (3)
C(23)	0.1198 (10)	0.1848 (9)	0.4148 (10)	0.057 (3)
C(24)	0.3136 (8)	0.0420 (7)	0.3503 (8)	0.036 (2)
C(25)	0.4248 (8)	0.0140 (7)	0.2878 (8)	0.035 (2)
N(10)	0.7631 (14)	0.1646 (12)	0.0923 (15)	0.110 (4)
O(1)	0.8401 (13)	0.1259 (11)	0.1959 (14)	0.160 (4)
O(2)	0.7705 (10)	0.0851 (9)	−0.0165 (11)	0.122 (3)
O(3)	0.6647 (15)	0.2495 (13)	0.0770 (14)	0.176 (5)
O(4)	0.7538 (8)	0.2866 (7)	0.4411 (8)	0.083 (2)
H(2)	0.4703	0.4118	0.3431	0.082
H(3)	0.4934	0.5438	0.2192	0.091
H(4)	0.3522	0.5698	−0.0060	0.084
H(6)	0.1528	0.5241	−0.2168	0.081
H(7)	−0.0002	0.4280	−0.3209	0.085
H(9)	−0.1153	0.2775	−0.2921	0.079
H(10)	−0.1203	0.1595	−0.1555	0.084
H(11)	0.0317	0.1452	0.0792	0.068
H(14)	0.5414	0.1535	0.1577	0.060
H(15)	0.7063	−0.0450	0.1252	0.070
H(16)	0.6889	−0.2052	0.1957	0.067
H(18)	0.5696	−0.2780	0.3163	0.070
H(19)	0.3973	−0.2360	0.4224	0.066
H(21)	0.1811	−0.0782	0.4981	0.067
H(22)	0.0283	0.1195	0.5140	0.076
H(23)	0.0519	0.2678	0.4190	0.070

[a] Standard deviations in parentheses. If no standard deviation is given, the parameter was not refined. Isotropic temperature factor of the form $\exp[-8\pi^2 U((\sin^2\theta)/\lambda^2)]$.

equatorial plane and large angles of 129.0° (C(1)–Cu–N(2)) and 132.4° (C(1)–Cu–N(3)) between the Cu–CN bond and the equatorial Cu–N bonds. The equatorial coordinating atoms are very close to coplanar, with the copper(II) ion lying only 0.03 Å below the best least-squares plane through the two cyanide atoms and the equatorial phenanthroline nitrogen atoms (see Table V). The remaining two phenanthroline nitrogen atoms, N(1) and N(4), are slightly removed from the "ideal" axial positions due to the small "bite" of the rigid bidentate phenanthroline ligands. The observed N–Cu–N bite angles of 79.9 and 80.7° are entirely normal for phenanthroline coordinated to copper(II).[15]

The bond lengths and angles involving the cyanide ion are all normal. The C–N bond length of 1.16 (1) Å is slightly longer than the observed C–N bond length in the dimeric $[Cu_2(tren)_2(CN)_2](BPh_4)_2$ (tren = 2,2′,2″-triaminoethylamine) of 1.13 Å[4] and very similar to the C–N bond lengths found in the hexacyanometalates of Mn(III) (C–N = 1.145 (6) Å), Fe(III) (1.148 (5) Å), and Co(III) (1.148 (5) Å).[16] The Cu–C(1) distance of 1.94 (1) Å found here compares favorably with the 1.97-Å distance found in the dimeric tren complex cited above.[4] The Cu–C(1)–N(5) system is linear (178 (1)°), as expected. The Cu–N(phen) bond lengths are within the normal range for binding to Cu(II).[15] The axial Cu–N bond lengths (2.00 (1), 2.01 (1) Å) are significantly shorter than the equatorial Cu–N bond lengths (2.102 (6), 2.123 (6) Å), in agreement with the pattern found in the pentachlorocuprate(II) anion.[17] However, this axial contraction may be due to other forces operating within the crystal and may not be a result of the influence of the $3d^9$ electronic distribution on the coordination geometry.[18]

As mentioned previously, a splitting in the ν_3 band of the nitrate ion has been interpreted[5] as indicating a weak interaction between the copper(II) ion and the nitrate ion, of the type referred to as "semicoordination." In the diagram of the unit cell and its contents (Figure 2) the nitrate ion is clearly well separated from the copper(II) ion. The origin of the infrared splitting lies, instead, in hydrogen bond formation between the water of hydration (O(4)) and atom O(1) of the nitrate anion, with the distance O(4)–O(1) = 2.83 (4) Å. This distance, being less than twice the oxygen van der Waals radius of 1.50 Å,[19] together with the observed nitrate splitting, strongly suggests the existence of a hydrogen bond between these two oxygen atoms. Similar distances have been observed in other H-bonded systems.[20] The O(4)–N(5) distance of 2.88 (2) Å and the O(1)–O(4)–N(5) angle of approximately 112° also strongly suggest the existence of a hydrogen bond between the water of hydration and the nitrogen atom of the coordinated cyanide. In the dimeric complex $[Cu_2(tren)_2(CN)_2](BPh_4)_2$ mentioned earlier,[4] hydrogen bonding between coordinated cyanide and hydrogen on one of the coordinated amine sites was established, with the N(H)···N distance being 3.05 Å. The C–N stretching frequency of 2136 cm^{-1} observed[5] for $[Cu(phen)_2CN](NO_3)\cdot H_2O$ is quite comparable to that observed in the H-bonded system of the dimeric tren complex (2140 cm^{-1}).

The position (axial or equatorial) of the cyanide ion in the trigonal-bipyramidal coordination geometry apparently does not control the relative lengths of axial and equatorial bonds for the other coordinating atoms and the pattern of angles in the equatorial plane. For example, in the complex $[Cu_2(tren)_2(CN)_2](BPh_4)_2$ (*vide ante*), cyanide occupies an axial position, leading to an axially compressed system and two angles greater than 120° in the equatorial plane. In the

Table II. Anisotropic Thermal Parameters (Å^2)[a]

Atom	10^4U_{11}	10^4U_{22}	10^4U_{33}	10^4U_{12}	10^4U_{13}	10^4U_{23}
Cu(II)	460 (6)	356 (6)	411 (6)	−156 (5)	133 (5)	55 (4)
N(1)	458 (46)	400 (43)	644 (54)	−153 (38)	240 (1)	19 (38)
N(2)	390 (41)	288 (37)	512 (45)	−92 (33)	201 (36)	16 (33)
N(3)	377 (41)	387 (40)	401 (42)	−121 (34)	93 (34)	82 (33)
N(4)	444 (44)	416 (43)	449 (45)	−168 (37)	130 (37)	87 (35)
C(1)	819 (76)	459 (62)	588 (70)	−166 (57)	179 (60)	233 (54)
N(5)	1997 (126)	636 (66)	630 (68)	−489 (76)	477 (76)	−67 (54)

[a] In the form $\exp[-2\pi^2(h^2a^{*2}U_{11} + \cdots + 2hka^*b^*U_{12} + \cdots)]$, with standard deviations in parentheses.

Table III. Bond Lengths (Å) and Angles (deg) Involving Cu(II)[a]

(a) Bond Lengths

Cu-N(1)	2.014 (10)	Cu-N(4)	2.001 (10)
Cu-N(2)	2.123 (6)	Cu-C(1)	1.935 (10)
Cu-N(3)	2.102 (6)	C(1)-N(5)	1.161 (13)

(b) Bond Angles

C(1)-Cu-N(2)	129.0 (3)	Cu-C(1)-N(5)	177.8 (13)
C(1)-Cu-N(3)	132.4 (3)	Cu-N(1)-C(2)	125.9 (7)
C(1)-Cu-N(1)	91.8 (5)	Cu-N(1)-C(13)	114.0 (7)
C(1)-Cu-N(4)	93.9 (5)	Cu-N(2)-C(11)	130.6 (7)
N(1)-Cu-N(2)	79.9 (3)	Cu-N(2)-C(12)	110.5 (6)
N(1)-Cu-N(3)	95.9 (3)	Cu-N(3)-C(14)	131.0 (6)
N(1)-Cu-N(4)	174.3 (3)	Cu-N(3)-C(25)	111.0 (6)
N(2)-Cu-N(3)	98.6 (2)	Cu-N(4)-C(23)	127.1 (6)
N(2)-Cu-N(4)	96.0 (3)	Cu-N(4)-C(24)	114.4 (7)
N(3)-Cu-N(4)	80.7 (3)		

[a] Standard deviations in parentheses.

Table IV. Bond Lengths (Å) and Angles (deg) for Ligands and Other Species[a]

(a) Bond Lengths

C(1)-N(5)	1.161 (13)		
N(1)-C(2)	1.332 (15)	N(3)-C(14)	1.323 (14)
N(1)-C(13)	1.349 (11)	N(3)-C(25)	1.365 (13)
C(2)-C(3)	1.420 (21)	C(14)-C(15)	1.403 (11)
C(3)-C(4)	1.308 (15)	C(15)-C(16)	1.351 (18)
C(4)-C(5)	1.385 (17)	C(16)-C(17)	1.393 (16)
C(5)-C(13)	1.440 (18)	C(17)-C(25)	1.383 (10)
C(5)-C(6)	1.421 (14)	C(17)-C(18)	1.431 (17)
C(6)-C(7)	1.253 (18)	C(18)-C(19)	1.326 (17)
C(7)-C(8)	1.468 (20)	C(19)-C(20)	1.446 (11)
C(8)-C(9)	1.392 (18)	C(20)-C(21)	1.390 (16)
C(8)-C(12)	1.441 (12)	C(20)-C(24)	1.405 (16)
C(9)-C(10)	1.303 (20)	C(21)-C(22)	1.334 (12)
C(10)-C(11)	1.421 (13)	C(22)-C(23)	1.415 (19)
N(2)-C(11)	1.319 (14)	N(4)-C(23)	1.326 (15)
N(2)-C(12)	1.351 (14)	N(4)-C(24)	1.345 (9)
C(12)-C(13)	1.403 (14)	C(24)-C(25)	1.431 (14)
N(10)-O(1)	1.169 (18)	N(10)-O(3)	1.148 (17)
N(10)-O(2)	1.255 (16)		

(b) Bond Angles

C(2)-N(1)-C(13)	120.0 (10)	C(14)-N(3)-C(25)	118.0 (6)
N(1)-C(2)-C(3)	120.6 (9)	N(3)-C(14)-C(15)	122.0 (10)
C(2)-C(3)-C(4)	118.4 (12)	C(14)-C(15)-C(16)	119.4 (11)
C(3)-C(4)-C(5)	124.9 (14)	C(15)-C(16)-C(17)	120.3 (8)
C(4)-C(5)-C(13)	114.1 (9)	C(16)-C(17)-C(18)	124.3 (8)
C(4)-C(5)-C(6)	131.0 (13)	C(16)-C(17)-C(25)	117.2 (10)
C(13)-C(5)-C(6)	114.8 (11)	C(25)-C(17)-C(18)	118.5 (9)
C(5)-C(6)-C(7)	127.5 (14)	C(17)-C(18)-C(19)	122.1 (8)
C(6)-C(7)-C(8)	120.6 (10)	C(18)-C(19)-C(20)	120.8 (11)
C(7)-C(8)-C(12)	115.9 (10)	C(19)-C(20)-C(21)	124.8 (11)
C(7)-C(8)-C(9)	128.1 (9)	C(19)-C(20)-C(24)	118.4 (10)
C(12)-C(8)-C(9)	116.0 (11)	C(24)-C(20)-C(21)	116.8 (8)
C(8)-C(9)-C(10)	122.2 (9)	C(20)-C(21)-C(22)	120.9 (12)
C(9)-C(10)-C(11)	119.4 (12)	C(21)-C(22)-C(23)	119.3 (11)
C(10)-C(11)-N(2)	121.9 (11)	C(22)-C(23)-N(4)	121.7 (8)
C(11)-N(2)-C(12)	119.0 (7)	C(23)-N(4)-C(24)	118.4 (9)
N(2)-C(12)-C(8)	121.5 (9)	N(4)-C(24)-C(20)	122.9 (9)
N(2)-C(12)-C(13)	117.6 (7)	N(4)-C(24)-C(25)	117.5 (9)
C(8)-C(12)-C(13)	121.0 (10)	C(20)-C(24)-C(25)	119.6 (7)
C(12)-C(13)-N(1)	117.8 (10)	C(24)-C(25)-C(17)	120.6 (9)
C(12)-C(13)-C(5)	120.2 (8)	C(24)-C(25)-N(3)	116.3 (6)
N(1)-C(13)-C(5)	122.0 (9)	N(3)-C(25)-C(17)	123.1 (9)
O(1)-N(10)-O(2)	112 (1)	O(2)-N(10)-O(3)	115 (1)
O(1)-N(10)-O(3)	131 (2)		

[a] Standard deviations in parentheses.

Table V. Deviations from Least-Squares Planes

(a) Deviations (Δ, Å) of Atoms from Ligand Planes[a]

Plane 1 ($n = 14$)		Plane 2 ($n = 14$)		Plane 3 ($n = 4$)	
Atom	Δ	Atom	Δ	Atom	Δ
N(1)	−0.005	N(3)	0.023	C(1)	−0.033
N(2)	0.036	N(4)	−0.034	N(5)	0.025
C(2)	−0.025	C(14)	0.037	N(2)	0.004
C(3)	−0.016	C(15)	−0.001	N(3)	0.005
C(4)	−0.003	C(16)	−0.031	Cu(II)	−0.027
C(5)	0.023	C(17)	−0.016	N(1)	1.952
C(6)	0.007	C(18)	−0.006	N(4)	−1.993
C(7)	−0.010	C(19)	0.016		
C(8)	0.006	C(20)	0.015		
C(9)	−0.022	C(21)	0.016		
C(10)	−0.025	C(22)	0.012		
C(11)	−0.001	C(23)	−0.023		
C(12)	0.017	C(24)	−0.005		
C(13)	0.018	C(25)	−0.003		
Cu(II)	0.126	Cu(II)	0.003		

(b) Equations of the Planes[b]

Plane	P	Q	R	S
1	−6.0915	5.4704	4.4200	0.9619
2	4.6171	3.0522	6.8296	3.9730
3	8.3367	9.7756	−6.5396	3.0556

[a] The first n atoms in each list generate the plane. [b] In the form $Px + Qy + Rz = S$.

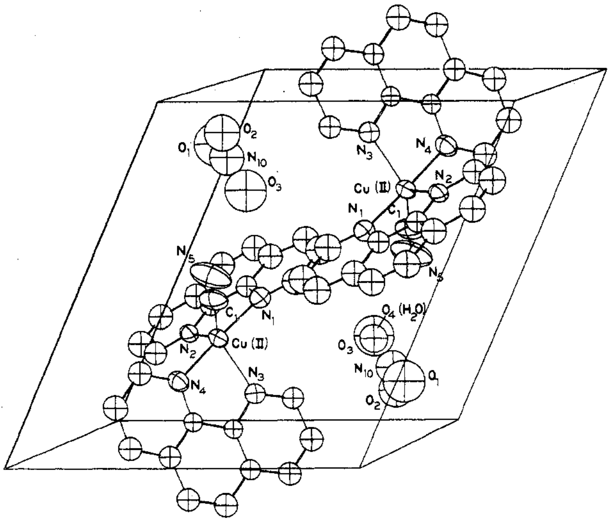

Figure 2. Unit cell of [Cu(phen)$_2$CN](NO$_3$)·H$_2$O. Origin in lower left-hand rear corner, with *a* horizontal, *b* vertical, and *c* coming out of the page toward the reader.

complex [Cu$_2$([14]-4,11-diene-N$_4$)$_2$CN](ClO$_4$)$_3$, where the cyanide ion bridges the two copper(II) ions directly, the cyanide occupies an equatorial position,[4] as it does in the monomeric [Cu(phen)$_2$CN](NO$_3$)·H$_2$O reported here. In the monocyano dimer, however, the axial Cu–N bonds were longer than the Cu–N equatorial bonds, in contrast to the monomer, which exhibits the "expected" axial compression. Also, the monomer exhibits two angles larger than 120° and one smaller than 120° in the equatorial plane, more like the tren dimer above than the monocyano dimer, which exhibits two small angles and one larger one. It appears that the rigidity of the other ligands and crystal forces are more important in establishing these patterns than the position of the cyanide ligand.

The geometries of the phenanthroline ligands and the nitrate counterion are satisfactory. The rigid phenanthroline rings are highly planar (see Table V), and the copper(II) ion is found in the plane of the N(3, 4) ligand and slightly out of the plane of the N(1, 2) ligand. The mean C–C bond distance in the two phenanthroline ligands is 1.39 (2) Å, while the mean C–N distance is 1.34 (1) Å, in good agreement with the results of earlier studies.[15,21] Intraligand angles average to the expected 120 (1)°. Thus, despite the size of the deviations from the average values for individual bonds and angles, the average configuration is very satisfactory. The mean N–O distance of 1.19 Å in the nitrate ion observed here is slightly shorter than earlier values[22] but must be considered satisfactory, and the O–N–O angles average to 119 (1)°.

The overall structure of the cation in [Cu(phen)$_2$CN]-

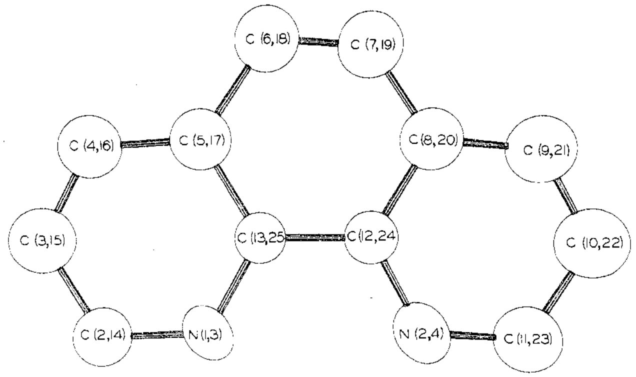

Figure 3. Numbering scheme for the phenanthroline ligands. Hydrogen atom numbers correspond to those of the carbon atoms to which they are bound.

$(NO_3){\cdot}H_2O$ is, as was suggested earlier, very similar to that of the compound $[Cu(bipy)_2I]I$,[7] where bipy = 2,2'-bipyridine. In that five-coordinate complex, iodide ion was stabilized in bonding directly to copper(II) and occupied the equatorial position in the trigonal-bipyramidal coordination sphere. The structures observed to date thus suggest that stable bonding of reducing ligands such as cyanide ion and iodide ion to copper(II) is associated with the formation of the relatively rare trigonal-bipyramidal coordination geometry about the cupric ion.

Acknowledgment. Computing funds for this work were supplied by the University of Michigan and the University of Michigan Computing Center. The Syntex diffractometer was purchased through NSF Grant No. GP18277. The author thanks M. Strumpel for helpful discussions.

Registry No. $[Cu(phen)_2CN](NO_3){\cdot}H_2O$, 53966-23-7.

Supplementary Material Available. Table VI, a listing of structure factor amplitudes, will appear following these pages in the microfilm edition of this volume of the journal. Photocopies of the supplementary material from this paper only or microfiche (105 × 148 mm, 24× reduction, negatives) containing all of the supplementary material for the papers in this issue may be obtained from the Journals Department, American Chemical Society, 1155 16th Street, N.W. Washington, D.C. 20036. Remit check or money order for $7.00 for photocopy or $2.00 for microfiche, referring to code number AIC40414F.

References and Notes

(1) F. A. Cotton and G. Wilkinson, "Advanced Inorganic Chemistry," 3rd ed, Wiley, New York, N.Y., 1972, p 907.
(2) A. Longo and T. Buch. *Inorg. Chem.*, **6**, 556 (1967).
(3) Y. M. Curtis and N. F. Curtis, *Aust. J. Chem.*, **19**, 609 (1966).
(4) D. M. Duggan, R. G. Jungst, K. R. Mann, G. D. Stucky, and D. N. Hendrickson, *J. Amer. Chem. Soc.*, **96**, 3443 (1974).
(5) M. Wicholas and T. Wolford, *Inorg. Chem.*, **13**, 316 (1974).
(6) B. J. Hathaway and D. E. Billing, *Coord. Chem. Rev.*, **5**, 143 (1970).
(7) G. A. Barclay, B. F. Hoskins, and C. H. L. Kennard, *J. Chem. Soc.*, 5691 (1963).
(8) (a) D. S. Brown, J. D Lee, B. G. A. Melson, B. J. Hathaway, I. M. Procter, and A. A. G. Tomlinson, *Chem. Commun.*, 369 (1967); (b) I. M. Procter, B. J. Hathaway, and P. Nicholls, *J. Chem. Soc. A*, 1678 (1968).
(9) Using the automated routines incorporated in the Syntex diffractometer package.
(10) Most of the calculations reported in this article made use of programs contained in "The X-RAY System–Version of June 1972," Technical Report TR-192 of the Computer Science Center, University of Maryland, June 1972. Exceptions were the use of the following programs: SYNOUT (*Lp* correction), CLS (a local version of ORFLS by J. W. Schilling for structure factor calculation and least-squares refinement), and ORTEP (Johnson's Oak Ridge thermal ellipsoid plotting program).
(11) "International Tables for X-Ray Crystallography," Vol. III, Kynoch Press, Birmingham, England, 1962.
(12) D. T. Cromer and J. Mann, *Acta Crystallogr., Sect. A*, **24**, 321 (1968).
(13) R. F. Stewart, E. Davidson, and W. Simpson, *J. Chem. Phys.*, **42**, 3175 (1968).
(14) D. T. Cromer, *Acta Crystallogr.*, **18**, 17 (1965).
(15) O. P. Anderson, *J. Chem. Soc., Dalton Trans.*, 1237 (1973).
(16) B. I. Swanson and R. R. Ryan, *Inorg. Chem.*, **12**, 283 (1973).
(17) K. N. Raymond, D. W. Meek, and J. A. Ibers, *Inorg. Chem.*, **7**, 1111 (1968).
(18) J. A. McGinnety, *J. Amer. Chem. Soc.*, **94**, 8406 (1972).
(19) A. Bondi, *J. Phys. Chem.*, **68**, 441 (1964).
(20) D. W. Lewis, K. T. McGregor, W. E. Hatfield, and D. J. Hodgson, *Inorg. Chem.*, **13**, 1013 (1974).
(21) B. P. Khare and R. Eisenberg, *Inorg. Chem.*, **9**, 2211 (1970); C. G. Pierpont and R. Eisenberg, *ibid.*, **9**, 2218 (1970).
(22) *Chem. Soc., Spec. Publ.*, **No. 11**, M141 (1958).
(23) "International Tables for X-Ray Crystallography," Vol. I, Kynoch Press, Birmingham, England, 1969, p 531.

Contribution from Dow Chemical U.S.A.,
Midland, Michigan 48640

Cyclomer Complexes. IV. Crystal Structure of a 1:1 Hexahydrate Complex of Magnesium Chloride with 1,4,7,10-Tetraoxacyclododecane

M. A. NEUMAN, E. C. STEINER, F. P. van REMOORTERE,* and F. P. BOER

Received July 12, 1974 AIC40465C

The crystal structure of $Mg(H_2O)_6Cl_2{\cdot}C_8H_{16}O_4$, where $C_8H_{16}O_4$ is 1,4,7,10-tetraoxacyclododecane, has been determined by a single-crystal X-ray diffraction study. This complex crystallizes in the monoclinic space group $C2/c$ with cell constants $a = 16.406 \pm 0.005$ Å, $b = 8.443 \pm 0.003$ Å, $c = 12.729 \pm 0.005$ Å, and $\beta = 93° 18' \pm 2'$, giving a calculated density of 1.432 g cm^{-3} for $Z = 4$. The intensities of 2006 independent reflections were measured using the θ–2θ scan mode of a Picker four-circle diffractometer and Mo Kα radiation. The structure was solved by Patterson and Fourier methods and all hydrogens were located. Full-matrix least-squares refinement, with the hydrogens assigned isotropic temperature factors and all heavier atoms anisotropic thermal parameters, converged to give an R factor of 3.5% for the 1646 reflections above background. The structure contains octahedral $Mg(H_2O)_6{}^{2+}$ units, very similar to those in $MgCl_2{\cdot}6H_2O$, located on crystallographic twofold axes. The Mg–O distances range from 2.054 to 2.082 Å with errors of 0.001–0.002 Å. Eight of the twelve water hydrogens form hydrogen bonds to six different chloride ions, which are located in tetrahedral holes, while the remaining four hydrogens of the $Mg(H_2O)_6{}^{2+}$ unit form hydrogen bonds to ether oxygens from four different cyclomer molecules. The $Mg(H_2O)_6{}^{2+}$ units and the chloride ions form two-dimensional layers, as do the 12-membered rings. The tetraoxacyclododecane molecule is situated on a crystallographic center of symmetry and has normal bond distances and angles.

Introduction

As part of a systematic effort[1-4] to determine the nature of the complexes formed between 1,4,7,10-tetraoxacyclododecane ($C_8H_{16}O_4$) and inorganic salts, we have performed an X-ray diffraction study of a hexahydrate complex formed by this novel ligand with $MgCl_2$. Previous work[1,2] has established that in the compounds $Na(C_8H_{16}O_4)_2Cl{\cdot}5H_2O$ and $Na(C_8H_{16}O_4)_2OH{\cdot}8H_2O$ the heterocycle adopts a C_4 conformation to form 2:1 octacoordinate complexes of overall D_4 (square-antiprismatic) symmetry. X-Ray powder diffraction