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Crystal and Molecular Structure of Cyano(2,2',2''-terpyridine)copper(II) Nitrate Monohydrate

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The crystal and molecular structure of cyano(2,2',2''-terpyridine)copper(II) nitrate monohydrate, [Cu(N₃C₁₅H₁₁)C-N](NO₃)·H₂O, has been determined from three-dimensional single-crystal x-ray diffraction data, collected by counter techniques. The blue-green crystals are monoclinic, space group $P2_1/c$ (No. 14), with four formula units in a unit cell of dimensions $a = 12.230$ (11) Å, $b = 7.742$ (6) Å, $c = 17.160$ (15) Å, and $\beta = 90.93$ (5)°. The structure was refined by full-matrix least-squares methods to an R of 0.069 ($R_w = 0.073$) for 1124 independent reflections with $F^2 > 3\sigma(F^2)$. The coordination geometry about the copper(II) ion is based on a distorted square pyramid. Three of the basal coordination positions are occupied by nitrogen atoms of the terpyridine ligand (Cu–N = 1.94 (1), 2.05 (1), 2.06 (1) Å), with the fourth position occupied by cyanide ion (Cu–C = 1.92 (2) Å). The copper(II) ion is displaced 0.26 Å out of the basal plane of four coordinating atoms, toward the nitrogen end (Cu–N = 2.21 (1) Å) of a cyanide bonded to a symmetry-related copper(II) ion. This extended interaction involving nonlinear (Cu–N–C = 164 (1)°) cyanide bridges between copper ions extends through the lattice along the crystallographic twofold screw axis.

Introduction

We have previously discussed[2] the intriguing aspects of the coordination chemistry of copper(II). Specifically, these include the variety of coordination geometries possible about copper(II), the subtle asymmetries induced in these geometries by the 3d⁹ electronic distribution, and the relative stabilities of the cupric and cuprous oxidation states.

The cyanide ion, which normally reduces the copper(II) ion to cuprous cyanide,[3] has been shown to engage in stable binding to the cupric ion, provided that the copper(II) is first protected against reduction by coordination of stabilizing ligands which prefer to bind to the metal in the dipositive oxidation state.[4,5] The structures of three complexes in which the cyanide ion is bonded directly to the cupric ion have been fully reported.[2,6,8] In the monomeric cyanobis(1,10-phenanthroline)copper(II) nitrate monohydrate,[2] the overall coordination geometry about copper(II) was found to be trigonal bipyramidal, with the cyanide ion occupying one of the equatorial sites. In that structure, the nitrogen end of the cyanide ligand was involved in hydrogen-bonding to the lattice water of hydration. In the dimeric complex [Cu₂A₂(CN)](ClO₄)₃ (A = 5,7,7,12,14,14-hexamethyl-1,4,8,11-tetraaza-cyclotetradeca-4,11-diene), cyanide was observed[6] to occupy an equatorial position in a trigonal-bipyramidal coordination geometry about each copper and to bridge the two cupric ions directly in a linear fashion. This bridging mode is generally accepted as normal for the cyanide ion, although other modes of bridging have occasionally been demonstrated.[7] Finally, in the complex [Cu₂(tren)₂(CN)₂](BPh₄)₂ (tren = 2,2',2''-triaminotriethylamine), each complex ion again exhibited trigonal-bipyramidal stereochemistry, with cyanide found to occupy an axial position in this case. The dimeric interaction in this last compound involved hydrogen bonds between the cyanide nitrogen and a hydrogen atom on a coordinated primary amine nitrogen of a second complex ion.[8]

As part of our continuing studies on the mode of binding of the cyanide ion to copper(II), we have synthesized the compound cyano(2,2',2''-terpyridine)copper(II) nitrate monohydrate. The most obvious possible coordination geometry for this complex, considering the known geometry of the terdentate 2,2',2''-terpyridine ligand (hereafter abbreviated as terpy), would involve square-planar coordination of the copper(II) ion, with bonding from the copper ion to the three nitrogen atoms of the terpy ligand and to the carbon atom of the cyano group. In view of the clear propensity already established for five-coordination at copper(II) when cyanide is involved in the bonding to the metal (vide supra) and in view of the well-established tendency of copper(II) to engage in the "4 + 1" mode of bonding,[9] it was considered to be quite possible that this complex might exhibit a five-coordinate, square-pyramidal structure, with water, or perhaps nitrate ion, occupying the out-of-plane coordination site at a long distance[10] from the copper(II) ion. Either of these possibilities would represent a new mode of participation for the cyanide ion in the copper(II) coordination sphere.

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, cyano(2,2',2''-terpyridine)copper(II) nitrate monohydrate.

Experimental Section

Synthesis of [Cu(terpy)CN](NO₃)·H₂O. A 0.25-g (1.07 × 10⁻³ mol) portion of 2,2',2''-terpyridine (terpy, purchased from G. F. Smith Chemical Co., Inc.) was dissolved in a 25-ml aqueous solution containing 0.24 g (1.05 × 10⁻³ mol) of Cu(NO₃)₂·3H₂O. Heating and stirring dissolved the terpy, with subsequent formation of a Cu^II–terpy complex. A 10-ml aqueous solution containing 0.070 g (1.07 × 10⁻³ mol) of KCN was added dropwise (with stirring) to the warm solution of the Cu^II–terpy complex. After filtration of the mixture while warm, the blue filtrate was allowed to cool slowly to room temperature. The resulting bluish green crystals were filtered, washed with distilled water, and dried over P₂O₅ for 24 h. The yield was 0.21 g (50%).

Characterization of [Cu(terpy)CN](NO₃)·H₂O. Analysis was performed by Galbraith Laboratories, Knoxville, Tenn. Anal. Calcd

for [Cu(N3C15H11)CN](NO3)·H2O: C, 47.70; H, 3.25; N, 17.39.
Found: C, 47.20; H, 3.11; N, 17.19.

Spectral characteristics are as follows: ν_{CN} 2171 cm^{-1} (Nujol mull, Perkin-Elmer 521); a single broad absorbance at 16 200 cm^{-1} in the visible–ultraviolet spectrum (Cary 14). The visible–uv spectrum was taken in Nujol also, due to the extreme insolubility of the compound in all common solvents.

Magnetic susceptibility is μ_{eff} = 1.98 μ_B at 24 °C (Faraday method, Hg[Co(SCN)4] as calibrant, Cahn Research magnetic susceptibility system).

Crystal Data. For [Cu(N3C15H11)CN](NO3)·H2O (mol wt 402.8, monoclinic) a = 12.230 (11) Å, b = 7.742 (6) Å, c = 17.160 (15) Å, β = 90.93 (5)°, V = 1624.5 Å^3, ρ_{obsd} = 1.64 g cm^{-3}, ρ_{calcd} = 1.65 g cm^{-3}, Z = 4, and $F(000)$ = 820; space group $P2_1/c$, Mo Kα radiation, λ_1 0.70930 Å, λ_2 0.71359 Å, μ(Mo K$_\alpha$) = 14.34 cm^{-1}.

Data Collection and Reduction. Preliminary Weissenberg and precession photographs revealed 2/m Laue symmetry and exhibited systematic absences: $h0l$, l = 2n + 1; 0$k0$, k = 2n + 1; consistent with the monoclinic space group $P2_1/c$ (No. 14).[11]

The crystal chosen for data collection was mounted on the En-raf-Nonius CAD-3 diffractometer, with the b axis nearly coincident with the diffractometer ϕ axis. The crystal was accurately centered, and the orientation matrix for data collection was obtained from least-squares calculations on the automatically determined[12] 2θ, χ, and ϕ settings of 20 reflections with 2θ values in the range of 20–32°. Measurement of the setting angles for 25 high-order reflections at 20 (±1)°C (positive and negative 2θ values were averaged for all 25) allowed calculation (by least-squares methods)[13] of the unit cell parameters reported above. The measured density reported was obtained by neutral buoyancy in chloroform–1,2-dibromoethane.

The intensities of 2648 unique reflections with 4.75° < θ < 25° were measured by θ–2θ scans, employing Zr-filtered Mo Kα radiation. At θ values less than 4.75°, reflections were cut off on the low-θ side by the beam stop. The scan range was 0.80 on either side of the calculated K$\bar{\alpha}$ peak position, with a constant scan rate of 10° min^{-1}. The number of scans for a given reflection varied according to the intensity, with weak reflections being scanned a maximum of 10 times. Background was counted at either end of the scan, for a total time equal to half of the scan time. The takeoff angle was 3.5°, and zirconium-foil attenuators were inserted automatically if the peak count rate exceeded 2500 counts s^{-1}. The intensity of one of the three reference reflections (0,0,10, 122, and $\bar{5}$00) was measured every 25 reflections. None of these controls showed any significant changes in intensity during the course of data collection.

Lorentz and polarization corrections were applied to the observed data. The standard deviation in the intensity for each reflection was calculated as[14]

$$\sigma(I) = [A + B + (gI)^2]^{1/2}$$

where A is the total scan count, B is the total background count, and I is the net intensity (scan minus background counts). The uncertainty parameter g was taken as 0.04. Reflections with $I > 3\sigma(I)$ were judged to be observed. The 1124 reflections which met this criterion were employed in the solution and refinement of the structure. An absorption correction was applied to these data,[13] employing a numerical Gaussian integration technique. For the crystal used for data collection, an elongated column of dimensions 0.05 mm ({102} → {$\bar{1}0\bar{2}$}) × 0.13 mm ({$\bar{1}01$} → {10$\bar{1}$}) × 0.46 mm ({010} → {0$\bar{1}$0}), extrema in the reciprocal transmission factor were 1.205 and 1.066 (2 × 2 × 4 sampling grid).

Solution and Refinement of the Structure. The position of the copper(II) ion was assigned from the double-intensity nonorigin peaks appearing in the Harker sections of the Patterson map. The positions of all nonhydrogen atoms were then obtained from a series of Fourier syntheses phased by the atoms in known positions. Scattering factors for copper(II), carbon, nitrogen, and oxygen were taken from ref 15. Scattering factors for spherically bonded hydrogen atoms[16] were also taken from ref 15, as were correction terms $\Delta f'$ and $\Delta f''$ for anomalous dispersion due to copper.

Three cycles of full-matrix least-squares refinement (on F) with isotropic thermal parameters for all atoms except copper(II), the cyanide ion, and the coordinating nitrogen atoms of the 2,2′,2″-terpyridine ligand, which were refined anisotropically, lowered R (=[$\sum \|F_o| - |F_c\| / \sum |F_o|$) from its initial value of 0.281 to 0.080 (unobserved values not included) and R_w (=[$\sum w(|F_o| - |F_c|)^2 /$

Table 1. Atomic Coordinates (Fractional) and Isotropic Thermal Parameters[a]

Atom	x	y	z	U, Å^2
Cu(II)	0.0092 (1)	0.0974 (2)	0.1485 (1)	
N1	0.1728 (9)	0.0523 (14)	0.1316 (7)	
N2	0.0314 (10)	0.1970 (14)	0.0462 (7)	
N3	−0.1497 (9)	0.1527 (13)	0.1174 (6)	
C20	−0.0142 (11)	−0.0728 (21)	0.2279 (9)	
N20	−0.0243 (9)	−0.1720 (16)	0.2765 (7)	
C1	0.2112 (10)	0.1183 (19)	0.0660 (8)	
C2	0.1305 (11)	0.2041 (18)	0.0141 (9)	
C3	−0.0590 (12)	0.2671 (17)	0.0061 (9)	
C4	−0.1620 (11)	0.2418 (18)	0.0518 (8)	
C5	−0.2359 (12)	0.1306 (20)	0.1636 (9)	
C6	−0.3382 (12)	0.1984 (21)	0.1384 (11)	
C7	−0.3479 (14)	0.2910 (23)	0.0733 (12)	
C8	−0.2587 (12)	0.3149 (19)	0.0279 (9)	
C9	−0.0439 (14)	0.3427 (17)	−0.0648 (10)	
C10	0.0605 (15)	0.3491 (18)	−0.0946 (8)	
C11	0.1471 (12)	0.2803 (18)	−0.0546 (9)	
C12	0.3208 (12)	0.1005 (24)	0.0486 (9)	
C13	0.3918 (12)	0.0194 (23)	0.0958 (9)	
C14	0.3528 (12)	−0.0468 (22)	0.1680 (10)	
C15	0.2413 (13)	−0.0270 (21)	0.1823 (9)	
N10	0.3767 (13)	−0.5235 (19)	0.1551 (9)	0.061 (4)
O10	0.2750 (10)	−0.5277 (16)	0.1558 (7)	0.073 (4)
O11	0.4273 (10)	−0.5662 (18)	0.2155 (8)	0.086 (4)
O12	0.4258 (11)	−0.4754 (18)	0.0996 (8)	0.091 (4)
O13(H2O)	0.3828 (10)	0.2312 (19)	0.3530 (7)	0.084 (4)
H5	−0.2276	0.0672	0.2128	0.058
H6	−0.4034	0.1768	0.1696	0.056
H7	−0.4177	0.3438	0.0598	0.069
H8	−0.2667	0.3794	−0.0203	0.053
H9	−0.1064	0.3898	−0.0935	0.055
H10	0.0713	0.4034	−0.1450	0.052
H11	0.2198	0.2872	−0.0762	0.045
H12	0.3468	0.1495	−0.0002	0.059
H13	0.4685	0.0064	0.0812	0.060
H14	0.4011	−0.1059	0.2038	0.065
H15	0.2120	−0.0703	0.2308	0.059

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

$\sum wF_o^2]^{1/2}$) from 0.320 to 0.086. The NUCLS refinement program minimizes $\sum w(|F_o| - |F_c|)^2$, where F_o and F_c are the observed and calculated structure amplitudes, respectively, and w is the weight (=$4F_o^2/\sigma^2(F_o^2)$). At this point a difference Fourier map clearly indicated the presence of the hydrogen atoms attached to the 2,-2′,2″-terpyridine ligand rings (electron densities 0.25–0.55 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 pronounced in the difference Fourier at this time and were not included in the structural model. Three final cycles of full-matrix least-squares refinement on all atoms other than hydrogen, with anisotropic thermal parameters for all atoms except those of the nitrate counterion and the oxygen of the water of hydration, reduced R to its final value of 0.069 and R_w to 0.073. On the final cycle of refinement, no shift in any parameter was greater than 10% of the standard deviation in that parameter. An extinction correction was not deemed necessary. A final difference Fourier map showed no peak higher than 0.57 e Å^{-3} and no depression lower than −0.43 e Å^{-3}.

Final atomic positional parameters and isotropic thermal parameters are listed in Table I. Anisotropic thermal parameters are listed 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 ligands and the nitrate anion are found in Table IV. In all cases, standard deviations reported include contributions from the standard deviations in the unit cell parameters and coordinate covariance.

Table II. Anisotropic Thermal Parameters (A²)ᵃ

Atom	10^3U_{11}	10^3U_{22}	10^3U_{33}	10^3U_{12}	10^3U_{13}	10^3U_{23}
Cu(II)	27 (1)	24 (1)	26 (1)	1 (1)	−1 (1)	3 (1)
N1	26 (6)	26 (8)	47 (8)	−2 (5)	−1 (6)	7 (6)
N2	40 (8)	18 (7)	29 (8)	−5 (6)	−10 (6)	−10 (5)
N3	30 (7)	31 (8)	26 (8)	−4 (5)	−7 (6)	7 (6)
C20	35 (9)	40 (11)	27 (9)	−15 (8)	14 (7)	2 (8)
N20	24 (7)	43 (8)	31 (8)	−6 (6)	9 (6)	−18 (7)
C1	18 (7)	36 (9)	34 (9)	−16 (8)	8 (7)	−20 (8)
C2	21 (8)	26 (8)	37 (10)	3 (7)	8 (8)	−9 (7)
C3	39 (9)	12 (7)	38 (9)	2 (7)	−14 (8)	−9 (7)
C4	31 (9)	25 (8)	37 (10)	−4 (7)	−2 (8)	−2 (8)
C5	33 (9)	42 (11)	55 (11)	−4 (8)	−11 (8)	2 (9)
C6	26 (9)	40 (10)	70 (13)	−6 (8)	−9 (9)	−17 (10)
C7	52 (12)	40 (11)	91 (16)	11 (10)	−31 (12)	−4 (11)
C8	34 (9)	32 (9)	45 (11)	4 (8)	−7 (8)	5 (8)
C9	60 (11)	20 (9)	43 (11)	−5 (8)	3 (9)	8 (7)
C10	78 (12)	34 (10)	17 (8)	−13 (8)	15 (9)	−12 (7)
C11	42 (10)	25 (9)	33 (10)	6 (8)	5 (8)	8 (7)
C12	48 (10)	44 (9)	47 (10)	−11 (11)	4 (8)	8 (11)
C13	36 (10)	61 (12)	48 (11)	3 (9)	5 (9)	−3 (9)
C14	31 (9)	62 (14)	72 (13)	16 (8)	−25 (9)	7 (10)
C15	39 (10)	62 (12)	40 (10)	15 (9)	−7 (8)	10 (9)

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

Table III. Bond Lengths (A) and Angles (deg) Involving Cu(II)ᵃ

(a) Bond Lengths

Cu–C20	1.920 (16)	Cu–N2	1.940 (12)
Cu–N20′	2.207 (14)	Cu–N3	2.052 (11)
Cu–N1	2.056 (11)		

(b) Bond Angles

C20–Cu–N1	98.0 (5)	N20′–Cu–N3	93.0 (4)
C20–Cu–N2	159.9 (5)	Cu–C20–N20	177.3 (13)
C20–Cu–N3	100.2 (5)	Cu–N20′–C20′	163.9 (12)
N1–Cu–N2	77.8 (5)	Cu–N1–C15	125.7 (10)
N1–Cu–N3	156.7 (5)	Cu–N1–C1	114.4 (9)
N2–Cu–N3	80.1 (5)	Cu–N2–C2	122.0 (10)
N20′–Cu–C20	98.8 (5)	Cu–N2–C3	118.5 (10)
N20′–Cu–N1	98.5 (4)	Cu–N3–C4	115.0 (9)
N20′–Cu–N2	101.2 (4)	Cu–N3–C5	124.8 (10)

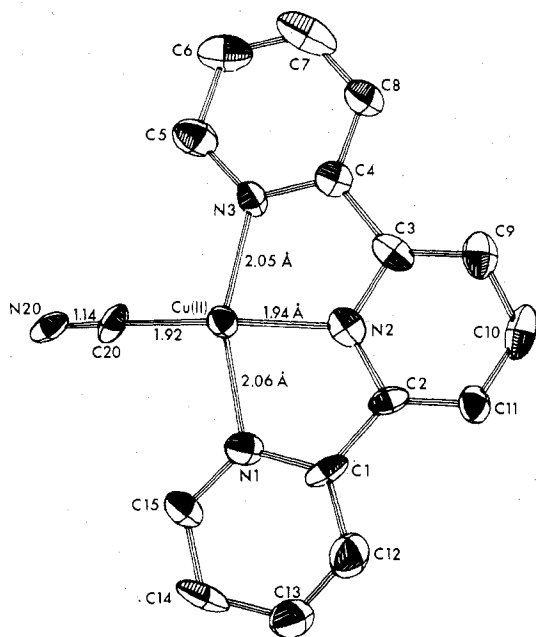ᵃ Standard deviations are in parentheses.

Figure 1. Coordination geometry of the [Cu(terpy)CN]⁺ unit. Hydrogen atoms have been omitted.

Figure 1 shows a view of the complex cation [Cu(terpy)-CN]⁺. At first glance, the coordination geometry seems to

Table IV. Bond Lengths (A) and Angles (deg) for Ligands and Other Speciesᵃ

(a) Bond Lengths

C20–N20	1.143 (16)	C9–C3	1.37 (2)
N1–C15	1.35 (2)	N2–C3	1.40 (2)
N1–C1	1.33 (2)	C3–C4	1.51 (2)
C1–C12	1.38 (2)	C4–C8	1.37 (2)
C12–C13	1.33 (2)	C8–C7	1.36 (2)
C13–C14	1.43 (2)	C7–C6	1.33 (2)
C14–C15	1.40 (2)	C6–C5	1.42 (2)
C1–C2	1.48 (2)	N3–C5	1.34 (2)
N2–C2	1.34 (2)	N3–C4	1.33 (2)
C2–C11	1.34 (2)		
C11–C10	1.36 (2)	N10–O10	1.25 (2)
C10–C9	1.38 (2)	N10–O11	1.24 (2)
		N10–O12	1.19 (2)
O13(H₂O)–O11	2.89 (2)		
O13(H₂O)–O12	2.94 (2)		

(b) Bond Angles

C15–N1–C1	120 (1)	C9–C3–N2	119 (1)
N1–C15–C14	122 (1)	C3–N2–C2	120 (1)
C15–C14–C13	117 (1)	N2–C3–C4	111 (1)
C14–C13–C12	118 (1)	C9–C3–C4	130 (1)
C13–C12–C1	123 (1)	C3–C4–C8	121 (1)
C12–C1–N1	120 (1)	C3–C4–N3	115 (1)
C12–C1–C2	124 (1)	N3–C4–C8	124 (1)
N1–C1–C2	116 (1)	C4–C8–C7	118 (1)
C1–C2–C11	128 (1)	C8–C7–C6	119 (2)
C1–C2–N2	110 (1)	C7–C6–C5	121 (2)
N2–C2–C11	122 (1)	C6–C5–N3	118 (1)
C2–C11–C10	119 (1)	C5–N3–C4	119 (1)
C11–C10–C9	121 (1)	O10–N10–O11	118 (2)
C10–C9–C3	119 (2)	O10–N10–O12	122 (2)
		O11–N10–O12	120 (2)

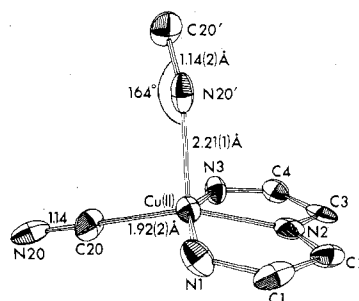ᵃ Standard deviations are in parentheses.

Figure 2. Square-pyramidal coordination environment of the copper(II) ion in the crystal. Only the connecting carbon atoms between the coordinating nitrogen atoms of the terpy ligand are shown.

be as expected, with approximate square-planar coordination about the metal ion. The true coordination geometry is seen in Figure 2, however. The cupric ion is clearly seen to be five-coordinate in this case, with approximate square-pyramidal geometry.

Four of the coordinating atoms do lie at the corners of a distorted square plane surrounding the cupric ion. Three of these four sites are occupied by nitrogen atoms of the 2,2′,-2″-terpyridine ligand. The two nitrogen atoms (N1 and N3) of the terminal pair of pyridine rings in the terpy ligand form bonds of equal length to the copper(II) ion (Cu–N1 = 2.06 (1) Å, Cu–N3 = 2.05 (1) Å). The nitrogen atom (N2) of the central pyridine ring is bonded to the cupric ion at a significantly shorter distance (Cu–N2 = 1.94 (1) Å), as a result of the constrained ligand geometry. This pattern of the two outer M–N bonds being longer than the middle M–N bond was also seen in the structure of bis(2,2′,2″-terpyridine)cobalt(II) bromide trihydrate,[17] where the mean Co–N(central) bond length was 1.89 (1) Å, and the mean Co–N(outer) bond

length was 2.10 (1) Å. This pattern of bond lengths is not seen when terpy is coordinated to larger cations such as tin(IV)[18] but appears from the above discussion to be typical of the constrained system that develops when terpy coordinates to the smaller dipositive first transition series ions. Other systems indicate the normality of these observed distances for strong Cu–N(pyridine) type bonding to copper(II). For example, similar bond lengths are observed in tris(2,2'-bi-pyridine)copper(II) perchlorate[19] (mean Cu–N distance for the four short equatorial bonds 2.031 (6) Å), in tris(1,10-phenanthroline)copper(II) perchlorate[20] (mean Cu–N distance for the four short equatorial bonds 2.04 Å), and in cyano-bis(1,10-phenanthroline)copper(II) nitrate monohydrate[2] (mean Cu–N(axial) = 2.00 Å, mean Cu–N(equatorial) = 2.11 Å). The cyanide carbon (C20) occupies the fourth position in this approximately square-planar array, with the copper to carbon bond appearing of normal length (Cu–C20 = 1.920 (16) Å). This bond length value for copper to cyanide carbon bonding may be compared with reported Cu–C bond lengths of 1.94 (1) Å in cyanobis(1,10-phenanthroline)copper(II) nitrate monohydrate[2] and 1.97 Å in [Cu₂(tren)₂(CN)₂]-(BPh₄)₂.[8] It is significantly shorter than the Cu–C bond length of 1.995 (4) Å in the cyanodiethylenetriaminecopper(II) complex ion, which has been the subject of a preliminary structural report.[21] Another long bond between copper(II) and cyanide carbon has been reported in the structure of μ-cyano-bis(5,7,7,12,14,14-hexamethyl-1,4,8,11-tetraaza-cyclotetradeca-4,11-diene)dicopper(II) perchlorate,[6] although here the bond length of 2.125 (3) Å reported is an average for the Cu–C(cyanide) and Cu–N(cyanide) bonding due to disorder in the linear bridging cyanide ion.

The angles in this square-planar array are distorted from the ideal square-planar angles, due in part to the constrained geometry of the chelating terpy ligand. The N–Cu–N(cis) angles are slightly unequal, and the values reported for N1–Cu–N2 (77.8 (5)°) and N3–Cu–N2 (80.1 (5)°) illustrate the typical small "bite" possible for this type of chelating ligand (compare the angle N–Cu–N of 80.4 (3)° in [Cu(bpy)₃]-(ClO₄)₂[19] and the mean of angles N–Cu–N(cis) of 79.2° in the [Co(terpy)₂]²⁺ cation[17]). The angles C20–Cu–N(cis) show the results of this constrained ligand geometry, both being significantly greater than 90° (C20–Cu–N1 = 98.0 (5)°, C20–Cu–N3 = 100.2 (5)°). The main element of the distortion, however, is clearly seen to be an out-of-plane displacement of the copper(II) ion (see Figure 2). This strong displacement, which puts the cupric ion 0.26 Å above the least-squares plane through the four square-planar coordinating atoms (C20, N1, N2, N3; see Table V), is attended by marked distortion of the angles at copper(II) involving trans ligands. The trans angle C20–Cu(II)–N2 is 159.9 (5)°, while the angle N1–Cu–N3 is found to be 156.7 (5)°. While both of these angles are seen to be greatly distorted from the 180° expected for a square-planar ligand array, it is felt that they represent a coordination geometry which is much closer to the square-planar case than to other alternatives.

The out-of-plane displacement of the copper(II) ion mentioned above is in the direction of the cyanide nitrogen atom (N20') of a cyanide ligand already bonded through carbon to another cupric ion. The Cu–N20' distance seen (see Figure 2), 2.207 (14) Å, is considerably longer than "normal" Cu–N bonds such as those quoted earlier but is well within the range usually taken as implying bonding in copper(II) complexes. It is considered normal, for example, to find the axial bond in a square-pyramidal coordination geometry about copper(II) to be 0.2–0.6 Å longer than the bonds in the equatorial plane.[22] In addition, it may also be pointed out that Cu–N bond distances of 2.2–2.4 Å are commonly taken as typical for "long" Cu–N bonds in Jahn–Teller distorted

Table V. Deviations from Least-Squares Planes

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

Plane 1 (n = 4)		Plane 2 (n = 6)		Plane 3 (n = 6)	
Atom	Δ	Atom	Δ	Atom	Δ
N1	0.07 (1)	N1	−0.01 (1)	N2	0.00 (1)
N2	−0.07 (1)	C1	0.01 (1)	C2	−0.01 (1)
N3	0.06 (1)	C12	0.00 (2)	C3	0.00 (1)
C20	−0.08 (1)	C13	−0.02 (2)	C9	−0.01 (1)
Cu(II)	0.26	C14	0.01 (2)	C10	0.00 (1)
N20	−0.26	C15	0.01 (2)	C11	0.01 (1)
		Cu(II)	0.06	Cu(II)	0.08

Plane 4 (n = 6)			Plane 5 (n = 4)	
Atom	Δ	Atom	Atom	Δ
N3	0.00 (1)	C7	0.01 (2)	N10	0.01 (1)
C4	−0.01 (1)	C8	0.01 (1)	O10	0.00 (1)
C5	0.02 (2)	Cu(II)	0.32	O11	0.00 (1)
C6	−0.02 (2)			O12	0.00 (1)

(b) Equations of the Planes[b]

Plane	A	B	C	D
1	1.5704	6.3099	9.6585	1.8045
2	2.2508	6.7372	7.7898	1.7753
3	1.8731	6.7962	7.7437	1.7510
4	2.6179	6.5094	8.4718	1.5983
5	0.3860	−7.2976	−5.7126	3.0697

(c) Dihedral Angles (deg) between Planes

Plane 1	Plane 2	Angle	Plane 1	Plane 2	Angle
1	2	7.65	2	3	1.83
1	3	7.46	2	4	3.33
1	4	6.43	3	4	4.78

[a] The first n atoms in each list generate the plane. Standard deviations are in parentheses. [b] In the form $Ax + By + Cz - D = 0$.

complexes of copper(II).[19,20] The Cu–N20' distance reported here of 2.207 (14) Å is much shorter than that reported in the structure of the cyanodiethylenetriaminecopper(II) complex ion (Cu–N(cyanide) = 2.348 (4) Å), where an asymmetric cyanide bridge has also been found to exist.[21]

This cyanide nitrogen thus completes the coordination sphere (no other atoms were found within 2.80 Å of the cupric ion position), the geometry of which is clearly (Figure 2) that of a distorted square pyramid, with N20' (cyanide nitrogen) at the apex and the cupric ion raised out of the basal plane toward the apical coordinating atom. The angles observed from N20' through copper(II) to the other coordinating atoms are very close to the typical 90° angles expected for this coordination geometry, with N20'–Cu–C20 = 98.8 (5)°, N20'–Cu–N1 = 98.5 (4)°, N20'–Cu–N2 = 101.2 (4)°, and N20'–Cu–N3 = 93.0 (4)°. The deviations from 90° clearly arise from the out-of-plane displacement of the copper(II) ion. This 0.26-Å deviation from the basal plane of coordinating atoms toward the axial ligand is typical, in both direction and magnitude, of copper(II) complexes with this coordination geometry.[22-25]

Although the angle from the copper(II) ion through the carbon-bonded cyano group is that expected for a linear metal–cyanide linkage (Cu–C20–N20 = 177.3 (13)°), the angle from the copper(II) ion through the nitrogen-bonded cyano group corresponds to a distinctly nonlinear bonding arrangement (Cu–N20'–C20' = 163.9 (12)°). This nonlinear cyanide bridge is extremely rare and represents one of the most intriguing aspects of this structure. Nonlinear cyanide bridges have been found in mixed-valence Cu(I)–Cu(II) complexes,[26,27] where Cu–C–N angles have been observed to range from 166.6 (4) to 175.1 (4)° and Cu–N–C angles to be in the range 159.7 (4)–174.6 (4)°. The nonlinear cyanide bridge observed here may also be directly compared to the dimeric cyano- and isocyanocobalt(III) systems recently studied by
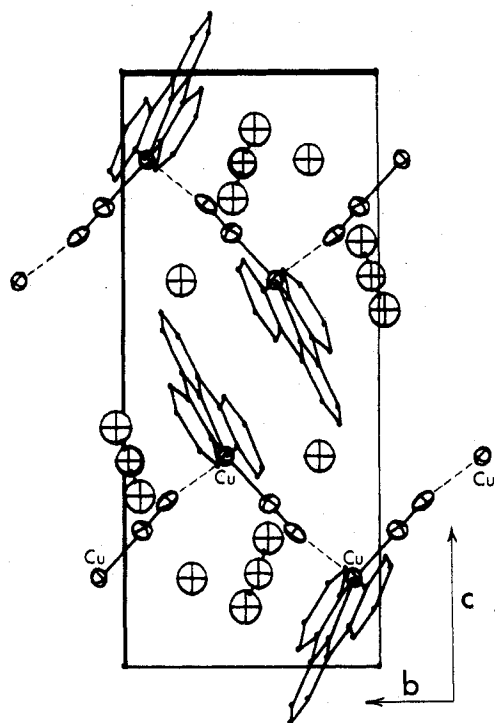
Figure 3. Projection, on the unit cell outline, of two interacting pairs of the polymeric [Cu(terpy)CN]$_n{}^+$ chains. Origin is in lower right-hand front corner, with axes defined as shown (right-handed system). Dashed lines indicate the Cu-N20' interaction.

Schaefer et al.[28,29] In these structural studies on the pentacyanocobalt(III)-μ-cyano-pentaamminecobalt(III) and the pentacyanocobalt(III)-μ-isocyano-pentaamminecobalt(III) complexes, distinctly nonlinear cyanide bridges between the cobalt(III) ions were found, with strong bending both at cyanide carbon and at cyanide nitrogen. The μ-cyano isomer provides the greatest degree of similarity to the copper(II) cyanide system reported here, as the angle Co-C-N was 172.4° and Co'-N-C was 159.8°. In this isomer also, the C-N(cyanide) distance was found to be 1.15 Å, in good agreement with the 1.14 (2) Å observed in the present copper(II) structure, and the cyanide stretching frequency was seen at 2180 cm^{-1} (cf. 2171 cm^{-1} for bridging CN$^-$ in the present study). It is not felt that there is any possibility of disorder in the cyanide bridge in this [Cu(terpy)CN]$^+$ system, as the final difference Fourier map does not indicate any appreciable residual electron density along the Cu-C-N-Cu' direction. The highest peaks in this final difference map are found in the immediate vicinity of the copper(II) ion and close to the positions expected for the hydrogen atoms of the water to nitrate oxygen hydrogen bonds (vide infra).

The nonlinear cyanide bridge observed here does not, however, give merely a dimeric interaction but instead gives rise to an extended polymeric chain running through the crystal. The individual complex ion links of the chain are related to one another by the crystallographic twofold screw axis. This extended interaction is shown in Figure 3, where the dashed lines indicate the bonding interaction between the cupric ion and atom N20' of another complex ion. In this figure, two pairs of interacting complex ions are seen, with the members of each pair being related to one another by the operation of the crystallographic twofold screw axis. For example, the cupric ion at (0.009, 0.097, 0.148) (lower right in Figure 3) is transformed by the crystallographic twofold screw axis running parallel to b at $x = 0$ and $z = {}^1/_4$ to the cupric ion at (-0.009, 0.597, 0.352). The cyanide of this second cupric ion is clearly seen to make a N20'-Cu bond to the first.

This pattern is then repeated, as the figure indicates, along this twofold screw axis (and along the axis at $x = 0$, $z = {}^3/_4$) throughout the crystal, to form the extended, cyanide-bridged polymeric chain alluded to above.

The geometry of the 2,2',2''-terpyridine ligand is satisfactory. The individual pyridine rings of the terpy ligand are highly planar, with all atoms of each ring within one standard deviation of the least-squares plane through the six ring atoms (see Table V). The ligand as a whole is not perfectly planar, with dihedral angles of 1.83 and 4.78° seen between the two outer rings of the ligand and the central ring. This sort of small dihedral twist motion is perfectly normal (indeed, perhaps a bit smaller than normal in this case) for a coordinated terpy ligand.[17,18] The mean bond distance for C-C bonds within the rings is 1.37 Å, for C-N bonds is 1.35 Å, and for C-C bonds (inter-ring) is 1.49 Å. These values may be compared with the corresponding values 1.38, 1.34, and 1.48 Å in the [Co(terpy)$_2$]$^{2+}$ system[17] and with the values 1.38, 1.34, and 1.48 Å in the Me$_2$(NCS)$_2$Sn(terpy) system.[18] The mean angle within the individual pyridine rings is the expected 120.0°, while the significant deviations from the expected 120° for angles such as N1-C1-C2 (116 (1)°) and C1-C2-N2 (110 (1)°) are common to other structures involving this type of ligand.[17-19]

The geometry of the nitrate counterion is also quite satisfactory, with the mean O-N-O angle found to be 120.0° and the mean N-O bond distance found to be 1.23 Å. These values are typical of the values found in other studies.[2,30] The nitrate ion is found to be highly planar (Table V). The position of the lattice water of hydration is such that it is capable of making simultaneous hydrogen bonds to oxygen atoms of two different nitrate groups. For example, the water oxygen O13 at (0.38, 0.23, 0.35) makes simultaneous hydrogen bonds to O11 of one nitrate ion (O11 at (0.43, 0.43, 0.22)) and to O12 of a second nitrate ion (O12 at (0.57, 0.02, 0.40)), as evidenced by calculated distances O13-O11 = 2.89 (2) Å and O13-O12 = 2.94 (2) Å. These distances, being significantly less than twice the oxygen van der Waals radius of 1.50 Å,[31] strongly suggest the existence of hydrogen bonds between these oxygen atoms. Similar distances have been observed in other H-bonded systems.[32] Further evidence in favor of this hydrogen-bonding system lies in the value of 111° calculated for the angle O11-O13-O12, which is quite close to the expected H-O-H angle, as indeed it must be if simultaneous hydrogen bonds as claimed above are to be reasonable.

The overall coordination geometry about copper(II) in this system falls within the normal pattern expected for five-coordinate cupric ion complexes based on the square-pyramidal coordination geometry, as explained above. Although a significant trans influence is expected for the cyanide ion in such a structure[33] and has been claimed to exist in similar complexes involving diethylenetriamine as ligand,[21,23] valid comparison data which would allow conclusions to be drawn on the existence of a corresponding trans influence in this system are lacking. The nonlinearity of the cyanide bridges between individual complex ion links in the extended polymeric chains running through the crystal lattice is not trivial to explain. It is felt to be highly likely that the nonlinearity of these cyanide bridges probably represents the best compromise available to the system between the geometric requirements of the bonding system about each copper(II) ion and the overall crystal packing requirements of this lattice, although specific packing interactions which would give rise to the necessity for this compromise cannot be demonstrated.

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Synthesis and Characterization of Cobalt(III) Complexes Containing a Coordinated Selenol. A Structural Trans Effect in (2-Selenolatoethylamine-N,Se)bis(ethylenediamine)cobalt(III) Nitrate

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The synthesis and characterization of (2-selenolatoethylamine-*N,Se*)bis(ethylenediamine)cobalt(III) and (2-selenolacetato-*O,Se*)bis(ethylenediamine)cobalt(III) salts are described. These complexes are the first well-defined examples of selenol coordination to cobalt(III). Coordinated selenols and thiols give rise to intense chalcogen-to-metal charge-transfer bands in the uv absorption spectra; the positions of these bands show that coordinated selenols are better reductants than the analogous coordinated thiols. A single-crystal x-ray structure analysis of the title compound shows that the average Co–N distance for those nitrogen atoms bonded cis to selenium is 1.971 (9) Å, whereas the trans Co–N length is 2.034 (2) Å. This corresponds to a ground-state trans effect, induced by the coordinated selenol, of 0.063 (9) Å which is larger than the 0.041 (10) Å effect of coordinated thiol in the analogous (2-thiolatoethylamine-*N,S*)bis(ethylenediamine)cobalt(III) ion. The influence of hydrogen bonding on the bond lengths and the conformation of the complex is discussed.

Introduction

Recent studies on the biochemical roles of selenium have indicated that this element is often associated with transition metals and electron-transfer processes.[1,2] The interactions between selenium (particularly as selenol) and transition metals are also of interest to us because of the periodic relationship between selenium and sulfur vis-a-vis recent reports on the remarkable properties of robust cobalt(III) and chromium(III) complexes containing coordinated thiols.[3] One particular property, the induction of a significant structural trans effect by thiolato sulfur in cobalt(III) complexes,[3d] may underlie several of the observed chemical and kinetic effects induced by coordinated sulfur.[3f-5] We therefore thought it worthwhile to probe the extent of the ground-state trans effect phenomenon in octahedral complexes by investigating selenol

analogues to the thiol complexes which exhibit both trans effects and unusual chemical properties. This paper describes the syntheses of two such complexes and the results of a single-crystal x-ray structure analysis of one of these compounds. To our knowledge these are the first well-defined selenolatocobalt(III) complexes to be reported.[6] Since these particular species are also robust and contain only "soft" Se and "hard" N and O as ligating atoms, they not only significantly extend the known types of selenol–metal complexes[7] but also provide useful models with which to probe biologically important selenium–metal interactions.

Experimental Section

General Data. Common laboratory chemicals were of reagent grade. Visible–uv spectra were recorded on a Cary 14 spectrophotometer at ambient temperature. Melting points (Thomas-Hoover apparatus)