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## Five- and Four-Coordinate Copper(II) Complexes of 2,2'-Bipyridine and Phenylcyanamide Anion Ligands: Crystal Structures, Cyclic Voltammetry, and Electronic Absorption Spectroscopy

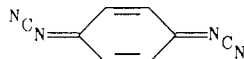
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A (bipyridine)copper(II) and seven bis(bipyridine)copper(II) complexes of phenylcyanamide anion ligands have been prepared and characterized by visible electronic and infrared spectroscopies and cyclic voltammetry. Crystal structures of the complexes [(bpy)<sub>2</sub>Cu(2,3-Cl<sub>2</sub>pcyd)][PF<sub>6</sub>] (**1**) and [(bpy)Cu(2,3-Cl<sub>2</sub>pcyd)] (**2**) are presented. For **1**, the coordination geometry around Cu(II) is shown to be a distorted square pyramid of nitrogen donor atoms in which the phenylcyanamide ligand occupies a basal coordination site. For **2**, the coordination geometry is distorted square planar. In both **1** and **2**, the anionic cyanamide group of the ligand (2,3-dichlorophenyl)cyanamide is shown to be nearly coplanar with the phenyl group due to strong  $\pi$  coupling and coordinated to copper(II) via the cyano nitrogen. Crystal data for **1**, C<sub>27</sub>H<sub>19</sub>N<sub>6</sub>F<sub>6</sub>PCl<sub>2</sub>Cu, are monoclinic crystal system and space group C2/c with  $a = 16.9094$  (21),  $b = 8.2073$  (7) Å,  $c = 40.224$  (4) Å,  $\beta = 94.485$  (9)°,  $V = 5565.2$  (10) Å<sup>3</sup>, and  $Z = 8$ . The structure was refined by using 3748 reflections with  $I > 2.5\sigma(I)$  to an  $R$  factor of 0.083. Crystal data for **2**, C<sub>24</sub>H<sub>14</sub>N<sub>6</sub>Cl<sub>4</sub>Cu, are monoclinic crystal system and space group P2<sub>1</sub>/n with  $a = 7.3244$  (16) Å,  $b = 40.200$  (4) Å,  $c = 16.1674$  (11) Å,  $\beta = 93.650$  (12)°,  $V = 4750.74$  (12) Å<sup>3</sup>, and  $Z = 8$ . The structure was refined by using 4838 Cu K $\alpha$  reflections with  $I > 2.5\sigma(I)$  to an  $R$  factor of 0.070. Crystal structure data, LMCT band intensity, and electrochemical potentials are compared with pentaammineruthenium(III) phenylcyanamide complexes. The results are consistent with a mostly  $\sigma$  bonding interaction between Cu(II) and the cyanamide anion group. The coordination chemistry of the copper(II) cyanamide complexes is relevant to an understanding of the mixed-valence state of copper in Cu(DCNQI)<sub>2</sub> molecular metals.

### Introduction

A new class of quinone derivatives, the *N,N'*-dicyanoquinone diimines (DCNQI), was recently synthesized by Aumuller and Hunig.<sup>1</sup>



These novel compounds are powerful acceptors and some charge transfer complexes of these compounds, having the stoichiometry M(DCNQI)<sub>2</sub>, show high electrical conductivity.<sup>2</sup> Indeed, the copper salt of the radical anion of 2,5-dimethyl-*N,N'*-dicyanoquinone diimine exhibited metallic conductivity down to 3.5 K with  $\sigma = 500\,000$  S cm<sup>-1</sup>.<sup>3</sup> Crystal structure data<sup>3,4</sup> indicate that the copper ions are interconnected by bridging DCNQI and that each copper ion is in a distorted tetrahedral environment coordinated by four cyanamide groups (-NCN). Segregated DCNQI  $\pi$  stacks are also revealed in the crystal lattice. Conductivity along  $\pi$  stacks has been observed in many other organic charge-transfer metals.<sup>5</sup> Examples of high conductivity in  $\pi$  acceptor stacks<sup>5</sup> are those in which each  $\pi$  acceptor molecule has a partial negative charge. The movement of electrons within a  $\pi$  stack can therefore occur without a Coulombic barrier. For this mechanism to operate in Cu(DCNQI)<sub>2</sub> molecular metals, copper must exist in a mixed-valence state and this is supported by low-temperature X-ray diffraction<sup>4b</sup> and XPS,<sup>2b</sup> which indicate an average oxidation state of 1.3 for Cu. Researchers have proposed that the mixed-valence state of copper arises from the direct coupling of copper d orbitals with radical anion DCNQI  $p\pi$  orbitals.<sup>2,3,6,7</sup>

In this study, we have synthesized and characterized by X-ray crystallography, visible absorption spectroscopy, and cyclic voltammetry copper phenylcyanamide complexes, in order to explore the nature of the interaction between copper(II) and the anionic cyanamide group. The results are compared to the coordination chemistry of ruthenium(III) phenylcyanamide complexes and the coordination environment of copper in Cu(DCNQI)<sub>2</sub> molecular metals.

### Experimental Section

**Equipment.** The equipment used to perform nonaqueous cyclic voltammetry and electronic absorption spectroscopy has been described in a previous paper.<sup>8</sup> Infrared spectra were obtained with a Perkin-Elmer

1600 series FTIR spectrophotometer.

**Materials.** Reagent grade cupric bromide, acetone, and acetonitrile (Anachemia), 2,2'-bipyridine (Aldrich), and ammonium hexafluorophosphate (Alfa) were used without further purification. Cu-(CF<sub>3</sub>SO<sub>3</sub>)<sub>2</sub>·*n*H<sub>2</sub>O (% Cu = 13.7)<sup>9</sup> was prepared by digesting copper metal turnings in triflic acid (Aldrich). Sephadex LH-20-100 was obtained from Sigma. Caledon HPLC grade acetonitrile, which had been dried with activated neutral alumina,<sup>10</sup> vacuum distilled, and stored over type 4A molecular sieves, was used in cyclic voltammetry experiments. Caledon HPLC grade acetonitrile and dimethylformamide (DMF) and spectrograde dichloromethane were used without further purification in the electronic absorbance measurements. Tetrabutylammonium hexafluorophosphate (TBAH) electrolyte (Aldrich) was recrystallized twice from ethanol/water and vacuum dried at 118 °C overnight. Elemental analysis was performed by Canadian Microanalytical Services, Ltd.

**Preparation of Phenylcyanamide Ligands.** The general preparation of neutral phenylcyanamide derivatives and their thallium salts is available in the literature.<sup>8,11,12</sup>

**Preparation of [(bpy)<sub>2</sub>CuBr][Br].** This complex has been prepared previously.<sup>13</sup> In our synthesis, 7.0 g of 2,2'-bipyridine was added to a

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boiling solution of 5.0 g of cupric bromide in 200 mL of distilled water. The blue color of the solution rapidly intensified as the product formed. The solution was allowed to cool in ice, resulting in green-blue needles of product which were filtered and washed with water and acetone. Yield: 10.5 g (88%).

**Preparation of [(bpy)<sub>2</sub>CuBr][PF<sub>6</sub>].** The procedure for the preparation of [(bpy)<sub>2</sub>CuBr][Br] was followed except that instead of allowing the reaction solution to cool, 4 g of ammonium hexafluorophosphate in 20 mL of water was added. The product immediately precipitated and was filtered and washed with water followed by ethanol. Yield: 13 g (97%).

**Preparation of [(bpy)<sub>2</sub>Cu(OH)<sub>2</sub>][CF<sub>3</sub>SO<sub>3</sub>]<sub>2</sub>.** The complex has been previously prepared as a S<sub>2</sub>O<sub>6</sub><sup>2-</sup> salt.<sup>14</sup> An aqueous solution of Cu-(CF<sub>3</sub>SO<sub>3</sub>)<sub>2</sub>·nH<sub>2</sub>O (10 g in 70 mL) was brought to a boil and then 7.2 g of 2,2'-bipyridine was added. After 5 min, the reaction solution was placed in an ice bath. The blue crystals that formed were washed with ice cold water and then air-dried. Yield: 12.5 g (84%). The coordinated water could be eliminated by recrystallization from ether diffusion into an acetone solution of the complex or by vacuum drying the complex at 120 °C for 48 h.

**Preparation of Copper Phenylcyanamide Complexes.** Two methods are presented that use either the neutral form of the phenylcyanamide ligand or its thallium salt.

**First Method. Preparation of [(bpy)<sub>2</sub>Cu(4-Cl)pcyd][PF<sub>6</sub>].** To a hot filtered solution of [(bpy)<sub>2</sub>CuBr][Br] (0.5 g in 70 mL of water) was added 0.1 g of potassium hydroxide, followed by 0.18 g of (4-chlorophenyl)cyanamide in 20 mL of acetone. While the reaction was heated to boil off acetone, a filtered solution of 4.5 g of ammonium hexafluorophosphate in 25 mL of water was slowly added. Almost immediately, a deep purple crystalline product formed. The hot reaction mixture was filtered and the product washed with water and ethanol and then vacuum dried at 118 °C for 3 h. Yield: 0.4 g (64%). Anal. Calcd for C<sub>27</sub>H<sub>20</sub>N<sub>6</sub>F<sub>6</sub>PClCu: C, 48.23; H, 3.00; N, 12.50; Cl, 5.27. Found: C, 48.56; H, 3.03; N, 12.62; Cl, 5.71.

**Second Method. Preparation of [(bpy)<sub>2</sub>Cu(2,3,5,6-Cl<sub>4</sub>)pcyd][PF<sub>6</sub>].** To a solution of 1.6 g of [(bpy)<sub>2</sub>CuBr][PF<sub>6</sub>] in 160 mL of acetonitrile was added 2.3 g of the thallium salt of anionic (2,3,5,6-tetrachlorophenyl)cyanamide, Tl(2,3,5,6-Cl<sub>4</sub>)pcyd. **Caution!** Thallium is extremely toxic. The reaction mixture was stirred for 16 h at approximately 45 °C, during which time the solution turned a deep brown. The solution was filtered from the thallium precipitate and the filtrate evaporated to dryness. The brown product was recrystallized by ether diffusion into an acetone solution of the product and then vacuum dried at 118 °C. Yield: 0.7 g (34%). Anal. Calcd for C<sub>27</sub>H<sub>17</sub>N<sub>6</sub>F<sub>6</sub>PCl<sub>4</sub>Cu: C, 41.80; H, 2.21; N, 10.83; Cl, 18.28. Found: C, 41.97; H, 2.34; N, 10.82; Cl, 18.66.

**Preparation of [(bpy)<sub>2</sub>Cu(2,4,5-Cl<sub>3</sub>)pcyd][PF<sub>6</sub>].** This complex was prepared by the second method. Yield: 30%. Anal. Calcd for C<sub>27</sub>H<sub>18</sub>N<sub>6</sub>F<sub>6</sub>PCl<sub>3</sub>Cu: C, 43.74; H, 2.45; N, 11.34; Cl, 14.35. Found: C, 43.70; H, 2.47; N, 11.24; Cl, 14.53.

**Preparation of [(bpy)<sub>2</sub>Cu(2,3-Cl<sub>2</sub>)pcyd][PF<sub>6</sub>].** This complex was prepared by the second method. Yield: 40%. Anal. Calcd for C<sub>27</sub>H<sub>19</sub>N<sub>6</sub>F<sub>6</sub>PCl<sub>2</sub>Cu: C, 45.88; H, 2.71; N, 11.89; Cl, 10.03. Found: C, 46.19; H, 2.87; N, 11.69; Cl, 10.33.

**Preparation of [(bpy)<sub>2</sub>Cu(2,6-Cl<sub>2</sub>)pcyd][PF<sub>6</sub>].** This complex was prepared by the second method. Yield: 35%. Anal. Calcd for C<sub>27</sub>H<sub>19</sub>N<sub>6</sub>F<sub>6</sub>PCl<sub>2</sub>Cu: C, 45.88; H, 2.71; N, 11.89; Cl, 10.03. Found: C, 46.04; H, 2.85; N, 11.93; Cl, 10.12.

**Preparation of [(bpy)<sub>2</sub>Cu(2-Cl)pcyd][PF<sub>6</sub>].** This complex was prepared by the first method and recrystallized by ether diffusion into an acetone solution of the complex. Yield: 55%. Anal. Calcd for C<sub>27</sub>H<sub>20</sub>N<sub>6</sub>F<sub>6</sub>PClCu: C, 48.23; H, 3.00; N, 12.50; Cl, 5.27. Found: C, 48.20; H, 3.01; N, 12.45; Cl, 5.75.

**Preparation of [(bpy)<sub>2</sub>Cu(3,4,5-MeO<sub>3</sub>)pcyd][PF<sub>6</sub>].** This complex could not be prepared pure. Attempts to prepare the complex using the first method yielded a product whose elemental analysis indicated an excess of PF<sub>6</sub><sup>-</sup>. The instability of the complex in solution precluded recrystallization. The best elemental analysis and cyclic voltammetry behavior were obtained with product prepared by the following procedure: to an aqueous solution of [(bpy)<sub>2</sub>Cu(OH)<sub>2</sub>][CF<sub>3</sub>SO<sub>3</sub>]<sub>2</sub> (1.0 g in 30 mL) at 60 °C was added an acetone solution of (3,4,5-trimethoxyphenyl)cyanamide (0.3 g in 30 mL). The pH of the blue solution was adjusted to 6.8 with 0.5 M NaOH. The resulting deep purple solution was concentrated to an oil, dissolved in acetonitrile, and placed on a Sephadex LH-20-100 column (dimensions were 25 cm by 2.2 cm diameter). The purple product band was rapidly eluted with CH<sub>3</sub>CN, leaving unreacted copper complex at the top of column. The eluent was concentrated to approximately 10 mL and ether added, precipitating the purple product. The product was filtered, washed with ether, and then vacuum dried over-

**Table I.** Crystal Data for [(bpy)<sub>2</sub>Cu(2,3-Cl<sub>2</sub>)pcyd][PF<sub>6</sub>] (**1**) and [(bpy)Cu(2,3-Cl<sub>2</sub>)pcyd]<sub>2</sub> (**2**)

	<b>1</b>	<b>2</b>
empirical formula	C <sub>27</sub> H <sub>19</sub> N <sub>6</sub> F <sub>6</sub> PCl <sub>2</sub> Cu	C <sub>24</sub> H <sub>14</sub> N <sub>6</sub> Cl <sub>4</sub> Cu
fw	700.42	519.77
cryst syst	monoclinic	monoclinic
space group	C2/c	P2 <sub>1</sub> /n
a, Å	16.9094 (21)	7.3244 (16)
b, Å	8.2073 (7)	40.200 (4)
c, Å	40.224 (4)	16.1674 (16)
β, deg	94.485 (9)	93.650 (12)
V, Å <sup>3</sup>	5565.2 (10)	4750.74 (12)
Z	8	8
ρ <sub>calcd</sub> , g/cm <sup>3</sup>	1.672	1.655
T, °C	22	22
radiation (λ, Å)	Cu Kα <sub>1</sub> (1.54056)	Cu Kα <sub>1</sub> (1.54056)
μ, cm <sup>-1</sup>	0.411	0.576
transmission coeff	0.324–0.550	
R factor <sup>a</sup>	0.083	0.070
R <sub>w</sub> factor <sup>a</sup>	0.084	0.053

$$^a R = \sum ||F_o| - |F_c|| / \sum |F_o|; R_w = (\sum w(|F_o| - |F_c|)^2 / \sum w|F_o|^2)^{1/2}.$$

night. Yield: 0.45 g (43%). Anal. Calcd for C<sub>31</sub>H<sub>27</sub>N<sub>6</sub>O<sub>6</sub>F<sub>3</sub>SCu: C, 50.85; H, 3.72; N, 11.48. Found: C, 47.58; H, 3.53; N, 10.41.

**Preparation of [(bpy)Cu(2,3-Cl<sub>2</sub>)pcyd]<sub>2</sub>.** This synthesis is a variation of the first method. To a hot filtered solution of [(bpy)<sub>2</sub>CuBr][Br] (2.0 g in 75 mL of water) was added a solution of (2,3-dichlorophenyl)cyanamide (1.4 g in 50 mL of acetone). Triethylamine (1.9 g) was then quickly added and almost immediately a black precipitate formed. The product was filtered and washed with water and ethanol and recrystallized from dimethylformamide/water solution. Yield: 1.4 g (63%). Anal. Calcd for C<sub>24</sub>H<sub>14</sub>N<sub>6</sub>Cl<sub>4</sub>Cu: C, 48.71; H, 2.38; N, 14.20; Cl, 23.96. Found: C, 48.70; H, 2.50; N, 14.28; Cl, 23.89.

**Crystallography Studies.** Deep brown rectangular prisms of [(bpy)<sub>2</sub>Cu(2,3-Cl<sub>2</sub>)pcyd][PF<sub>6</sub>] (**1**) were grown by the diffusion of ether into a concentrated acetone solution of the complex. Intensity data were collected on a Picker diffractometer using Cu Kα radiation (graphite monochromator). Data were corrected for decay, Lorentz-polarization effects, secondary extinction, and absorption. The structure was solved by direct methods and refined by cycles of least-squares calculations. Weights based on counting statistics were used. Hydrogen atom positions were calculated and included in structure factor calculations. The copper, chloride, nitrogen, phosphorus, and cyanamide carbon atoms were refined anisotropically. Other non-hydrogen atoms were refined isotropically. Merging R for **1** = 3.6% for 148 differences. All computations were carried out using the NRCVAX system of crystal structure programs.<sup>15a</sup> Scattering factors were taken from ref 15b.

In the original solution and refinement of **1**, the PF<sub>6</sub><sup>-</sup> was found to be disordered. Attempts to prepare the halide salts of this complex were unsuccessful and a triflate salt again showed disorder of the anion. During this time, the NRCVAX system of programs was expanded to include the possibility of group refinement. The resolution of the disordered PF<sub>6</sub><sup>-</sup> into two or more orientations seemed more feasible than the resolution of the CF<sub>3</sub>SO<sub>3</sub><sup>-</sup> disorder, so we returned to this structure. From earlier efforts of refinement, it was clear that more than one PF<sub>6</sub><sup>-</sup> orientation existed but that one was obviously prevalent. The top six peaks surrounding the phosphorus gave a convincing octahedron with reasonable P-F distances. This was fitted to a rigid group; a tetragonal bipyramid with a central atom. All P-F bonds were fixed at 1.58 Å. The remaining four major peaks were found to be coplanar with four of the original fluorines; i.e., the disorder of the octahedron was confined to the equatorial plane. These four peaks were fitted to an idealized square plane with no central atom. Complementary refinements were refined for the two sets of equatorial fluorines. The axial fluorines and phosphorus were assigned occupancies of 1. After refinement of the group origins and angles, the fluorines were allowed to refine anisotropically. The occupancies of the dominant equatorial fluorines were refined to 0.677.

Black rectangular prisms of [(bpy)Cu(2,3-Cl<sub>2</sub>)pcyd]<sub>2</sub> (**2**) were grown from a hot concentrated dimethylformamide/water solution that was allowed to slowly cool to room temperature. Data were collected on a Picker diffractometer using Cu Kα radiation and corrected for decay,

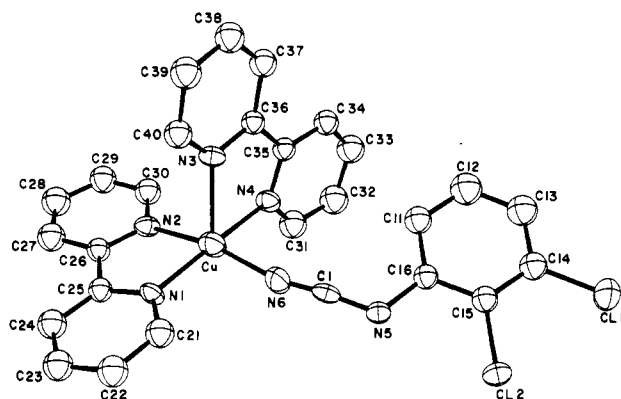
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**Table II.** Atomic Parameters and  $B_{iso}^a$  for  $[(bpy)_2Cu(2,3-Cl_2pcyd)] [PF_6] (1)$ 

	<i>x</i>	<i>y</i>	<i>z</i>	$B_{iso}^b$
Cu	0.04841 (6)	0.15347 (11)	0.109352 (24)	3.45 (4)
Cl1	-0.20044 (13)	0.3512 (3)	0.29652 (5)	4.28 (10)
Cl2	-0.12244 (15)	0.57193 (24)	0.24414 (5)	4.75 (11)
N1	0.1119 (3)	0.3242 (6)	0.08853 (13)	2.4 (3)
N2	0.0609 (3)	0.0473 (7)	0.06477 (13)	2.6 (3)
N3	-0.0247 (3)	-0.0206 (7)	0.12625 (13)	2.6 (3)
N4	0.1331 (3)	-0.157 (7)	0.13674 (13)	2.5 (3)
N5	-0.0425 (4)	0.3947 (7)	0.19342 (14)	2.9 (3)
N6	0.0231 (4)	0.2897 (7)	0.14662 (14)	3.7 (3)
C1	-0.0092 (4)	0.3327 (8)	0.16941 (16)	2.5 (3)
C11	-0.0713 (4)	0.1227 (9)	0.21450 (17)	3.19 (15)
C12	-0.1062 (5)	0.0298 (11)	0.23783 (19)	4.34 (19)
C13	-0.1467 (5)	0.0979 (10)	0.26264 (18)	3.92 (17)
C14	-0.1510 (4)	0.2667 (9)	0.26507 (17)	3.05 (15)
C15	-0.1150 (4)	0.3617 (9)	0.24207 (16)	2.75 (14)
C16	-0.0745 (4)	0.2939 (8)	0.21642 (16)	2.47 (13)
C21	0.1336 (4)	0.4686 (10)	0.10271 (17)	3.28 (15)
C22	0.1758 (5)	0.5836 (10)	0.08628 (18)	3.70 (17)
C23	0.1975 (5)	0.5500 (10)	0.05546 (18)	3.60 (16)
C24	0.1757 (4)	0.4021 (10)	0.04011 (18)	3.53 (16)
C25	0.1324 (4)	0.2900 (9)	0.05782 (16)	2.49 (13)
C26	0.1063 (4)	0.1311 (9)	0.04480 (16)	2.53 (13)
C27	0.1275 (5)	0.0676 (10)	0.01507 (18)	3.74 (17)
C28	0.0997 (5)	-0.0860 (10)	0.00530 (19)	4.22 (18)
C29	0.0552 (5)	-0.1707 (10)	0.02563 (18)	3.79 (17)
C30	0.0352 (4)	-0.1026 (9)	0.05502 (18)	3.37 (16)
C31	-0.1025 (5)	-0.0126 (10)	0.12081 (19)	3.89 (17)
C32	-0.1532 (5)	-0.1151 (10)	0.13690 (19)	4.25 (18)
C33	-0.1198 (5)	-0.2297 (10)	0.15930 (18)	3.89 (17)
C34	-0.0389 (4)	-0.2382 (9)	0.16466 (16)	2.94 (15)
C35	0.0082 (4)	-0.1333 (8)	0.14797 (15)	2.42 (13)
C36	0.0954 (4)	-0.1326 (8)	0.15319 (15)	2.38 (13)
C37	0.1384 (4)	-0.2462 (9)	0.17346 (17)	3.09 (15)
C38	0.2202 (4)	-0.2360 (10)	0.17675 (18)	3.56 (16)
C39	0.2580 (5)	-0.1181 (10)	0.16027 (18)	3.74 (17)
C40	0.2125 (4)	-0.0092 (9)	0.13997 (17)	3.14 (15)

<sup>a</sup> Estimated standard deviations are in parentheses. <sup>b</sup>  $B_{iso}$  is the mean of the principal axes of the thermal ellipsoid, Å<sup>2</sup>.

**Figure 1.** Plot of  $[(bpy)_2Cu(2,3-Cl_2pcyd)] [PF_6] (1)$  with atom number scheme. The  $PF_6$  anion has been omitted for clarity.

Lorentz-polarization effects, and secondary extinction. For the space group  $P2_1/n$ ,  $Z = 8$ , there are two crystallographically distinct molecules in the asymmetric unit. The copper positions were identified from a Patterson synthesis; other non-hydrogen atoms were located by using difference Fourier maps. Hydrogen atoms were included in idealized positions.

The structure was refined by least-squares calculations. Weights were based on counting statistics. Copper, chlorine, and nitrogen atoms were refined anisotropically and other non-hydrogen atoms were refined isotropically. Merging  $R$  for  $2 = 0.9\%$  for 1942 duplicates.

Crystal structure data and atomic coordinates and thermal parameters of significant atoms for **1** and **2** are given in Tables I, II, and III. Figure 1 shows the coordination geometry of the ligands about copper for **1** and the atom numbering scheme used to describe the corresponding bond lengths and bond angles in Table IV. The crystal structure of **2** showed two unique copper ions per unit cell (see Figures 2 and 3). Important

**Table III.** Atomic Parameters and  $B_{iso}^a$  for  $[(bpy)Cu(2,3-Cl_2pcyd)] (2)$ 

	<i>x</i>	<i>y</i>	<i>z</i>	$B_{iso}^b$
Cu1	0.30951 (19)	0.74381 (3)	0.21295 (7)	4.27 (7)
Cu2	0.86293 (20)	0.44400 (3)	1.02399 (8)	4.79 (7)
Cl1	0.2399 (4)	0.73974 (6)	-0.22917 (14)	4.57 (14)
Cl2	0.3685 (4)	0.80096 (7)	-0.33145 (14)	5.65 (16)
Cl3	0.1319 (4)	0.90025 (6)	0.02688 (15)	4.71 (14)
Cl4	-0.2790 (5)	0.91988 (8)	-0.00413 (20)	8.66 (21)
Cl5	0.5650 (4)	0.48691 (7)	0.61494 (14)	5.31 (15)
Cl6	0.1600 (4)	0.47526 (7)	0.55009 (15)	5.45 (15)
Cl7	0.6750 (4)	0.61967 (6)	1.01303 (14)	4.01 (13)
Cl8	0.4884 (4)	0.65375 (6)	0.85566 (16)	4.81 (14)
N1	0.3113 (12)	0.73909 (17)	0.0943 (4)	4.7 (5)
N2	0.2454 (11)	0.74989 (17)	-0.515 (4)	3.8 (4)
N3	0.2896 (11)	0.79215 (16)	0.2090 (4)	3.9 (4)
N4	0.1933 (10)	0.84053 (15)	0.1297 (4)	2.8 (3)
N5	0.3679 (9)	0.69532 (15)	0.2384 (4)	2.6 (3)
N6	0.2720 (9)	0.74312 (16)	0.3347 (4)	2.6 (3)
N7	0.7989 (12)	0.43537 (18)	0.9070 (4)	4.9 (5)
N8	0.6600 (11)	0.45985 (17)	0.7804 (4)	4.0 (4)
N9	0.7801 (12)	0.48963 (17)	1.0184 (5)	5.8 (5)
N10	0.7409 (12)	0.54834 (17)	0.9954 (4)	4.3 (4)
N11	0.9004 (10)	0.39519 (15)	1.0494 (4)	2.8 (4)
N12	0.9530 (10)	0.44733 (17)	1.1438 (4)	3.1 (4)
C1	0.2794 (13)	0.74670 (21)	0.0264 (5)	3.23 (19)
C2	0.2349 (13)	0.81487 (21)	0.1710 (5)	2.94 (19)
C11	0.2932 (12)	0.77843 (20)	-0.0939 (5)	2.82 (18)
C12	0.2994 (12)	0.77661 (19)	-0.1794 (5)	2.72 (18)
C13	0.3502 (13)	0.80381 (22)	-0.2261 (5)	3.43 (20)
C14	0.3915 (13)	0.83388 (22)	-0.1879 (5)	3.88 (21)
C15	0.3804 (13)	0.83562 (22)	-0.1025 (6)	4.04 (22)
C16	0.3340 (13)	0.80911 (21)	-0.0564 (5)	3.43 (20)
C21	0.0097 (12)	0.84899 (20)	0.1163 (5)	2.45 (17)
C22	-0.0369 (13)	0.87746 (20)	0.0680 (5)	2.94 (19)
C23	-0.2206 (14)	0.88580 (23)	0.0548 (5)	4.22 (23)
C24	-0.3521 (14)	0.86683 (23)	0.0866 (6)	4.51 (24)
C25	-0.3098 (15)	0.83910 (23)	0.1335 (6)	4.61 (24)
C26	-0.1264 (13)	0.83053 (21)	0.1484 (5)	3.34 (20)
C31	0.4081 (13)	0.67242 (22)	0.1815 (5)	3.54 (20)
C32	0.4432 (14)	0.63974 (22)	0.2049 (5)	3.96 (21)
C33	0.4333 (14)	0.63121 (23)	0.2864 (6)	4.49 (23)
C34	0.3939 (14)	0.65445 (22)	0.3441 (5)	3.91 (21)
C35	0.3607 (12)	0.68702 (20)	0.3191 (5)	2.71 (18)
C36	0.3117 (12)	0.71379 (20)	0.3734 (5)	2.51 (17)
C37	0.3049 (13)	0.71145 (21)	0.4574 (5)	3.69 (21)
C38	0.2509 (14)	0.73837 (22)	0.5032 (5)	4.15 (22)
C39	0.2067 (13)	0.76725 (21)	0.4637 (5)	3.66 (21)
C40	0.2207 (13)	0.76920 (21)	0.3796 (5)	3.53 (20)
C41	0.7240 (14)	0.44731 (23)	0.8491 (6)	3.81 (21)
C42	0.7594 (14)	0.51700 (24)	1.0032 (6)	3.85 (21)
C51	0.4775 (13)	0.45517 (21)	0.7547 (5)	3.13 (19)
C52	0.4208 (13)	0.46654 (20)	0.6751 (5)	3.01 (19)
C53	0.2361 (13)	0.46081 (21)	0.6469 (5)	3.53 (20)
C54	0.1191 (14)	0.44482 (23)	0.6950 (6)	4.42 (23)
C55	0.1724 (14)	0.43482 (22)	0.7739 (6)	4.32 (23)
C56	0.3504 (13)	0.44036 (21)	0.8038 (5)	3.42 (20)
C61	0.6422 (13)	0.56176 (21)	0.9270 (5)	3.17 (19)
C62	0.6092 (12)	0.59632 (20)	0.9272 (5)	2.90 (18)
C63	0.5184 (13)	0.61084 (20)	0.8575 (5)	3.20 (19)
C64	0.4576 (13)	0.59257 (22)	0.7902 (5)	3.66 (21)
C65	0.4831 (13)	0.55851 (22)	0.7906 (5)	3.97 (21)
C66	0.5750 (13)	0.54310 (21)	0.8587 (5)	3.59 (20)
C71	0.8639 (13)	0.37043 (22)	0.9943 (5)	3.88 (22)
C72	0.8888 (14)	0.33790 (22)	1.0177 (6)	4.17 (22)
C73	0.9551 (14)	0.33066 (22)	1.0964 (6)	4.10 (22)
C74	0.9957 (13)	0.35549 (21)	1.1528 (5)	3.45 (20)
C75	0.9650 (12)	0.38857 (20)	1.1265 (5)	2.55 (18)
C76	0.9982 (12)	0.41763 (20)	1.1803 (5)	2.68 (18)
C77	1.0680 (13)	0.41664 (21)	1.2613 (5)	3.67 (21)
C78	1.0919 (14)	0.44542 (23)	1.3057 (5)	4.34 (23)
C79	1.0443 (14)	0.47471 (22)	1.2685 (5)	4.20 (22)
C80	0.9759 (13)	0.47514 (21)	1.1866 (5)	3.61 (21)

<sup>a</sup> Estimated standard deviations are in parentheses. <sup>b</sup>  $B_{iso}$  is the mean of the principal axes of the thermal ellipsoid, Å<sup>2</sup>.

bond lengths and bond angles are given in Table V. Additional crystal structure data are available (see supplementary material).

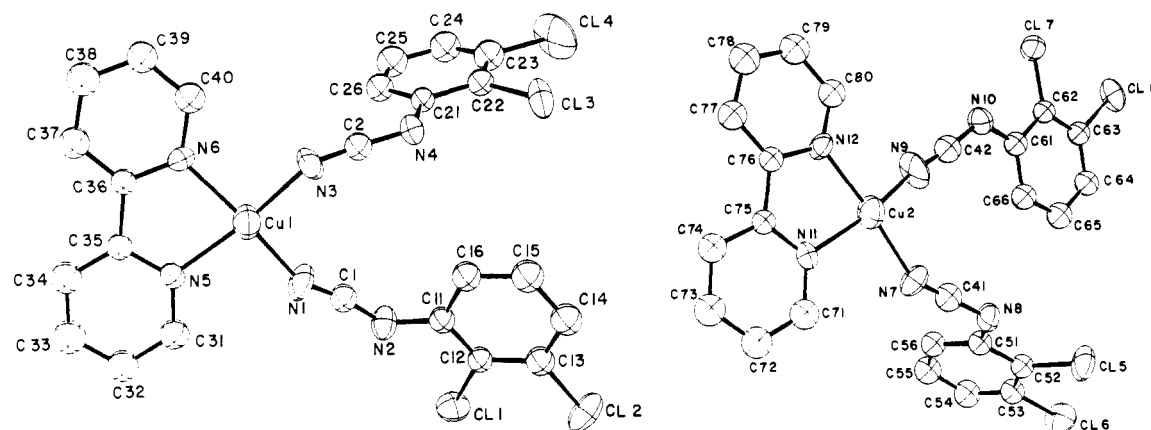


Figure 2. Plot of the two inequivalent configurations of  $[(\text{bpy})\text{Cu}(2,3\text{-Cl}_2\text{pcyd})_2]$  (2) with atom number scheme.

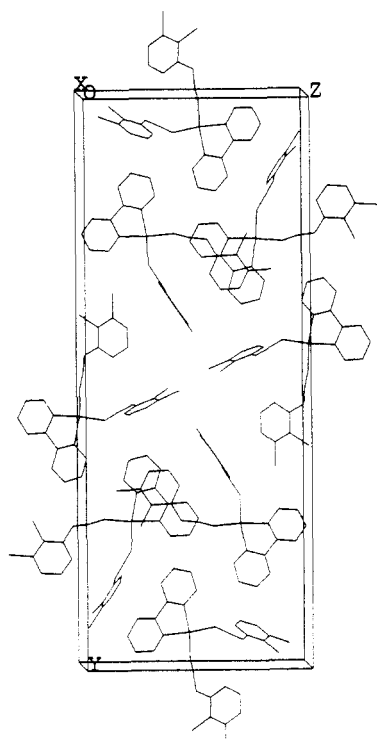


Figure 3. Packing diagram of the crystal unit cell of  $[(\text{bpy})\text{Cu}(2,3\text{-Cl}_2\text{pcyd})_2]$ .

Table IV. Selected Crystal Structure Data<sup>a</sup> for  $[(\text{bpy})_2\text{Cu}(2,3\text{-Cl}_2\text{pcyd})][\text{PF}_6]$

Bond Lengths, Å			
Cu-N1	1.989 (5)	Cu-N6	1.944 (6)
Cu-N2	2.020 (5)	N6-C1	1.159 (9)
Cu-N3	2.040 (5)	C1-N5	1.262 (9)
Cu-N4	2.224 (5)	N5-C16	1.382 (8)
Bond Angles, deg			
N1-Cu-N2	80.37 (22)	N3-Cu-N4	77.39 (21)
N1-Cu-N3	173.92 (22)	N3-Cu-N6	88.29 (24)
N1-Cu-N4	107.47 (21)	N4-Cu-N6	98.57 (24)
N1-Cu-N6	94.49 (23)	Cu-N6-C1	158.6 (6)
N2-Cu-N3	95.84 (22)	N6-C1-N5	174.0 (7)
N2-Cu-N4	93.59 (21)	C1-N5-C16	119.5 (6)
N2-Cu-N6	167.75 (25)		

Distances to the Phenyl Ring Plane of Cyanamide Atoms, Å  
 N6 -0.161 (16) C1 -0.112 (13) N5 -0.048 (11)

<sup>a</sup> Estimated standard deviations are in parentheses.

## Results and Discussion

There are many examples of four-, five-, and six-coordinate copper(II) complexes and this is a reflection of the general lability of the copper(II) ion.<sup>16a</sup> This property complicated the synthesis

Table V. Selected Crystal Structure Data<sup>a</sup> for  $[(\text{bpy})\text{Cu}(2,3\text{-Cl}_2\text{pcyd})_2]$

Bond Lengths, Å			
Cu1-N1	1.928 (7)	Cu2-N7	1.951 (7)
Cu1-N3	1.950 (6)	Cu2-N9	1.933 (7)
Cu1-N5	2.032 (6)	Cu2-N11	2.020 (6)
Cu1-N6	2.004 (6)	Cu2-N12	2.011 (6)
N1-C1	1.150 (11)	N7-C41	1.158 (12)
N2-C1	1.274 (11)	N8-C41	1.281 (11)
N2-C11	1.393 (11)	N8-C51	1.387 (12)
N3-C2	1.158 (11)	N9-C42	1.135 (12)
N4-C2	1.255 (11)	N10-C42	1.272 (12)
N4-C21	1.391 (11)	N10-C61	1.392 (11)
Bond Angles, deg			
N1-Cu1-N3	94.1 (3)	N7-Cu2-N9	93.9 (3)
N1-Cu1-N5	95.3 (3)	N7-Cu2-N11	92.6 (3)
N1-Cu1-N6	170.2 (3)	N7-Cu2-N12	171.9 (3)
N3-Cu1-N5	167.7 (3)	N9-Cu2-N11	165.9 (3)
N3-Cu1-N6	91.8 (3)	N9-Cu2-N12	93.7 (3)
N5-Cu1-N6	80.1 (3)	N11-Cu2-N12	80.6 (3)
Cu1-N1-C1	155.5 (7)	Cu2-N9-C42	165.3 (9)
Cu1-N2-C11	145.7 (7)	Cu2-N7-C41	141.4 (7)
N1-C1-N2	170.3 (9)	N7-C41-N8	172.6 (11)
N3-C2-C4	173.8 (10)	N9-C42-N10	173.1 (10)
C1-N2-C11	122.0 (7)	C41-N8-C51	119.8 (8)
C2-N4-C21	118.9 (7)	C42-N10-C61	120.6 (8)

Distances to the Phenyl Ring Plane of Cyanamide Atoms, Å			
N1	0.74 (2)	C1	0.37 (2)
N3	0.05 (2)	C2	0.04 (2)
N7	0.45 (2)	C41	0.23 (2)
N9	0.17 (2)	C42	0.04 (2)
N2	0.02 (1)	N4	0.01 (1)
N4	0.01 (1)	N8	0.07 (1)
N8	0.07 (1)	N10	-0.07 (1)

<sup>a</sup> Estimated standard deviations are in parentheses.

of bis(bipyridine)(phenylcyanamido)copper(II) complexes in aqueous solution. While the more basic phenylcyanamide ligands ( $(2\text{-Cl})\text{pcyd}^-$ ,  $(4\text{-Cl})\text{pcyd}^-$ , and  $3,4,5\text{-(MeO)}_3\text{pcyd}^-$ ) appeared to form, using the first method, bis(bipyridine) copper complexes, the same reaction with the more acidic phenylcyanamide ligands ( $2,3\text{-Cl}_2\text{pcyd}^-$ ,  $2,6\text{-Cl}_2\text{pcyd}^-$ , and  $2,4,5\text{-Cl}_3\text{pcyd}^-$ ) resulted in the elimination of a coordinated bipyridine ligand and the precipitation of the insoluble bis(phenylcyanamido)(bipyridine)copper(II) complexes. To prepare the bis(bipyridine)copper complexes of the more acidic phenylcyanamide ligands, a metathesis reaction (second method) was developed in which substitution under mild conditions of the coordinated bromide by the phenylcyanamide anion was driven to completion by the precipitation of TlBr. All of the bis(bipyridine)(phenylcyanamido)copper(II) complexes gave good elemental analyses and were stable in acetonitrile solution with the exception of  $[(\text{bpy})_2\text{Cu}(3,4,5\text{-(MeO)}_3\text{pcyd})][\text{CF}_3\text{SO}_3]$ . This complex could not be prepared pure due in part to its instability in nonaqueous solutions. Acetonitrile solutions of this

(16) Lever, A. B. P. *Inorganic Electronic Spectroscopy*, 2nd ed.; Elsevier Publishing Co.: Amsterdam, 1985: (a) p 554, (b) p 556, (c) p 776, and (d) p 175.

**Table VI.** Visible Electronic Absorption<sup>a</sup> and IR Data<sup>b</sup> for Bis(bipyridine)copper(II) Complexes of Anionic Phenylcyanamide Ligands (pcyd<sup>-</sup>) and the Complex [(bpy)Cu(2,3-Cl<sub>2</sub>pcyd)<sub>2</sub>]

no.	complex	LMCT( $\pi \rightarrow \sigma^*$ )	d-d transitions	$\nu(\text{NCN})$
1	[(bpy) <sub>2</sub> Cu(3,4,5-(OMe) <sub>3</sub> pcyd)] [PF <sub>6</sub> ]	541 <sup>c</sup>	730 <sup>c</sup>	2182 s <sup>d</sup>
2	[(bpy) <sub>2</sub> Cu(4-Cl)pcyd] [PF <sub>6</sub> ]	513 (1450) <sup>e</sup>	715 (640) <sup>e</sup>	2122 s <sup>d</sup>
3	[(bpy) <sub>2</sub> Cu(2-Cl)pcyd] [PF <sub>6</sub> ]	505 (1370) <sup>e</sup>	710 (540) <sup>e</sup>	2108 s <sup>d</sup>
4	[(bpy) <sub>2</sub> Cu(2,6-Cl <sub>2</sub> pcyd)] [PF <sub>6</sub> ]	484 (1410) <sup>e</sup>	709 (460) <sup>e</sup>	2149 w, 2109 s <sup>d</sup>
5	[(bpy) <sub>2</sub> Cu(2,3-Cl <sub>2</sub> pcyd)] [PF <sub>6</sub> ]	495 (1410) <sup>e</sup>	704 (490) <sup>e</sup>	2154 s, 2117 w <sup>d</sup>
6	[(bpy) <sub>2</sub> Cu(2,4,5-Cl <sub>3</sub> pcyd)] [PF <sub>6</sub> ]	494 (1720) <sup>e</sup>	702 (570) <sup>e</sup>	2155 s, 2125 s <sup>d</sup>
7	[(bpy) <sub>2</sub> Cu(2,3,5,6-Cl <sub>4</sub> pcyd)] [PF <sub>6</sub> ]	469 (1280) <sup>e</sup>	702 (350) <sup>e</sup>	2151 s <sup>d</sup>
	[(bpy)Cu(2,3-Cl <sub>2</sub> pcyd) <sub>2</sub> ]	508 (2270) <sup>f</sup> 480 (1900) <sup>g</sup>	642 (1920) <sup>f</sup> 666 (410) <sup>g</sup>	2134 s <sup>f</sup> 2112 s <sup>g</sup> 2181 s, 2136 s, 2110 s <sup>d</sup>

<sup>a</sup> In nm ( $\epsilon$  in M<sup>-1</sup> cm<sup>-1</sup> in parentheses). <sup>b</sup> In cm<sup>-1</sup>. <sup>c</sup> In acetonitrile solution this complex slowly decomposes. <sup>d</sup> Nujol mull between NaCl plates. <sup>e</sup> In acetonitrile. <sup>f</sup> In dichloromethane. <sup>g</sup> In DMF.

**Table VII.** Formal Reduction Potentials<sup>a</sup> of Bis(bipyridine)copper(II) Phenylcyanamide Complexes and Bromobis(bipyridine)copper(II)

anion ligand	Cu(II/I) <sup>b</sup>	Cu(I/0) <sup>c</sup>	L(0/-) <sup>d</sup>
3,4,5-(OMe) <sub>3</sub> pcyd	-0.056 (190)	-0.789	0.636
(4-Cl)pcyd	-0.007 (158)	-0.853	0.783
(2-Cl)pcyd	0.007 (194)	-0.776	0.941
2,6-Cl <sub>2</sub> pcyd	-0.013 (203)	-0.814	1.039
2,3-Cl <sub>2</sub> pcyd	0.020 (187)	-0.772	0.909
2,4,5-Cl <sub>3</sub> pcyd	-0.023 (192)	-0.859	1.021
2,3,5,6-Cl <sub>4</sub> pcyd	0.012 (170)	-0.867	1.075
Br	0.016 (106)	-0.619	1.033

<sup>a</sup> In volts vs NHE, at 25 °C. Cyclic voltammetry experiments were performed in 0.1 M TBAH acetonitrile solution, at a scan rate of 100 mV/s with a platinum disk (1.6 mm diameter) working electrode. <sup>b</sup> Quasi-reversible with the separation between anodic and cathodic peaks in parentheses in mV. <sup>c</sup> Irreversible, the position of the cathodic peak is indicated. <sup>d</sup> Irreversible, the position of the anodic peak is indicated.

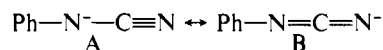
complex showed a slow decrease of visible LMCT band intensity with time, suggesting either ligand substitution with loss of 3,4,5-(OMe)<sub>3</sub>pcyd<sup>-</sup> or a chemical modification of the cyanamide anion group. The decomposition reaction was not investigated further. [(bpy)<sub>2</sub>Cu(3,4,5-(OMe)<sub>3</sub>pcyd)]<sup>+</sup> has a visible spectrum (Table VI) and cyclic voltammogram (Table VII) that are consistent with the other bis(bipyridine)(phenylcyanamido)copper(II) complexes and this gives confidence to its suggested formula.

The crystal structure of the complex [(bpy)<sub>2</sub>Cu(2,3-Cl<sub>2</sub>pcyd)] [PF<sub>6</sub>] (Figure 1 and Table IV) indicates that the coordination environment around Cu(II) is that of a distorted square pyramid of nitrogen donor atoms. This type of coordination geometry is unusual since crystal structures of bis(bipyridine)-copper(II) halogen complexes have generally shown a distorted trigonal bipyramid of donor atoms about copper(II).<sup>16b</sup> The distortion from trigonal bipyramidal geometry is largely due to the plasticity of the coordination sphere about Cu(II), which makes it susceptible to crystal packing forces. In one study,<sup>17</sup> simply changing the nature of the counteranion was enough to induce varying degrees of distortion toward square-pyramidal geometry for a series of five [(bpy)<sub>2</sub>CuCl]<sup>+</sup> salts. The crystal structure of [(bpy)<sub>2</sub>CuCl][ClO<sub>4</sub>] showed the greatest distortion of the five salts in which the chloride ligand together with three bipyridine nitrogens make up the basal plane about copper(II). It is interesting to note that the crystal structure of [(bpy)<sub>2</sub>Cu(2,3-Cl<sub>2</sub>pcyd)]<sup>+</sup> also shows the pseudohalide ligand, (2,3-dichlorophenyl)cyanamide anion, occupying a coordination site in the basal plane. The axial pyridine nitrogen N4-Cu bond of 2.224 (9) Å is considerably larger than that of the basal pyridine nitrogens and reflects preferred coordination in the basal plane.

The crystal structure of the complex [(bpy)Cu(2,3-Cl<sub>2</sub>pcyd)<sub>2</sub>] (Figure 2 and Table V) revealed two unique copper ions per unit cell (Figure 3) which differ significantly only in the manner the

phenyl groups of the (2,3-dichlorophenyl)cyanamide ligands are oriented relative to the (bipyridine)copper(II) moiety. The slight differences in bond lengths and angles (Table IV) between the two copper ions should be ascribed to crystal packing forces. The coordination environment around each Cu(II) ion is that of a distorted square plane of nitrogen donor atoms. This is in contrast to the Cu(II) coordination environment found in the crystal structure of the complex [(bpy)Cu(pcyd)<sub>2</sub>].<sup>18</sup> In this complex, one phenylcyanamide ligand is monodentate and the other is bidentate, bridging two copper ions via the cyano and amido nitrogens of the cyanamide group. In the solid state, this complex is more accurately described as a copper dimer in which each Cu(II) ion is surrounded by a distorted square pyramid of nitrogen donor atoms. In Figure 3, the packing diagram of the crystal unit cell of [(bpy)Cu(2,3-Cl<sub>2</sub>pcyd)<sub>2</sub>] clearly demonstrates that dimer formation does not occur for this complex. The reason why dimer formation does not occur in the crystal lattice of [(bpy)Cu(2,3-Cl<sub>2</sub>pcyd)<sub>2</sub>] may be due to the greater steric crowding of the chlorine atoms. Another possible explanation is that the inductive effect of the chlorine atoms makes the cyanamide group less basic and therefore a less effective bridging ligand.

The bond angle between a cyanamide group and a metal ion is largely determined by the resonance

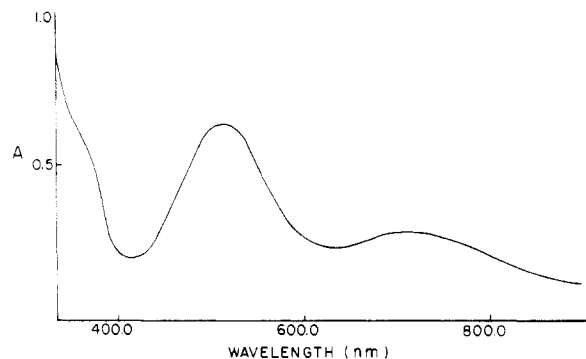


If only  $\sigma$  bonding interactions to the terminal cyanamide nitrogen are considered, resonance structure A will coordinate to a metal ion via the nitrile lone pair, resulting in an ideal bond angle of 180°. Coordination of resonance structure B to a metal ion ought to result in an ideal bond angle of 120°. In reality, the bonding description of the cyanamide group will have contributions from both resonance structures A and B and an expected coordination bond angle between 120 and 180°. Furthermore, coordination of the anionic cyanamide group to a strongly polarizing metal ion should increase the contribution of resonance structure B to the molecular orbital description of the cyanamide anion group, and if the metal ion has significant  $\pi$  acceptor properties, the preferred bond angle will be close to 180° in order to maximize the metal's interaction with the two terminal lone electron pairs of resonance structure B. In this regard, Ru(III), a strong  $\pi$  acceptor, has been shown<sup>11</sup> to coordinate to 2,3-Cl<sub>2</sub>pcyd<sup>-</sup> with a bond angle of 171.4 (10)°. Cu(II) has far weaker  $\pi$  acceptor properties compared to Ru(III) and, as shown in Tables IV and V, has Cu(II)-cyanamide bond angles between 141.4 (7) and 165.3 (9)°.

For [(bpy)Cu(2,3-Cl<sub>2</sub>pcyd)<sub>2</sub>], examination of the bond angles and lengths in Table V reveals that the two cyanamide ligands do not coordinate equivalently to Cu(II). Each copper ion has one cyanamide ligand that bonds in a more linear fashion (Cu1-N1-C1 = 155.5 (7) and Cu2-N9-C42 = 165.3 (9)°) and another whose coordination mode is more bent (Cu1-N2-C11 = 145.7 (7) and Cu2-N7-C41 = 141.4 (7)°). The Nujol mull IR spectrum of this complex shows multiple  $\nu(\text{NCN})$  bands (Table

(17) Harrison, W. D.; Kennedy, D. M.; Power, M.; Sheahan, R.; Hathaway, B. J. *J. Chem. Soc., Dalton Trans.* **1981**, 1556.

(18) Brader, M. L.; Ainscough, E. W.; Baker, E. N.; Brodie, A. M. *Polyhedron* **1989**, *8*, 2219.



**Figure 4.** Visible spectrum of  $[(bpy)_2Cu((4-Cl)pcyd)][PF_6]$ ,  $4.45 \times 10^{-4}$  M in acetonitrile.

VI), further illustrating the inequivalence of the cyanamide groups. However, in dichloromethane solution, the IR spectrum of this complex shows only a single  $\nu(NCN)$  at  $2134\text{ cm}^{-1}$ , suggesting that, in the absence of crystal packing forces, both phenylcyanamide ligands bind to copper(II) equivalently. Since linear coordination of Cu(II) to an anionic cyanamide group is not predicted based on the above discussion, we suggest that crystal packing forces prevent their both adopting the bent coordination mode in the crystal lattice.

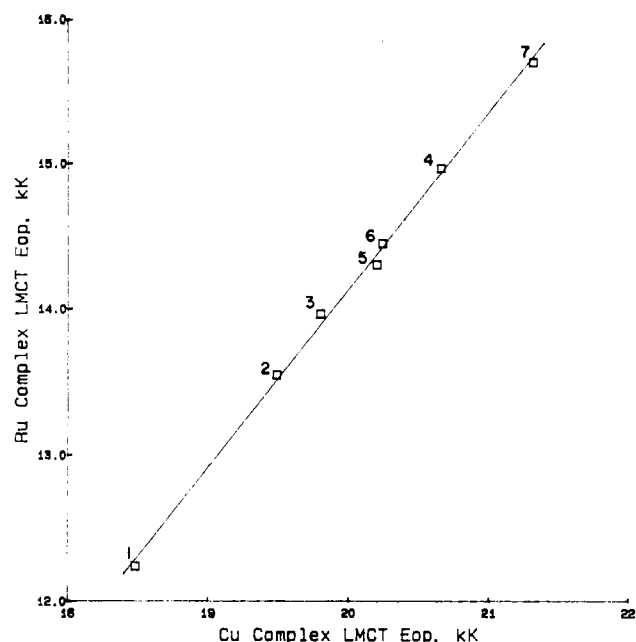
Free anionic phenylcyanamide ligands are expected to be planar in the absence of steric effects<sup>19</sup> due to the strong coupling of the cyanamide group with the phenyl ring  $\pi$  system. This interaction is apparently maintained upon coordination to Cu(II), as shown by the out of phenyl ring plane distances of the cyanamide atoms in Tables IV and V and the short bond lengths between cyanamide group nitrogen and phenyl ring carbon, indicating some double bond character. The ligand, (2,3-dichlorophenyl)cyanamide anion, has also been shown to retain planarity when coordinated to Ru(III).<sup>11</sup>

Crystal structures of a number of  $Cu(DCNQI)_2$  molecular metals have been performed,<sup>4c</sup> and it is of interest to contrast the coordination environment of the copper ion in these salts with this study. In these systems, copper occupies a distorted tetrahedron of terminal cyanamide nitrogens. Evidence<sup>2b,4b</sup> suggests that the oxidation state of copper is 1.3, requiring a partial negative charge to be assigned to each DCNQI. The copper–cyanamide bond angle at room temperature was shown to range from  $167.0$  (6) to  $177.6$  (5)°. This would indicate, based on the above discussion of the cyanamide resonance, that the resonance favors A. This is expected, since the two cyanamide groups of DCNQI share only a partial negative charge and its effect on the resonance will be less than that experienced by a fully anionic cyanamide group. The copper–cyanamide bond length at room temperature was shown to range from  $1.963$  (7) to  $1.988$  (5) Å. This bond range is only a little greater than that determined for Cu(II) bonded to anionic (2,3-dichlorophenyl)cyanamide, Tables IV and V. Future studies will provide information on Cu–cyanamide bond lengths as a function of copper oxidation state and cyanamide charge.<sup>20</sup> The distorted tetrahedral coordination environment of copper in  $Cu(DCNQI)_2$  molecular metals is consistent with its oxidation state of 1.3. Cu(I) is known to prefer tetrahedral geometry while Cu(II) complexes (i.e.  $[(bpy)Cu(2,3-Cl_2pcyd)_2]$ ) can undergo considerable tetragonal distortion.<sup>21</sup>

(19) We have determined the crystal structures of the tetraphenylarsonium salts of dianion 1,4-dicyanamidobenzene ( $Dicyd^{2-}$ ), 1,4-dicyanamido-2,3,5,6-tetrachlorobenzene ( $Cl_4Dicyd^{2-}$ ), and 1,4-dicyanamido-2,3,5,6-tetramethylbenzene ( $Me_4Dicyd^{2-}$ ): Aquino, M. A. S.; Lee, F. L.; Gabe, E. J.; Grodzan, J. E.; Crutchley, R. J. To be submitted for publication.  $Dicyd^{2-}$  and  $Cl_4Dicyd^{2-}$  are both planar molecules. However, for  $Me_4Dicyd^{2-}$ , the cyanamide groups are out of the phenyl ring plane and in an anti configuration relative to each other. It is probable that the steric repulsion of the methyl groups is enough to overcome the  $\pi$  interaction between the phenyl ring and the cyanamide groups.

(20) Work in progress.

(21) Rorabacher, D. B.; Martin, M. J.; Koenigbauer, M. J.; Malik, M.; Schroeder, R. R.; Endicott, J. F.; Ochrymowycz, L. A. In *Copper Coordination Chemistry: Biochemical and Inorganic Perspectives*; Adenine Press: New York, 1983; p 167.



**Figure 5.** Correlation of lowest energy LMCT transitions for the complexes  $[(NH_3)_5Ru(L)][ClO_4]_2$  (from ref 11) and  $[(bpy)_2Cu(L)][PF_6]$  in acetonitrile solutions. The phenylcyanamide ligand L is given by the number index in Table VI.

Researchers investigating the properties of  $Cu(DCNQI)_2$  molecular metals have suggested that the mixed-valence state of copper is obtained through the mixing of copper d orbitals and DCNQI  $p\pi$  orbitals.<sup>2,3,6,7</sup> The extent of this interaction will be reflected by the oscillator strength of the lowest energy LMCT band originating from the Cu(II)–cyanamide chromophore.<sup>22</sup> For this reason the visible electronic spectra of the copper complexes were investigated.<sup>23</sup> It has been shown that the  $\sigma$  and  $\pi$  donor properties of the cyanamide anion group can be “tuned” by varying the nature of the substituents on the phenyl ring.<sup>11</sup> Seven bis(bipyridine)copper(II) phenylcyanamide complexes were prepared to give a reasonable range of phenylcyanamide basicity.

The visible absorption spectral data of the (phenylcyanamido)bis(bipyridine)copper(II) complexes, in acetonitrile, are found in Table VI. A representative visible absorption spectrum of these complexes is illustrated by the spectrum of  $[(bpy)_2Cu((4-Cl)pcyd)][PF_6]$  (Figure 4). The spectrum shows two major bands and is in contrast to the visible spectrum of  $[(bpy)_2CuBr][PF_6]$ , which has only one broad absorption band at  $744\text{ nm}$  in acetonitrile. The low energy band at wavelengths  $>700\text{ nm}$  is suggested to originate from ligand field transitions, by analogy with  $[(bpy)_2CuBr][PF_6]$ .<sup>24</sup> This ligand field band (Table VI) shifts to slightly lower energies as the cyanamide ligand becomes a better  $\sigma$  and  $\pi$  donor. The high-energy band at wavelengths  $<550\text{ nm}$  shifts to higher energy as the number of electron-withdrawing substituents increases on the phenyl ring or as the donor number<sup>25</sup> of the solvent is increased. This behavior is consistent with a LMCT transition, which we have assigned to cyanamide anion  $p\pi \rightarrow d_{x^2-y^2}$  Cu(II).

In an analysis of the LMCT transitions of pentaammine-ruthenium(III) complexes of phenylcyanamide anion ligands, two LMCT transitions at approximately  $380$  and  $650\text{ nm}$  arose from

(22) The relationship between oscillator strength  $f$  and the extent of electronic coupling between donor and acceptor wavefunctions is given by the expression  $f \approx (1.085 \times 10^{-5})G\nu S^2 R^2$ , where  $G$  refers to the degeneracy of the states concerned,  $\nu$  is the energy, in  $\text{cm}^{-1}$  of the transition,  $R$  is the transition dipole length in Å and  $S$  is the overlap between donor and acceptor wavefunctions: Saleh, A. A.; Crutchley, R. J. *Inorg. Chem.* **1990**, *29*, 2132.

(23) The UV region was composed of overlapping phenyl and bipyridine  $\pi \rightarrow \pi^*$  transition as well as high-energy CT transitions.

(24) Elliott, H.; Hathaway, B. J.; Slade, R. C. *J. Chem. Soc. A* **1966**, 1443.

(25) Gutmann, V. *The Donor-Acceptor Approach to Molecular Interactions*; Plenum Press: New York, 1978.

two nondegenerate  $\pi$  nonbonding electron pairs on the cyanamide anion group.<sup>8,11</sup> For the bis(bipyridine)copper complexes, the high-energy LMCT  $p\pi \rightarrow d_{x^2-y^2}$  transition is probably buried under the ligand-centered transitions in the UV region. It should be possible to correlate the energies of the lowest energy LMCT bands of  $[(\text{NH}_3)_5\text{Ru}(\text{L})]^{2+}$  and  $[(\text{bpy})_2\text{Cu}(\text{L})]^+$  (where L is a phenylcyanamide anion ligand), provided the LMCT bands have the same origin. Figure 5 shows the correlation that is excellent ( $R = 0.999$ ). The slope of the line (1.22) is a measure of the greater sensitivity of the  $(\text{NH}_3)_5\text{Ru}^{\text{III}}$  moiety to the nature of the cyanamide ligand. This may not be due exclusively to the  $\pi$  acceptor properties of ruthenium(III), since the nature of the ligands and the coordination geometry have also changed in the correlation.

A number of linear correlations between charge transfer band energies and the difference between metal–ligand redox couples have appeared in the literature.<sup>26</sup> The working hypothesis has been to suggest that the energy of a photoinduced charge transfer event, in which a donor is oxidized and an acceptor is reduced, can be approximated by the difference between appropriate electrochemical couples.<sup>16c</sup> The electrochemical data in Table VII would appear to suggest that variation in LMCT energy is due largely to changes in the  $\text{L}(-/0)$  couple. A plot of  $[(\text{bpy})_2\text{Cu}(\text{L})]^+$  LMCT energies vs  $\text{L}(-/0)$  couples can be fitted to the linear relationship,  $\text{LMCT energy} = 0.62[\text{L}(-/0)] + 1.92$  in units of volts with  $R = 0.87$ . This fit is not as good as others in the literature and may be due to the irreversibility of the  $\text{L}(-/0)$  couple.

The intensity of the visible LMCT band of  $[(\text{bpy})_2\text{Cu}(\text{L})]^+$  complexes (Table VI) is significantly less than that found for  $[(\text{NH}_3)_5\text{Ru}(\text{L})]^{2+}$  complexes ( $\epsilon$  ranges from 5000 to 8000  $\text{M}^{-1} \text{cm}^{-1}$ ).<sup>11</sup> This is not surprising since the copper(II)  $d_{x^2-y^2}$  orbital has mostly  $\sigma^*$  character and the visible LMCT band of the copper complexes may be formally described as a forbidden  $2p\pi \rightarrow d\sigma^*$  transition. The low symmetry of the  $[(\text{bpy})_2\text{Cu}(\text{L})]^+$  complexes probably mixes some  $\pi$  character into the  $d_{x^2-y^2}$  orbital, reducing the forbiddenness of the LMCT transition.

The visible spectrum of  $[(\text{bpy})\text{Cu}(2,3\text{-Cl}_2\text{pcyd})_2]$  in dichloromethane consists of two bands at 508 ( $\epsilon = 2270 \text{ M}^{-1} \text{cm}^{-1}$ ) and 642 nm ( $1920 \text{ M}^{-1} \text{cm}^{-1}$ ), which we have assigned to  $p\pi \rightarrow d\sigma^*$  LMCT and ligand field transitions, respectively (Table VI). The apparent intensity of the ligand field band is somewhat misleading as it does overlap with the LMCT band. Nevertheless, taking this into account, the intensity of this band is still significantly greater than that of the  $[(\text{bpy})_2\text{Cu}(\text{L})]^+$  complexes. Ligand field bands are known to gain intensity by an intensity stealing mechanism involving charge transfer bands.<sup>16d</sup> It would appear for these systems that this mechanism is more important for copper(II) in a distorted square-planar geometry than a square-pyramidal geometry. For example, the coordination geometry of  $[(\text{bpy})\text{Cu}(2,3\text{-Cl}_2\text{pcyd})_2]$  is expected to be retained in dichloromethane but not in DMF (a strong donor solvent), where the coordination sphere of copper(II) is likely to expand to accommodate a DMF molecule. This perturbation in DMF solution results in a significant reduction in ligand field band intensity (Table VI).

The  $[(\text{bpy})_2\text{Cu}(\text{L})]^+$  complexes were found to have very similar cyclic voltammograms with the greatest variation associated with the oxidation of the phenylcyanamide ligand (Table VII). The cathodic voltammogram (Figure 6) of  $[(\text{bpy})_2\text{Cu}(4\text{-Cl}_2\text{pcyd})][\text{PF}_6]$  illustrates this general behavior. The Cu(II/I) reduction couple (Figure 6a) occurs at  $-0.007 \text{ V}$  vs NHE and has some reversible behavior as indicated by the equivalent current intensity of cathodic and anodic peaks. The irreversible character of this couple is shown by the large separation between anodic and cathodic peaks of 158 mV at 100 mV/s and the greater loss in current intensity of the anodic wave relative to the cathodic wave at slower scan rates. Since Cu(I) prefers to be four coordinate, the irreversibility of the Cu(II/I) couple may be due to the loss

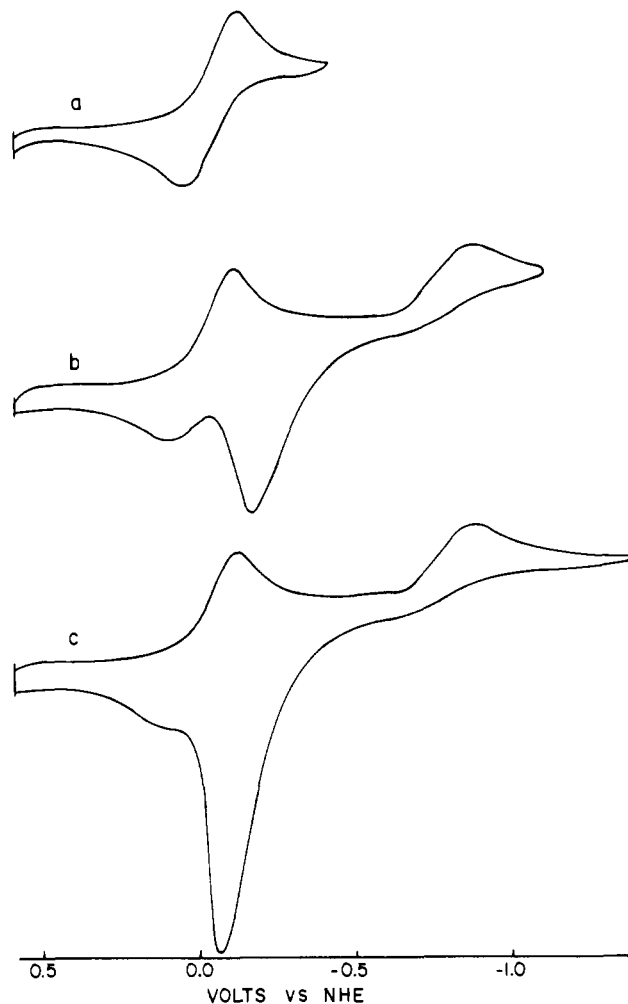


Figure 6. Cyclic voltammogram of the complex  $[(\text{bpy})_2\text{Cu}((4\text{-Cl})\text{pcyd})][\text{PF}_6]$ , 20 mM in acetonitrile at 100 mV/s scan rate using a platinum disk working electrode: (a) scan range 0.62 to  $-0.38 \text{ V}$ ; (b) scan range 0.62 to  $-1.07 \text{ V}$ ; (c) scan range 0.62 to  $-1.38 \text{ V}$ .

of the phenylcyanamide ligand. The Cu(II/I) reduction couples in Table VII are largely insensitive to the nature of the phenylcyanamide ligand even though the  $\sigma$  and  $\pi$  donor properties of this ligand vary significantly. In contrast, the Ru(III/II) reduction couple of  $[(\text{NH}_3)_5\text{Ru}(\text{L})]^{2+}$  complexes undergoes a modest cathodic shift as the basicity of the phenylcyanamide anion ligand increases.<sup>8,11</sup> This can be interpreted by the stabilization of Ru(III) oxidation state by strong  $\pi$  donors. Cu(II) has little  $\pi$  acid properties and so its oxidation state is largely indifferent to the  $\pi$  donor properties of its ligands.

If more cathodic sweeps are investigated (Figure 6b), an irreversible reduction wave appears at  $-0.853 \text{ V}$  vs NHE, which is assigned to the Cu(I/0) couple. The return anodic sweep results in the appearance of a large oxidation wave at approximately  $-0.05 \text{ V}$ . The current intensity of this anodic wave increases dramatically the longer the working electrode is at a more negative potential than the Cu(I/0) couple (compare Figure 6b and Figure 6c) and is clearly inconsistent with the diffusion controlled current intensity of the Cu(II/I) redox couple. The data strongly support electrode deposition of the Cu(I/0) reduction product followed by surface oxidation. This reaction fouls the electrode, which had to be cleaned for each sweep.

The anodic sweep showed only an irreversible wave at 0.783 vs NHE which is assigned to the cyanamide ligand  $\text{L}(0/-)$  couple. In comparison, the  $\text{L}(-/0)$  couples of  $[(\text{NH}_3)_5\text{Ru}(\text{L})]^{2+}$  complexes<sup>11</sup> are anodically shifted by approximately  $250 \pm 100 \text{ mV}$  relative to those of the corresponding  $[(\text{bpy})_2\text{Cu}(\text{L})]^+$  complexes. This may be due to the difference in metal ion oxidation states or the  $\pi$  acceptor properties of Ru(III). The range of  $\text{L}(0/-)$  couples (Table VII) of  $[(\text{bpy})_2\text{Cu}(\text{L})]^+$  complexes is a consequence

(26) For example see Curtis, J. C.; Sullivan, B. P.; Meyer, T. J. *Inorg. Chem.* **1983**, *22*, 224, and Dodsworth, E. S.; Lever, A. B. P. *Chem. Phys. Lett.* **1984**, *112*, 567. Erratum. *Ibid.* **1985**, *116*, 254.



of the coupling of the cyanamide group with the phenyl ring and the perturbation introduced by the nature of the phenyl ring substituents. It is to be expected that electron-withdrawing substituents will stabilize the anion ligand whereas electron-donating substituents will have the opposite effect.

In conclusion, the interaction of Cu(II) with phenylcyanamide anion ligands has been investigated. Crystal structure data, LMCT band intensity, and electrochemical potentials are consistent with a mostly  $\sigma$  bonding interaction between Cu(II) and the cyanamide anion group. Nevertheless, some  $\pi$  interaction must occur for the  $p\pi \rightarrow d_{x^2-y^2}$  transition to be partially allowed. This is relevant to the mechanism by which the mixed-valence state of copper in Cu(DCNQI)<sub>2</sub> molecular metals is achieved. In future studies,

we hope to more accurately model the coordination environment of copper in Cu(DCNQI)<sub>2</sub> molecular metals by preparing tetrahedral copper(I) and -(II) complexes of radical anion DCNQI molecules.

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**Supplementary Material Available:** Tables listing crystal data, atomic positional parameters, bond lengths, bond angles, anisotropic thermal parameters for non-hydrogen atoms, and least-squares planes and deviations therefrom for **1** and **2** (16 pages); structure factor tables for **1** and **2** (55 pages). Ordering information is given on any current masthead page.

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## A Homoleptic Uranium Thiolate: Synthesis, Structure, and Fluxional Behavior of [Li(dme)]<sub>4</sub>[U(SCH<sub>2</sub>CH<sub>2</sub>S)<sub>4</sub>] and Reaction with CS<sub>2</sub>

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We have synthesized and fully characterized a tetrakis(ethane-1,2-dithiolato)uranate(IV), [Li(dme)]<sub>4</sub>[U(edt)<sub>4</sub>] (**1**), the first homoleptic dithiolate complex of an f element. The complex crystallizes with an additional DME solvent molecule, and its structure was determined by an X-ray study. The coordination geometry about the uranium center is dodecahedral, and four lithium cations surround the [U(edt)<sub>4</sub>]<sup>4-</sup> anion. Each lithium bridges two sulfur atoms and is further coordinated by a dme molecule. We have analyzed the nature of the U-S bonds, using the extended Hückel method, to find that U 6d, 7s, and 7p orbitals are responsible for interactions with sulfur orbitals, thus, no significant U 5f participation in bonding is discernible, and that U-S  $\pi$  interactions are weak. The low-temperature <sup>1</sup>H NMR spectra in THF-*d*<sub>6</sub> exhibit four resonances associated with the edt protons. The relative size of their paramagnetic isotropic shifts can be interpreted on the basis of the pseudocontact (dipolar) term, the analysis of which suggests the solid-state dodecahedral structure to be retained in solution. According to the temperature dependence of the edt proton resonances, there are two fluxional processes, (1) a conformational change of the USSCS chelate rings and (2) an exchange of the A and B sites in the dodecahedral US<sub>8</sub> frame. The free energies of activation,  $\Delta G^\ddagger$ , are 9.3–9.6 kcal/mol and 12.9 kcal/mol, respectively, which are rather high probably due to coordination of lithium ions to sulfurs. The complex **1** reacts with CS<sub>2</sub> to give [Li(dme)<sub>2</sub>]<sub>2</sub>(S<sub>2</sub>CSC<sub>2</sub>H<sub>2</sub>SCS<sub>2</sub>) (**2**) as an isolable product. The crystal structure analysis of **2** reveals a zigzag form of the ethane-1,2-diyl bis(trithiocarbonate) skeleton and  $\eta^2$  coordination of each trithiocarbonate to a lithium. Crystal data: **1**, solvated by DME, monoclinic space group *P*2<sub>1</sub>/*n* with *a* = 11.330 (3) Å, *b* = 38.454 (8) Å, *c* = 11.047 (2) Å,  $\beta$  = 95.31 (2)°, *Z* = 4, *R* = 0.0538 for 3047 independent reflections; **2**, monoclinic space group *P*2<sub>1</sub>/*n* with *a* = 8.827 (3) Å, *b* = 15.191 (8) Å, *c* = 13.304 (8) Å,  $\beta$  = 107.13 (4)°, *Z* = 2, *R* = 0.0503 for 1581 independent reflections.

### Introduction

In contrast to the extensive coordination chemistry of actinide metal ions with oxygen donors,<sup>1</sup> development of their chemistry with S-donor ligands is limited. Some (thiocarbamato)- and (dithiocarbamato)uranyl complexes,<sup>2</sup> (dithiaacetato)uranyl complexes,<sup>2h</sup> a dmsO adduct of uranyl,<sup>2i</sup> tetrakis(dithiocarbamato) and tetrakis(dithiophosphinato) complexes of thorium and/or neptunium,<sup>3</sup> a pentasulfido complex of bis(pentamethylcyclopentadienyl)thorium,<sup>4a</sup> a series of binary and ternary uranium sulfides,<sup>4b-c</sup> and an intriguing  $\eta^2$ -disulfide complex of uranyl<sup>2c</sup> have been structurally characterized. Recently the reactions of tris-(cyclopentadienyl)uranium(III) with CS<sub>2</sub> and SPPH<sub>3</sub> (or COS) were reported to form the tetravalent binuclear uranium complexes consisting of CS<sub>2</sub> and S atom bridges, respectively.<sup>5</sup> Although synthesis of the pyrophoric U(SEt)<sub>4</sub> and U(S<sup>i</sup>Bu)<sub>4</sub> was reported as early as 1956,<sup>6a</sup> actinide thiolate complexes have been virtually ignored,<sup>6b-c</sup> in spite of the fact that thiolates may be useful for the separation of actinide ions from dilute aqueous solution.<sup>6d</sup> This is somewhat surprising in light of the richness of d-transition-metal thiolate chemistry that has been developed partly due to its biological and catalytic implication.

As an outgrowth of our recent studies on alkanedithiolate complexes of group 5 metals,<sup>7a-f</sup> we are interested in the behavior of dithiolate ligands with other electron-deficient metals. Here

we report the synthesis, X-ray structure, and variable-temperature <sup>1</sup>H NMR study of a tetrakis(ethane-1,2-dithiolato) (edt) complex

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