Synthetic, Spectroscopic, and *X*-Ray Crystallographic Studies on Phenylcyanamidocopper(II) Complexes. The Characterization of Three Different Co-ordination Modes for Phenylcyanamide Anions *

Mark L. Brader, Eric W. Ainscough, Edward N. Baker, Andrew M. Brodie, and Scott L. Ingham
Department of Chemistry and Biochemistry, Massey University, Palmerston North, New Zealand

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Phenylcyanamidocopper(II) complexes of the type $[\{CuL(L')_2\}_2]$ [L = 2,2′-bipyridine (bipy) or 1,10-phenanthroline (phen), L′ = a phenylcyanamide ion, $XC_6H_4NCN^-$], $[CuL_2(L')_2]$ (L = pyridine or piperidine), and $[\{CuL(L')(CH_3CO_2)\}_2]$ (L = bipy or phen) have been prepared from the reaction of the neutral phenylcyanamides with copper(II) acetate monohydrate in the presence of the appropriate N-donor co-ligand. They have been characterized by magnetic, i.r., and electronic spectral techniques and the crystal and molecular structures of $[\{Cu(bipy)(PhNCN)_2\}_2]$ and $[\{Cu(phen)(3\text{-}ClC_6H_4NCN)(CH_3CO_2)\}_2]\cdot 2H_2O$ determined by single-crystal *X*-ray diffraction techniques. Crystals of $[\{Cu(bipy)(PhNCN)_2\}_2]$ are monoclinic, space group $P2_1/c$, with $a = 9.625(3)$, $b = 20.945(5)$, $c = 9.956(3)$ Å, $\beta = 97.10(2)°$, and $Z = 2$. The complex consists of discrete centrosymmetric dimers. The copper atom of each monomeric unit is co-ordinated equatorially to two bipy nitrogens [Cu–N 2.012(5) and 2.052(5) Å] and to the cyano-nitrogens of two phenylcyanamide ligands [Cu–N 1.938(5) and 1.942(6) Å]. The distorted square-pyramidal

Table 1. Atomic co-ordinates (× 10^4) for $[\{Cu(bipy)(PhNCN)_2\}_2]$ with standard deviations in parentheses

Atom	*x*	*y*	*z*
Cu	772(1)	−87	2 489(1)
N(1)	−136(6)	537(2)	1 237(5)
N(2)	−705(5)	981(2)	−1 049(5)
N(3)	2 651(7)	208(3)	2 302(5)
N(4a)	4 547(10)	524(5)	811(10)
N(4b)	3 706(10)	1 269(5)	2 422(9)
N(5)	1 444(6)	−572(2)	4 191(4)
N(6)	−1 099(6)	−398(2)	3 054(5)
C(1)	−333(6)	764(3)	158(6)
C(2)	−21(6)	1 527(3)	−1 469(5)
C(3)	−731(7)	1 896(2)	−2 507(6)
C(4)	−99(7)	2 411(3)	−3 021(6)
C(5)	1 255(7)	2 580(3)	−2 528(6)
C(6)	1 959(7)	2 229(3)	−1 475(6)
C(7)	1 324(6)	1 703(3)	−959(5)
C(8a)	3 576(14)	385(6)	1 566(14)
C(8b)	3 126(13)	727(7)	2 320(12)
C(9)	4 486(6)	1 574(3)	1 494(6)
C(10)	5 036(7)	1 133(3)	664(7)
C(11)	6 017(7)	1 333(3)	−171(7)
C(12)	6 431(7)	1 963(3)	−165(6)
C(13)	5 866(7)	2 401(3)	655(7)
C(14)	4 921(7)	2 200(3)	1 495(7)
C(15)	2 782(8)	−633(3)	4 707(6)
C(16)	3 220(8)	−1 007(3)	5 829(6)
C(17)	2 185(9)	−1 332(3)	6 438(7)
C(18)	808(9)	−1 274(3)	5 910(6)
C(19)	453(8)	−886(3)	4 761(6)
C(20)	−977(8)	−802(3)	4 114(6)
C(21)	−2 149(8)	−1 112(3)	4 478(7)
C(22)	−3 437(9)	−991(3)	3 763(7)
C(23)	−3 546(8)	−564(3)	2 694(6)
C(24)	−2 345(8)	−270(3)	2 353(7)

were measured on a Cahn model 7550 Millibalance with $Hg[Co(SCN)_4]$ as standard and diamagnetic corrections were made using Pascal's constants. Microanalyses were performed by the Microanalytical Laboratory, University of Otago and data for the complexes are summarized in Table 3. The phenylcyanamide ligands were prepared from the appropriate anilines following the literature methods[9] for the unsubstituted compound.

Satisfactory microanalytical data were obtained in all cases. 4-Chlorophenylcyanamide, m.p. 184—186 °C, ν(CN) 2 243 cm^{-1} (Nujol); 3-chlorophenylcyanamide, m.p. 68—70 °C, ν(CN) 2 245 cm^{-1} (Nujol); 2-chlorophenylcyanamide, m.p. 85—88 °C, ν(CN) 2 242 cm^{-1} (Nujol); 4-bromophenylcyanamide, m.p. 107—109 °C, ν(CN) 2 239 cm^{-1} (Nujol); 4-fluorophenylcyanamide, m.p. 116—118 °C, ν(CN) 2 241 cm^{-1} (Nujol); 4-methylphenylcyanamide, ν(CN) 2 227 cm^{-1} (Nujol); 2-methylphenylcyanamide, ν(CN) 2 235 cm^{-1} (Nujol); 4-methoxyphenylcyanamide, m.p. 74—77 °C, ν(CN) 2 225 cm^{-1} (Nujol).

Preparation of the Copper Complexes.—$[\{Cu(bipy)L_2\}_2]$ (L = XC_6H_4NCN; X = H, 4-Cl, 3-Cl, 2-Cl, 4-Br, 4-F, 4-Me, 2-Me, *or* 4-MeO). The appropriate phenylcyanamide, HL (2 mmol), dissolved in ethanol (10 cm^3) was added slowly to a solution of copper(II) acetate monohydrate (0.20 g, 1 mmol) and 2,2′-bipyridine (0.16 g, 1 mmol) in the same solvent (30 cm^3). The intensely coloured solution which formed was filtered and allowed to stand overnight. The resulting crystals were filtered off, washed with ethanol, and dried *in vacuo*. For X = 4-MeO the complex was obtained as a dihydrate. Yields 40—60%.

$[\{Cu(phen)L_2\}_2]$ (L = XC_6H_4NCN; X = H, 4-Cl, 2-Cl, 4-Br, 4-F, 4-Me, 4-MeO, *or* 2-MeO). These were prepared using an analogous method to that for the bipy complexes. For X = 4-Me or 4-MeO the complexes were obtained as monohydrates and for X = 2-MeO the complex was a trihydrate. Yields 40—60%.

$[\{Cu(phen)(3\text{-}ClC_6H_4NCN)_2\}_2]$. 3-Chlorophenylcyanamide (0.31 g, 2 mmol) in ethanol (10 cm^3) was deprotonated by reaction with sodium (0.05 g, 2 mmol) in ethanol (5 cm^3). The resulting solution was slowly added to copper(II) acetate monohydrate (0.20 g, 1 mmol) and 1,10-phenanthroline (0.20 g, 1 mmol) dissolved in ethanol (30 cm^3). The solution was filtered and allowed to stand overnight whereupon the product formed as dark red crystals. These were filtered off, washed with ethanol, and dried *in vacuo*. Yield 0.38 g (70%).

$[\{Cu(phen)(3\text{-}ClC_6H_4NCN)(CH_3CO_2)\}_2]\cdot 2H_2O$. To a solution of copper(II) acetate monohydrate (0.20 g, 1 mmol) and 1,10-phenanthroline (0.20 g, 1 mmol) in ethanol (30 cm^3) was added 3-chlorophenylcyanamide (0.15 g, 1 mmol) dissolved in ethanol (10 cm^3). The dark green plate-like crystals obtained from the resulting solution upon standing overnight were filtered off, washed with ethanol, and air dried. Yield 0.28 g (60%). The other acetate complexes, $[\{Cu(bipy)(2\text{-}MeC_6H_4NCN)(CH_3CO_2)\}_2]$ and $[\{Cu(phen)(3\text{-}MeOC_6H_4NCN)(CH_3CO_2)\}_2]\cdot H_2O$, were prepared in a similar fashion.

$[Cu(py)_2L_2]\cdot 0.5H_2O$ (L = XC_6H_4NCN; X = H, 4-Cl, 3-Cl, 4-Br, *or* 4-F). The appropriate phenylcyanamide, HL (2 mmol), dissolved in ethanol (10 cm^3), was added to a warm solution of copper(II) acetate monohydrate (0.20 g, 1 mmol) and pyridine (1 cm^3) in ethanol (30 cm^3). The resulting intense dark red solution was filtered and on cooling the product was obtained. It was filtered off, washed with ethanol and air dried. Yields 40—50%.

$[Cu(pip)_2L_2]$ (L = XC_6H_4NCN; X = H, 4-Cl, *or* 4-Br). These were prepared as described above for the pyridine complexes. Yields 40–50%.

Crystal Structure Determination of Bis(μ*-phenylcyanamido*)*-*1:2κ^{2}N^1:N^3; 1:2κ^{2}N^3:N^1*-bis*[(2,2′*-bipyridine*)(*phenylcyanamido-*κN^3)*copper*(II)], $[\{Cu(bipy)(PhNCN)_2\}_2]$.—Suitable crystals were obtained by the slow evaporation of an ethanol solution.

Crystal data. $C_{48}H_{36}Cu_2N_{12}$, *M* = 907.0, monoclinic, space group $P2_1/c$, $a = 9.625(3)$, $b = 20.945(5)$, $c = 9.956(3)$ Å, $\beta = 97.10(2)°$, $U = 1\,992(1)$ Å^3 (by least-squares refinement on diffractometer angles of 25 automatically centred reflections, $\lambda = 0.710\,69$ Å), $D_m = 1.53$ g cm^{-3}, $Z = 2$, $D_c = 1.51$ g cm^{-3}. Dark red platelets, crystal dimensions 0.06 × 0.03 × 0.34 mm, $\mu(Mo\text{-}K_\alpha) = 10.63$ cm^{-1}.

Data collection and processing. Nicolet R3M diffractometer at 153 K, ω—2θ scan mode with graphite-monochromated Mo-K_α radiation, scan range 1.6°, scan speed 5.86° min^{-1}, 2 702 reflections measured ($5 \leqslant 2\theta \leqslant 45°$, *h*, *k*, $\pm l$), 1 914 unique [merging $R = 0.0191$ after data corrected for Lorentz and polarization effects and absorption correction applied (maximum, minimum transmission factors = 0.9348, 0.8653] giving 1 689 with $I > 3\sigma(I)$.

Structure analysis and refinement. Patterson and Fourier methods. Full-matrix least-squares refinement with all non-hydrogen atoms anisotropic and hydrogen atoms in calculated positions (C–H 1.08 Å). The terminal phenylcyanamide ligand was found to possess two orientations leading to a two-fold disorder of the amido nitrogen, N(4), and the cyano carbon, C(8), atoms. Since site-occupancy values for these atoms were found to be approximately 0.5, these values were assumed for refinement. Final *R* and *R′* values were 0.0429 and 0.0430 with the weighting scheme $w = 1.2365/(\sigma^2 F_o + 0.000\,642 F_o^2)$. For this and the following structure, computations were performed using SHELXTL 86[10] and SHELX 76[11] programs. Fractional

Table 2. Atomic co-ordinates ($\times 10^4$) for $[\{Cu(phen)(3\text{-}ClC_6H_4NCN)(CH_3CO_2)\}_2]\cdot 2H_2O$ with standard deviations in parentheses

Atom	*x*	*y*	*z*
Cu	3 429(1)	6 081(1)	5 487(1)
Cl	7 937(3)	1 759(2)	9 674(1)
N(1)	4 171(8)	3 982(6)	5 761(4)
N(2)	4 252(8)	1 554(6)	6 830(4)
N(3)	1 814(7)	6 326(5)	4 355(4)
N(4)	2 660(7)	8 255(5)	5 016(4)
O(1)	4 738(7)	6 051(5)	6 644(4)
O(2)	2 275(8)	5 907(5)	7 446(4)
O(3a)	96(14)	5 527(11)	266(8)
O(3b)	−1 429(17)	6 007(11)	811(8)
C(1)	4 208(9)	2 832(8)	6 332(5)
C(2)	5 205(9)	882(7)	7 744(5)
C(3)	5 999(9)	1 608(7)	8 213(5)
C(4)	6 938(9)	841(7)	9 095(5)
C(5)	7 136(10)	−615(8)	9 537(5)
C(6)	6 341(10)	−1 307(7)	9 062(6)
C(7)	5 367(10)	−571(7)	8 172(5)
C(8)	4 672(12)	5 698(8)	8 459(6)
C(9)	3 803(13)	5 900(7)	7 468(6)
C(10)	1 436(9)	5 318(7)	4 030(5)
C(11)	333(10)	5 655(7)	3 914(5)
C(12)	−316(9)	7 071(7)	2 653(5)
C(13)	105(9)	8 159(7)	2 957(5)
C(14)	−504(9)	9 663(7)	2 442(5)
C(15)	−38(9)	10 647(7)	2 770(5)
C(16)	1 048(9)	10 230(7)	3 642(5)
C(17)	1 595(9)	11 207(7)	4 035(6)
C(18)	2 604(10)	10 687(7)	4 895(6)
C(19)	3 136(9)	9 201(7)	5 374(5)
C(20)	1 633(8)	8 773(7)	4 172(5)
C(21)	1 155(9)	7 725(7)	3 817(5)

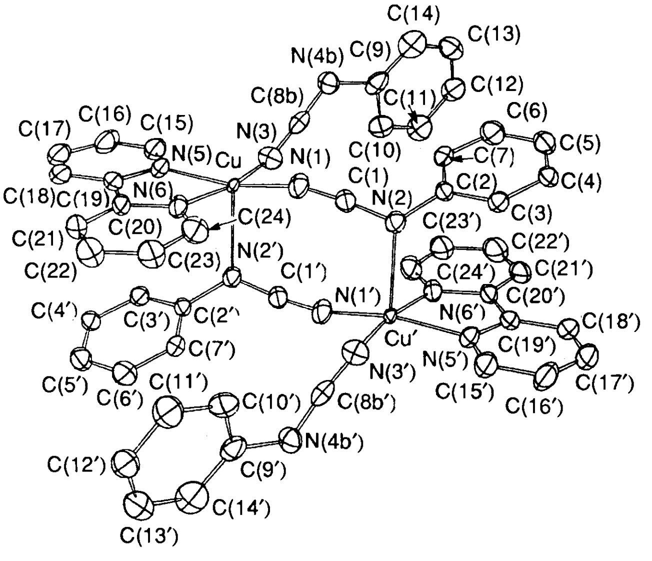

Figure 1. Structure of the complex $[\{Cu(bipy)(PhNCN)_2\}_2]$ showing the numbering system used

atomic co-ordinates are given in Table 1 and selected bond lengths and angles in Table 4.

Crystal Structure Determination of Bis(*μ*-3-*chlorophenylcyanamido*-κN³)-*bis*[*acetato*-κO(1,10-*phenanthroline*)*copper*(II)] *Dihydrate*, $[\{Cu(phen)(3\text{-}ClC_6H_4NCN)(CH_3CO_2)\}_2]\cdot 2H_2O$.—Crystals were obtained by the slow evaporation of an ethanol solution.

Crystal data. $C_{42}H_{30}Cl_2Cu_2N_8O_4$, $M = 944.0$, triclinic, space group $P\bar{1}$, $a = 8.171(5)$, $b = 10.060(6)$, $c = 13.377(7)$ Å, $\alpha = 74.33(4)$, $\beta = 84.79(5)$, $\gamma = 72.24(4)°$, $U = 1\,008(1)$ Å^3 (by least-squares refinement on diffractometer angles of 21 automatically centred reflections, $\lambda = 0.710\,69$ Å), $D_m = 1.51$ g cm^{-3}, $Z = 1$, $D_c = 1.54$ g cm^{-3}. Dark green diamond-shaped crystals, crystal dimensions 0.26 × 0.25 × 0.10 mm, $\mu(\text{Mo-}K_\alpha) = 11.74$ cm^{-1}.

Data collection and processing. Nicolet R3M diffractometer at 153 K, ω—2θ scan mode with graphite-monochromated Mo-K_α radiation, scan range 2.4°, scan speed 7.32° min^{-1}, 2 727 reflections measured ($5 \leqslant 2\theta \leqslant 45°$, h, $\pm k$, $\pm l$), 2 640 unique [merging $R = 0.0530$ after data corrected for Lorentz and polarization effects and absorption correction applied (maximum, minimum transmission factors = 0.892, 0.769)] giving 2 142 with $I > 3\sigma(I)$.

Structure analysis and refinement. Patterson and Fourier methods. Full-matrix least-squares refinement with all non-hydrogen atoms anisotropic and non-water hydrogen atoms in calculated positions (C–H 1.08 Å). The lattice water molecule was found to be disordered over two sites which were assigned site-occupancy factors of 0.5 for refinement. Final R and R' values were 0.0558 and 0.0581 with the weighting scheme $w = 4.227\,60/(\sigma^2 F_o + 0.000\,391 F_o^2)$.

Fractional atomic co-ordinates are given in Table 2 and selected bond lengths and angles in Table 5.

For both structures additional material available from the Cambridge Crystallographic Data Centre comprises H-atom co-ordinates, thermal parameters, and remaining bond lengths and angles.

Results and Discussion

The phenylcyanamidocopper(II) complexes were, in general, prepared by the reaction of the neutral phenylcyanamides with copper(II) acetate monohydrate, in the presence of the appropriate N-donor co-ligand (*i.e.* bipy, phen, pip, or py). Analytical data are given in Table 3 and while dimeric structures are assumed for the bipy and phen complexes, by analogy with the structure of $[\{Cu(bipy)(PhNCN)_2\}_2]$ characterized by *X*-ray crystallography (see below), the nature of the monomeric N-donor co-ligand (pip or py) complexes is less certain and further structural work is required.

To prepare the complex $[\{Cu(phen)(3\text{-}ClC_6H_4NCN)_2\}_2]$ it was necessary to deprotonate the neutral 3-chlorophenylcyanamide using sodium ethoxide. In the absence of added base, the complex $[\{Cu(phen)(3\text{-}ClC_6H_4NCN)(CH_3CO_2)\}_2]\cdot 2H_2O$ was obtained. This only involves one cyanamide ligand per copper(II), the positive charge being balanced by the inclusion of an acetate ion. The presence of acetate was deduced from the appearance of a strong i.r. band at 1 591 cm^{-1}, consistent with the ν(CO) frequency of co-ordinated acetate[12] and confirmed by *X*-ray crystallography (see below).

Two other mixed anionic ligand complexes, *viz.* $[\{Cu(bipy)(2\text{-}MeC_6H_4NCN)(CH_3CO_2)\}_2]$ and $[\{Cu(phen)(3\text{-}MeOC_6H_4NCN)(CH_3CO_2)\}_2]$, were obtained, illustrating that the final outcome of a particular reaction is determined by factors other than the acidity of the neutral phenylcyanamide (*e.g.* the basicity of the co-ligands and the relative solubilities of the complexes).

Crystal Structure of $[\{Cu(bipy)(PhNCN)_2\}_2]$.—A diagram of the complex is given in Figure 1 showing the atomic numbering scheme used. Selected bond distances and angles are given in Table 4. The complex consists of centrosymmetric dimers separated by normal van der Waals distances.[13] The dimerization occurs *via* end-to-end 'NCN' bridging of two phenylcyanamide ligands between the two copper atoms. The two phenylcyanamide ligands in the asymmetric unit exhibit

Table 3. Colours and analytical data for the complexes (L = XC_6H_4NCN)

Complex[a]	X	Colour	Analyses (%)[b] C	H	N	X[c]
$[\{Cu(bipy)L_2\}_2]$	H	Dark red	63.3 (63.5)	4.3 (4.0)	18.5 (18.5)	
	4-Cl	Dark red	54.9 (55.1)	3.0 (3.0)	16.0 (16.1)	
	3-Cl	Dark red	55.1 (55.1)	3.1 (3.0)	16.1 (16.1)	13.5 (13.6)
	2-Cl	Dark red	54.9 (55.1)	3.1 (3.0)	15.8 (16.1)	13.5 (13.6)
	4-Br	Dark red	47.2 (47.1)	2.5 (2.6)	13.7 (13.7)	26.3 (26.1)
	4-F	Dark red	58.9 (58.8)	3.4 (3.3)	16.9 (17.2)	7.5 (7.8)
	4-Me	Purple	64.5 (64.8)	4.5 (4.6)	17.7 (17.4)	
	2-Me	Green	64.5 (64.8)	4.6 (4.6)	17.4 (17.4)	
	4-MeO	Purple	60.5 (60.5)	4.1 (4.7)	16.1 (16.3)	
$[\{Cu(phen)L_2\}_2]$	H	Dark red	64.7 (65.3)	3.7 (3.9)	17.4 (17.6)	
	4-Cl	Dark red	57.0 (57.1)	2.8 (2.9)	15.1 (15.4)	12.9 (13.0)
	3-Cl	Dark red	57.2 (57.1)	3.0 (2.9)	15.2 (15.4)	13.1 (13.0)
	2-Cl	Dark red	56.9 (57.1)	2.9 (2.9)	15.3 (15.4)	13.0 (13.0)
	4-Br	Dark red	48.8 (49.1)	2.5 (2.5)	12.9 (13.2)	25.2 (25.1)
	4-F	Dark red	60.7 (60.8)	3.1 (3.1)	16.2 (16.4)	7.3 (7.4)
	4-Me	Purple	65.2 (65.3)	4.5 (4.5)	16.3 (16.3)	
	4-MeO	Black	61.7 (61.5)	4.05 (4.2)	15.6 (15.4)	
	2-MeO	Black	59.4 (59.5)	4.4 (4.5)	15.0 (14.9)	
$[Cu(pip)_2L_2]$	H	Orange red	61.3 (61.6)	7.1 (6.8)	18.1 (18.0)	
	4-Cl	Orange red	53.3 (53.3)	5.7 (5.6)	14.9 (15.6)	13.0 (13.2)
	4-Br	Orange red	45.6 (45.1)	4.8 (4.8)	13.2 (13.4)	25.3 (25.6)
$[Cu(py)_2L_2]$	H	Purple	62.0 (62.0)	4.4 (4.5)	17.4 (18.1)	
	4-Cl	Purple	54.4 (54.0)	3.5 (3.6)	15.2 (15.8)	13.5 (13.3)
	3-Cl	Purple	54.4 (54.0)	3.4 (3.6)	16.1 (15.8)	13.4 (13.3)
	4-Br	Purple	46.8 (46.3)	3.0 (3.1)	13.0 (13.5)	25.2 (25.7)
	4-F	Purple	57.7 (57.5)	3.7 (3.8)	16.4 (16.8)	7.5 (7.6)
$[\{Cu(bipy)L(CH_3CO_2)\}_2]$	2-Me	Khaki	60.4 (60.9)	4.0 (4.2)	13.0 (12.9)	
$[\{Cu(phen)L(CH_3CO_2)\}_2]$	3-Cl	Green	55.5 (55.5)	3.8 (3.3)	12.1 (12.3)	7.9 (7.8)
	3-MeO	Green	57.7 (57.6)	4.45 (4.2)	12.6 (12.2)	

[a] Some complexes were obtained as hydrates, see Experimental section. [b] Calculated values given in parentheses. [c] Halogen.

Table 4. Selected bond lengths (Å) and angles (°) for $[\{Cu(bipy)(PhNCN)_2\}_2]$ with standard deviations in parentheses *

Cu–N(1)	1.938(5)	N(3)–C(8a)	1.277(15)
Cu–N(2′)	2.355(6)	N(3)–C(8b)	1.179(14)
Cu–N(3)	1.942(6)	N(4a)–C(8a)	1.302(16)
Cu–N(5)	2.012(5)	N(4b)–C(8b)	1.263(16)
Cu–N(6)	2.052(5)	N(4a)–C(10)	1.374(11)
N(1)–C(1)	1.169(7)	N(4b)–C(9)	1.413(11)
C(1)–N(2)	1.293(7)	Cu ··· Cu′	5.009(6)
N(2)–C(2)	1.409(7)		
N(1)–Cu–N(3)	94.3(2)	N(1)–C(1)–N(2)	172.7(7)
N(1)–Cu–N(2′)	99.7(2)	C(1)–N(2)–Cu′	105.6(6)
N(1)–Cu–N(5)	162.6(2)	C(2)–N(2)–Cu′	116.5(6)
N(1)–Cu–N(6)	92.4(2)	C(1)–N(2)–C(2)	118.3(5)
N(3)–Cu–N(2′)	98.5(2)	Cu–N(3)–C(8a)	150.7(7)
N(3)–Cu–N(5)	92.0(2)	Cu–N(3)–C(8b)	131.0(8)
N(3)–Cu–N(6)	169.7(2)	N(3)–C(8a)–N(4a)	175.9(13)
N(5)–Cu–N(6)	79.4(2)	N(3)–C(8b)–N(4b)	175.2(12)
N(2′)–Cu–N(5)	95.4(2)	C(8a)–N(4a)–C(10)	123.2(10)
N(2′)–Cu–N(6)	88.0(2)	C(8b)–N(4b)–C(9)	128.2(9)
Cu–N(1)–C(1)	151.0(5)		

* The equally populated disorder sites for atoms N(4) and C(8) are represented by N(4a), N(4b) and C(8a), C(8b) respectively.

different co-ordination modes: a monodentate ligand which co-ordinates to the copper through the terminal cyano-nitrogen N(3), and a bidentate ligand which bridges the two copper atoms of the dimer through the cyano-N(1) and amido-N(2) nitrogen atoms. The centrosymmetric $(CuNCN)_2$ bridging unit forms an approximately planar eight-membered ring (maximum deviation 0.14 Å).

Each copper atom has a distorted square-pyramidal geometry. Two phenylcyanamido cyano nitrogens [Cu–N(1) 1.938(5) and Cu–N(3) 1.942(6) Å] and two 2,2′-bipyridine nitrogens [Cu–N(5) 2.012(5) and Cu–N(6) 2.052(5) Å] make a distorted basal square plane. A longer apical bond [Cu–N(2′) 2.355(6) Å] to the amido nitrogen of the symmetry-related bridging phenylcyanamide ligand completes the co-ordination.

The four basal atoms N(1), N(3), N(5), and N(6) exhibit poor planarity with deviations of ≈0.08 Å from their mean plane. The copper atom is displaced by 0.19 Å from this plane, towards the apical donor atom, N(2′). The dihedral angles between the planes through atoms Cu, N(1), N(3) and Cu, N(5), N(6) is 16.6° (*cf.* 0° for a square plane), due in part to a tetrahedral distortion of the basal plane as well as to the displacement of the copper atom out of this plane. The distortion from square pyramidal is also seen in the N(2′)–Cu–N(1) and N(2′)–Cu–N(3) bond angles which are somewhat larger than 90° [99.7(2) and 98.5(2)° respectively]. The axial Cu–N(2′) bond is thus tilted towards the bipyridine ligand. The phenylcyanamide ligands are arranged such that the phenyl rings are virtually orthogonal to each other (the dihedral angle between the best planes through these phenyl rings is 85.2°). In addition the phenyl ring of the bridging ligand is approximately parallel to the phenyl rings of the bipyridine group (the dihedral angle between the best plane through the bipy group and that through the phenyl ring of the bridging $[PhNCN]^-$ ligand is 17.3°). Such an arrangement of ligands evidently minimizes the intramolecular interactions within the dimer. An inspection of the intra- and inter-molecular distances show that the shortest H ··· H contacts are in fact between the phenylcyanamide H atoms of neighbouring molecules rather than within the dimer. This suggests that the

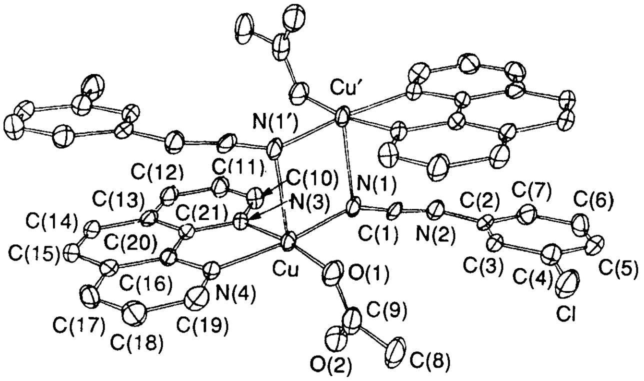

Figure 2. Structure of the complex [{Cu(phen)(3-ClC$_6$H$_4$NCN)-(CH$_3$CO$_2$)}$_2$]·2H$_2$O. The numbering system is shown for one monomer unit

basal distortion towards tetrahedral arises, at least in part, to optimize the molecular packing efficiency.

The Cu–N(bipy) bond distances are consistent with values in previously reported structures.[14] The copper–phenylcyanamide distances, Cu–N(1) and Cu–N(3) [1.938(5) and 1.942(6) Å respectively], are significantly shorter than the Cu–N(bipy) distances (mean 2.03 Å) indicating strong bonding between the copper and the phenylcyanamide ligands. Their equivalence suggests that the donor properties of the cyano-N(1) atom are not significantly modified by the involvement of the amido-nitrogen N(2) in bonding to the second copper atom. The Cu–N(2′) bond is clearly elongated with a value of 2.355(6) Å and represents a typical lengthening of an apical bond in a five-co-ordinate copper(II) complex.[15]

The terminal phenylcyanamide ligand. The terminally bound phenylcyanamide ligand is partially disordered. The nitrogen and carbon atoms of the cyanamido group each occupy two positions [C(8a), C(8b), N(4a), and N(4b)] with site-occupancy factors of 0.5 [N(4a) is bound to C(9) of the phenyl ring and N(4b) to C(10)]. The bond lengths of each conformation are equivalent within the limits of experimental error, with the exception of N(3)–C(8a) [1.277(15) Å] and N(3)–C(8b) [1.179(14) Å]. The latter bond distance agrees with the value expected for a CN triple bond (1.16 Å)[16] whereas the former is substantially longer. The remaining bond lengths [C(8a)–N(4a), N(4a)–C(9), C(8b)–N(4b), and N(4b)–C(10)] agree with the corresponding bond lengths in the bridging ligand which suggests the longer bond distance for N(3)–C(8a) can be attributed to limitations in modelling the disorder rather than to steric or electronic factors. Thus an accurate comparison of the bond lengths and angles associated with bridging and terminally bound phenylcyanamide ligands cannot be made.

The disorder is such that the orientation of the phenyl ring is the same but the two orientations of the NCN group make angles to the copper of 150.7(7) [Cu–N(3)–C(8a)] and 131.0(8)° [Cu–N(3)–C(8b)].

The bridging phenylcyanamide ligand. The observed bond distances for the cyanamido moiety [N(1)–C(1) 1.169(7) and C(1)–N(2) 1.293(7) Å] emphasize the importance of resonance structure (**a**) in the bonding description. However the length of C(1)–N(2) is close to the value expected for a CN double bond (1.29 Å),[13] indicating that there is also an important contribution from resonance form (**b**). A concomitant lengthening of the N(1)–C(1) distance to a value greater than predicted for a triple bond (1.16 Å)[16] is not seen but would not necessarily be expected.[17] For instance for the neutral cyanamide, Me$_2$NCN, the CN bond lengths are 1.351 and 1.160 Å,[18] and for co-ordinated Et$_2$NCN in [Cr(CO)$_5$(Et$_2$NCN)], the distances are 1.314 and 1.139 Å.[5d] The C(2)–N(2) bond distance of 1.409(7) Å is somewhat less than the value expected for a single CN bond (1.47 Å),[13] implying that the negative charge on N(2) is also partially delocalized on to the phenyl ring.

Table 5. Selected bond lengths (Å) and angles (°) for [{Cu(phen)-(3-ClC$_6$H$_4$NCN)(CH$_3$CO$_2$)}$_2$]·2H$_2$O with standard deviations in parentheses

Cu–N(1)	1.950(6)	C(1)–N(2)	1.269(9)
Cu–N(3)	2.014(5)	N(2)–C(2)	1.402(9)
Cu–N(4)	2.016(5)	C(8)–C(9)	1.497(10)
Cu–O(1)	1.948(5)	C(9)–O(1)	1.285(9)
Cu–N(1′)	2.454(6)	C(9)–O(2)	1.249(9)
N(1)–C(1)	1.196(8)	Cu • • • Cu′	3.247(5)
N(1)–Cu–N(3)	93.2(2)	N(3)–Cu–N(1′)	90.7(2)
N(1)–Cu–N(4)	172.8(2)	N(4)–Cu–N(1′)	89.9(2)
N(1)–Cu–N(1′)	85.7(2)	C(1)–N(1)–Cu	149.1(5)
N(1)–Cu–O(1)	92.7(2)	C(1)–N(1)–Cu′	113.9(5)
O(1)–Cu–N(3)	172.1(2)	Cu–N(1)–Cu′	94.3(2)
O(1)–Cu–N(4)	93.3(2)	C(1)–N(2)–C(2)	120.2(6)
O(1)–Cu–N(1′)	95.0(2)	N(1)–C(1)–N(2)	172.2(7)
N(3)–Cu–N(4)	81.2(2)	Cu–O(1)–C(9)	108.1(5)

Consideration of the bond angles around N(1) and N(2) also shows that neither resonance structure (**a**) or (**b**), by itself, can adequately describe the bonding for the co-ordinated phenylcyanamide anion. Angles around N(2) range from 105.6(6) to 118.3(5)° whereas for structure (**a**) the amide nitrogen should be tetrahedral and for (**b**) trigonal. Similarly, with a value of 151.0(5)°, the Cu–N(1)–C(1) angle lies approximately midway between linear and trigonal. The N(2)–C(1)–N(1) bond angle of 172.7(7)° shows a significant deviation from linearity.

The few crystal structures reported[5] of metal–cyanamide complexes are somewhat removed from [{Cu(bipy)-(PhNCN)$_2$}$_2$] because they contain neutral cyanamides which are generally co-ordinated *via* the terminal CN bond.[5a–c] The most comparable previously reported structure is that of [Cu$_2$(C$_9$H$_{21}$N$_3$)$_2$(μ-HNCN)$_2$][ClO$_4$]$_2$·H$_2$O (C$_9$H$_{21}$N$_3$ = *N*,*N*′,*N*″-trimethyl-1,4,7-triazacyclononane) which also possesses an end-to-end 'NCN' bridge between two copper(II) atoms.[6] The copper co-ordination environment in this cationic complex is dictated largely by the constraints of the tridentate cyclic amine. The resulting co-ordination geometry is approximately trigonal bipyramidal. The major difference between the co-ordination of the [HNCN]$^-$ ligand in this complex and the bridging [PhNCN]$^-$ anion in [{Cu(bipy)(PhNCN)$_2$}$_2$] is seen in the Cu–N distances. The [HNCN]$^-$ anion bridges approximately symmetrically, with Cu–N distances ranging from 1.962(5) to 2.017(6) Å, whereas the phenylcyanamide is asymmetrically co-ordinated [Cu–N(1) 1.938(5) and Cu–N(2′) 2.355(6) Å]. The mean CN distances for the bridging [HNCN]$^-$ ion (1.28 and 1.15 Å) are in agreement with the corresponding distances in the [PhNCN]$^-$ complex.

Crystal Structure of [{Cu(phen)(3-ClC$_6$H$_4$NCN)(CH$_3$CO$_2$)}$_2$]·2H$_2$O.—A diagram of the complex is shown in Figure 2 together with the atomic numbering scheme used. Selected bond distances and angles are listed in Table 5. The complex consists of centrosymmetric dimers separated by normal van der Waals distances.[13] The dimerization is achieved *via* the terminal nitrogen N(1) of the 3-chlorophenylcyanamide anion which asymmetrically bridges the two copper atoms and hence is an example of a third type of co-ordination for a phenylcyanamide anion.

Each copper atom has an approximately square-pyramidal co-ordination geometry. The 3-chlorophenylcyanamide cyano nitrogen [Cu–N(1) 1.950(6) Å], the two phenanthroline nitrogen atoms [Cu–N(3) 2.014(5) and Cu–N(4) 2.016(5) Å], and an acetate oxygen [Cu–O(1) 1.948 (5) Å] make an 'ON$_3$'

Table 6. Magnetic, i.r., and electronic spectra data for the complexes ($L = XC_6H_4NCN$)

Complex	X	$\mu_{eff.}$[a]	$\nu(CN)$[b]/cm^{-1}			$\lambda_{max.}$[c]/nm	
$[\{Cu(bipy)L_2\}_2]$	H	1.98	2 175	2 147 (sh)	2 103	496 (1 900)	658 (400)
	4-Cl	1.96	2 179	2 159	2 111	498 (2 476)	662 (462)
						515	720 (sh)[d]
	3-Cl	1.95	2 169	2 141	2 107	488 (2 314)	674 (370)
	2-Cl	1.93	2 187	2 139	2 119	476 (1 272)	678 (382)
						500	690 (sh)[d]
	4-Br	1.94	2 171	2 151	2 111	489 (1 930)	663 (447)
	4-F	1.95	2 173	2 137	2 111	486 (1 821)	658 (398)
	4-Me	1.90	2 179	2 155 2 143	2 111	570	750 (sh)[d,e]
	2-Me	1.92	2 141	2 105	2 091 (sh)	530	745 (sh)[d]
						492 (1 900)	613 (400)[f]
	4-MeO	1.82	2 183	2 143	2 107 (sh)	585	770 (sh)[d]
						519 (865)	664 (480)
$[\{Cu(phen)L_2\}_2]$	H	1.82	2 175	2 141	2 103	498 (1 364)	670 (641)
	4-Cl	1.95	2 179	2 147	2 095	493 (1 898)	662 (511)
	3-Cl	1.89	2 155		2 107	481 (1 560)	686 (400)
	2-Cl	1.91	2 185	2 119	2 103	477 (988)	692 (353)
	4-Br	2.11	2 165	2 123	2 111	494 (1 774)	669 (576)
	4-F	1.93	2 175	2 149	2 087	493 (1 194)	669 (585)
	4-Me	1.88	2 195	2 121 (sh)	2 095	520	760 (sh)[d,e]
	4-MeO	2.03	2 181	2 147	2 117 (sh)	590	755 (sh)[d]
						525 (1 290)	698 (484)
	2-MeO	1.89	2 227	2 157	2 107 (sh)	575	760 (sh)[d]
						520 (680)	660 (388)
$[Cu(pip)_2L_2]$	H	1.85	2 175	2 143		474 (931)	659 (403)
	4-Cl	1.78	2 161	2 145		476 (940)	655 (403)
	4-Br	1.97	2 179	2 143		476 (1 030)	671 (430)
$[Cu(py)_2L_2]$	H	1.89	2 171	2 142		494 (861)	752 (240)
						525	740 (sh)[d]
	4-Cl	1.93	2 167	2 143		485 (807)	732 (265)
						515	720 (sh)[d]
	3-Cl	1.96	2 173	2 075		481 (1 656)	775 (233)
	4-Br	2.07	2 159	2 107		496 (807)	757 (234)
	4-F	1.93	2 155	2 109		492 (865)	736 (227)
$[\{Cu(bipy)L(CH_3CO_2)\}_2]$	2-Me	2.00	2 143	2 089		490	640 (sh)[d]
						488 (820)	662 (220)[f]
$[\{Cu(phen)L(CH_3CO_2)\}_2]$	3-Cl	1.89	2 159	2 107		462 (820)	677 (167)
	3-MeO	—	2 127	2 107		490	630 (sh)[d]

[a] Measured at 293 K. [b] Recorded as Nujol mulls. [c] Unless otherwise stated in dimethyl sulphoxide. Molar absorption coefficients per monomer (ε/dm^3 mol^{-1} cm^{-1}) are given in parentheses. [d] Nujol mull transmittance. [e] Not sufficiently soluble in dimethyl sulphoxide. [f] In dimethylformamide.

distorted basal square plane. A longer apical bond to the cyanamide ligand of the other half of the dimer [Cu–N(1′) 2.454(6) Å] completes the co-ordination sphere. The apical Cu–N(1′) bond deviates by 3.4° from the normal to the best plane through the basal atoms. The plane through atoms O(1), N(1), N(3), and N(4) shows that these four atoms are not coplanar (deviations 0.08—0.09 Å) but that the Cu atom does not deviate significantly (deviation 0.01 Å) from the best plane through them. The dihedral angle between the planes through atoms Cu, N(3), N(4) and Cu, N(1), O(1) is 7.4° which indicates a small distortion of the basal atoms away from square planar towards tetrahedral. This distortion is similar to that observed for $[\{Cu(bipy)(PhNCN)_2\}_2]$ and could arise from steric interactions between the basal ligands and the apical ligand. The 3-chlorophenylcyanamide and phenanthroline ligands are orientated such that their aromatic rings are virtually parallel to each other. (The dihedral angle between the best planes through these groups is 8°.)

The Cu–N(phen) bond lengths [Cu–N(3) 2.014(5) and Cu–N(4) 2.016(5) Å] agree with values previously reported for equatorially co-ordinated phenanthroline ligands.[19] The Cu–O(1) distance, at 1.948(5) Å, is within the range of values expected for monodentate carboxylate co-ordination (1.95—1.99 Å).[20] The Cu–N(1) bond distance [1.950(6) Å] is shorter than the Cu–N(phen) bond lengths (mean 2.015 Å) and similar to the equatorial Cu–N(cyanamide) distances found in $[\{Cu(bipy)(PhNCN)_2\}_2]$.

There are two water molecules of crystallization associated with each dimer, each of which is disordered over two positions. They are not hydrogen bonded to the dimer which is presumably why the disorder occurs.

The 3-*chlorophenylcyanamide ligand.* The values of the N(1)–C(1), C(1)–N(2), and N(2)–C(2) bond lengths [1.196(8), 1.269(9), and 1.402(9) Å respectively] again indicate that electronic charge is delocalized along the cyanamide moiety and, as for the cyanamide ligands in $[\{Cu(bipy)(PhNCN)_2\}_2]$, both resonance structures are important but with (**a**) dominating. A comparison of the geometries of the 'NCN' bridging phenylcyanamide ligand in the bipy complex, with the 'end-on' bridged 3-chlorophenylcyanamide ligand in the phen complex, shows that they are very similar. For instance some relevant bond parameters (with the $[PhNCN]^-$ data listed first) are: N(1)–C(1) 1.169(7), 1.196(8); C(1)–N(2) 1.293(7), 1.269(9) Å; C(1)–N(2)–C(2) 118.3(5), 120.2(6)°. These differences cannot be regarded as statistically significant, but overall the data are consistent with an enhanced contribution from resonance form (**b**) for $[3\text{-}ClC_6H_4NCN]^-$ since for this ligand N(1)–C(1) is longer, C(1)–N(2) is shorter, and the C(1)–N(2)–C(2) angle is closer to the trigonal value of 120°. Form (**b**) would allow a greater charge build up on the terminal N, required for end-on bridging, for donation into the copper orbitals. However the N(1)–C(1)–N(2) bond angle, at 172.7(7)°, is the same as the corresponding angle observed for the 'NCN' bridged [PhNCN]$^-$ ligand, a reminder that the geometry of phenylcyanamide ligands will also be influenced by the need for an efficient packing arrangement of atoms around the copper in which steric interactions are minimized.

Physicochemical Studies.—Molar conductivity measurements using dimethyl sulphoxide or dimethylformamide (*e.g.* for $[\{Cu(bipy)(2\text{-}MeC_6H_4NCN)(CH_3CO_2)\}_2]$, Λ (per monomer) is 2 S cm^2 mol^{-1}) as solvent indicate that the complexes are non-electrolytes and therefore the anionic phenylcyanamide ligands remain co-ordinated in solution. The i.r. spectra (Table 6) all exhibit intense bands in the 2 090—2 180 cm^{-1} range, assignable to ν(CN) frequencies. That these values are less than those observed for the neutral cyanamides (2 220—2 245 cm^{-1}, see Experimental section) is consistent with an increased contribution of resonance form (**b**) to the bonding scheme on deprotonation and co-ordination. When neutral cyanamide ligands co-ordinate to transition metals a positive shift in the ν(CN) frequency is seen.[1] Within a series, with a particular N-donor co-ligand, the ν(CN) band profiles are reasonably consistent, although not all shoulders are resolved, suggesting a common structural type for each group of compounds. However, there does not appear to be a correlation between the ν(CN) frequencies and the position or electronic properties of the substituent on the phenyl ring, nor do the frequencies distinguish between terminal or bridging phenylcyanamides. The magnetic moments for the complexes are listed in Table 6 and lie in the range 1.8—2.1, close to the spin-only value for Cu^{II}. In contrast, the complex $[Cu_2(C_9H_{21}N_3)_2(\mu\text{-}HNCN)_2][ClO_4]_2\cdot H_2O$, which as mentioned previously contains symmetrically, 'end-to-end', bridged [HNCN]$^-$ cyanamide anions, has intramolecularly antiferromagnetically coupled copper(II) centres and exhibits a magnetic moment of 1.35 at 298 K.[6] The solution electronic spectra (Table 6) show two absorption maxima. The band in the range 650—775 nm is assigned as a predominantly *d–d* transition and the second more intense band in the region 460—590 nm to a charge-transfer transition. The former is consistent with the '4 + 1' co-ordination geometry[21] as shown by *X*-ray crystallography for $[\{Cu(bipy)(PhNCN)_2\}_2]$ and $[\{Cu(phen)(3\text{-}ClC_6H_4NCN)(CH_3CO_2)\}_2]\cdot 2H_2O$. The latter is assigned as a ligand-to-metal charge-transfer (l.m.c.t.) transition from the π-type orbitals on the phenylcyanamide to empty *d*-type copper-based orbitals. The observed values may be compared with bands in the same range (410—545 nm) observed for a number of copper(II) phenolato complexes which have been assigned as l.m.c.t., $p_\pi \longrightarrow d_{\sigma^*}$, transitions,[22] and the lowest-energy l.m.c.t. band for the ruthenium(III) 2,3-dichlorophenylcyanamido complex, $[Ru(NH_3)_5(2,3\text{-}Cl_2C_6H_3NCN)]^{2+}$, which occurs at 629 nm. Without a detailed knowledge of solvation effects or the structures of the complexes in solution, comments on the energies of the l.m.c.t. bands should be made with caution.[23] Nevertheless, it does appear that electron-donating substituents on the phenyl ring of the cyanamide anion (*e.g.* methyl or methoxy) cause the l.m.c.t. band to be at lower energy ($\lambda > \approx 500$ nm) than the electron-withdrawing halogen substituents ($\lambda < \approx 500$ nm) (Table 6). Similar trends have been observed for the l.m.c.t. absorption band of a series of phenoxocopper(II) complexes.[22] The solid-state spectra are poorly resolved and hence only a few examples have been included in Table 6. In general the *d–d* band appears as a broad shoulder on the more intense l.m.c.t. absorption making it difficult conclusively to deduce structural information. However it does appear that for the pyridine complexes the *d–d* band is observed at lower energy (λ > *ca.* 700 nm) in both the solid-state and solution spectra, when compared to the majority of the bipyridine complexes (λ < *ca.* 700 nm). This difference may indicate another structural type for the $[Cu(py)_2L_2]$ series, especially when coupled with the ν(CN) i.r. data. The pyridine complexes exhibit two ν(CN) bands in their i.r. spectra whereas the bipyridine complexes are generally typified by a three ν(CN) band pattern. Clearly a single-crystal *X*-ray structure is required for one of the pyridine complexes.

Conclusion

The complexes reported in this study represent the first examples of transition-metal complexes, incorporating anionic phenylcyanamide ligands, that have been characterized by *X*-ray crystallography. The synthetic results show that the phenylcyanamide anion is a versatile ligand that readily forms complexes with copper(II). The outcome of a particular interaction is influenced by ring substitution as well as the nature of the co-ligands present. The bonding parameters obtained from the crystallographic studies establish that the phenylcyanamide anions in these complexes possess electronic structures corresponding to resonance forms (**a**) and (**b**), but with (**a**) predominating.

Collectively these results lead to the observation that the ligating characteristics of the phenylcyanamide anion bear a close resemblance to those of the pseudohalide class of anions. The co-ordination chemistry of pseudohalides has been extensively documented[24] and these anions are known to form an exceedingly diverse array of compounds which possess many interesting and important properties. Thus the current paucity of structural and synthetic data available on transition-metal phenylcyanamide complexes is surprising. We anticipate that the stoicheiometries and basic structural types identified in this study will be expanded by extending this work to the co-ordination chemistry of phenylcyanamides with a wide range of transition metals.

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