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2-Cyanoguanidine: a versatile hydrogen-bonding ligand in copper(II)–2,2′-bipyridine–2-cyanoguanidine complexes

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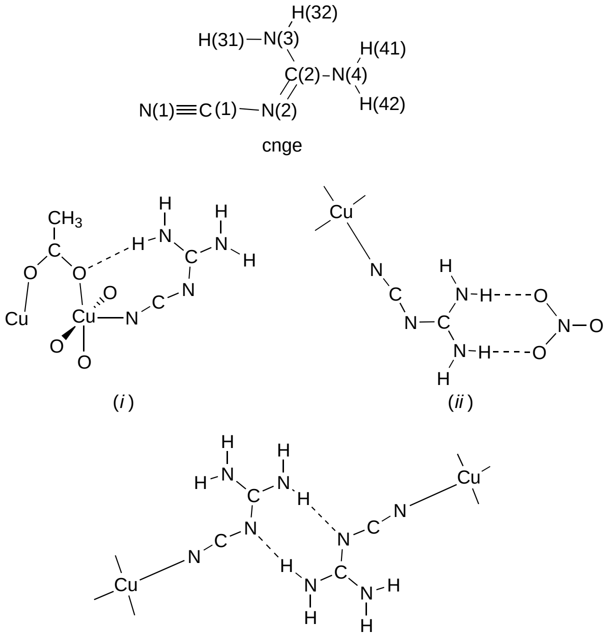
The copper(II)–2,2′-bipyridine (bipy)–2-cyanoguanidine (cnge) complexes, $[Cu(bipy)(cnge)_2(FBF_3)_2]$ **1**, $[Cu(bipy)(cnge)Cl_2]\cdot H_2O$ **3**, and $[Cu(bipy)_2(cnge)][BF_4]_2\cdot H_2O$ **5**, have been synthesised and structurally characterised. Their copper(II) co-ordination geometries vary from *cis*-distorted tetragonally elongated octahedral (for **1**) through square pyramidal (for **3**) to trigonal bipyramidal (for **5**). That in **1** comprises one bidentate chelating bipy and two monodentate cnge as equatorial ligands plus two BF_4^- anions as axial ligands, that in **3** comprises one bidentate chelating bipy, one monodentate cnge and one chlorine in equatorial positions with the other chlorine in the axial position, and that in **5** comprises two bidentate bipy ligands which straddle equatorial and axial sites and an equatorially located monodentate cnge ligand. The weak $Cu-FBF_3^-$ co-ordinate bond in **1** is supported by an intramolecular $N-H\cdots F$ hydrogen bond from an adjacent cnge amino moiety. A similar intramolecular $N-H\cdots Cl$ interaction occurs in **3**. Intermolecular hydrogen bonds exist in all three complexes; they include pairs of $N-H\cdots N$ donor–acceptor interactions between centrosymmetrically related cnge ligands (in **3**) and double $N-H\cdots F$ contacts (in **5**) as well as more conventional single $N-H\cdots X$ (X = F, Cl, O or N) interactions.

2-Cyanoguanidine (cnge; Scheme 1) readily co-ordinates the later transition metals, complexes with copper(II),[1–6] copper(I)[7–9] and cadmium[10] having been structurally characterised. Co-ordination preferentially occurs through the nitrile nitrogen [N(1)]; secondary co-ordination through the imino nitrogen [N(2)] only occurs when the nitrile function is already in use and the metal is sterically unhindered.[7]

Hydrogen-bonding interactions have long been considered to be of importance in biological systems[11] and in crystal engineering.[12] More recently their significance in co-ordination chemistry has been recognised.[5,9,13] In a number of earlier papers,[3,5,9] we attributed the versatility of cnge as a hydrogen-bonding ligand to the presence of guanidine functionalities which can act as donor [amino groups; $N(3)H_2$, $N(4)H_2$] and acceptor [imino nitrogen; N(2)] sites (Scheme 1). Its hydrogen-bonding potential is similar to that of melamine[13] to which it is structurally related, cnge and melamine being the dimer and trimer, respectively, of cyanamide (H_2NCN). When co-ordinated to copper(II) it can form both intra- and inter-molecular hydrogen-bonded contacts. Intramolecular interactions [Scheme 1(*i*)] have been reported in $[Cu_2(\mu-O_2CMe)_4(cnge)_2]$[4] and $[Cu(bipy)(cnge)_2(FBF_3)_2]$.[5] Intermolecular contacts are many and diverse. The more unusual are the double N−H donor systems in which both amino groups of a cnge molecule provide contacts to separate acceptor atoms of an anion, typically, NO_3^- or BF_4^- [Scheme 1(*ii*)], and the paired donor–acceptor contact between two (often centrosymmetric) cnge molecules in which each cnge molecule provides a donor and acceptor function [Scheme 1(*iii*)]. This latter system promotes two-dimensional sheet structures with the planar cnge molecule coplanar with the equatorial plane of the copper(II) co-ordination sphere; similar sheet structures are generated by the former system when a planar anion (*e.g.*, NO_3^-) is used.[3]

In the absence of multidentate ligands, copper(II) generally binds two *trans*-located cnge ligands in the equatorial plane of the tetragonally elongated octahedral copper(II) co-ordination sphere.[2,3] In a recent preliminary publication,[5] we reported the first example of a *cis*-located bis(cnge) copper(II) complex. This arrangement is dictated by the presence of the bidentate chelating ligand, 2,2′-bipyridine (bipy), and is supported by an intramolecular hydrogen bond involving a cnge amino proton and a weakly co-ordinated, axially located, tetrafluoroborate anion.



Scheme 1 2-Cyanoguanidine (cnge) and its modes of hydrogen bonding: (*i*) intramolecular N−H donor, (*ii*) intermolecular double N−H donor, and (*iii*) intermolecular paired $N-H\cdots N$ donor–acceptor

To further our understanding of the co-ordination behaviour of cnge, and of the influence of hydrogen-bonding interactions, we have undertaken a structural study of copper(II)–bipy–cnge complexes of differing stoichiometry (1:1:2, 1:1:1, 1:2:1) and with diverse anions (BF_4^-, NO_3^-, Cl^- and Br^-). Thus, in this paper we report the preparation and characterisation of

Table 1 Interatomic distances (Å) and angles (°) in the copper co-ordination spheres of **1**, **3** and **5***

1		**3**		**5**	
Cu–N(1)	1.931(5)	Cu–N(1)	1.946(4)	Cu–N(1)	2.014(5)
Cu–N(11)	1.983(5)	Cu–N(11)	2.007(3)	Cu–N(11)	1.985(4)
Cu–F(1)	2.599(2)	Cu–N(21)	2.023(3)	Cu–N(21)	2.058(4)
		Cu–Cl(1)	2.546(1)	Cu–N(31)	1.989(4)
		Cu–Cl(2)	2.300(1)	Cu–N(41)	2.128(4)
N(1)–Cu–N(11)	93.4(2)	N(1)–Cu–N(11)	168.2(1)	N(1)–Cu–N(11)	93.1(2)
N(1)–Cu–N(1^{I})	91.3(2)	N(1)–Cu–N(21)	91.6(1)	N(1)–Cu–N(21)	138.1(2)
N(1)–Cu–N(11^{I})	175.3(2)	N(1)–Cu–Cl(1)	95.9(1)	N(1)–Cu–N(31)	90.3(2)
N(1)–Cu–F(1^{I})	89.7(2)	N(1)–Cu–Cl(2)	88.6(1)	N(1)–Cu–N(41)	108.6(2)
N(11)–Cu–N(11^{I})	81.9(2)	N(11)–Cu–N(21)	80.3(1)	N(11)–Cu–N(21)	80.4(2)
N(11)–Cu–F(1)	89.7(2)	N(11)–Cu–Cl(1)	93.0(1)	N(11)–Cu–N(31)	176.6(2)
N(1)–Cu–F(1)	91.8(2)	N(11)–Cu–Cl(2)	95.7(1)	N(11)–Cu–N(41)	100.0(2)
N(11)–Cu–F(1^{I})	89.7(2)	N(21)–Cu–Cl(1)	101.0(1)	N(21)–Cu–N(31)	96.8(2)
F(1)–Cu–F(1^{I})	177.9(2)	N(21)–Cu–Cl(2)	157.9(1)	N(21)–Cu–N(41)	113.2(2)
		Cl(1)–Cu–Cl(2)	100.92(4)	N(31)–Cu–N(41)	79.1(2)
Cu–N(1)–C(1)	151.0(5)	Cu–N(1)–C(1)	152.8(3)	Cu–N(1)–C(1)	146.0(5)
Cu–N(11)–C(12)	114.5(3)	Cu–N(11)–C(16)	125.3(3)	Cu–N(11)–C(12)	115.7(3)
Cu–N(11)–C(16)	126.7(4)	Cu–N(11)–C(12)	115.4(2)	Cu–N(11)–C(16)	125.1(4)
Cu–F(1)–B(1)	129.6(4)	Cu–N(21)–C(26)	125.2(2)	Cu–N(21)–C(22)	113.2(3)
		Cu–N(21)–C(22)	115.3(2)	Cu–N(21)–C(26)	127.8(4)
				Cu–N(31)–C(32)	117.5(4)
				Cu–N(31)–C(36)	122.8(4)
				Cu–N(41)–C(42)	112.9(4)
				Cu–N(41)–C(46)	128.3(4)

* Symmetry relationship: I $-x, y, 1.5 - z$.

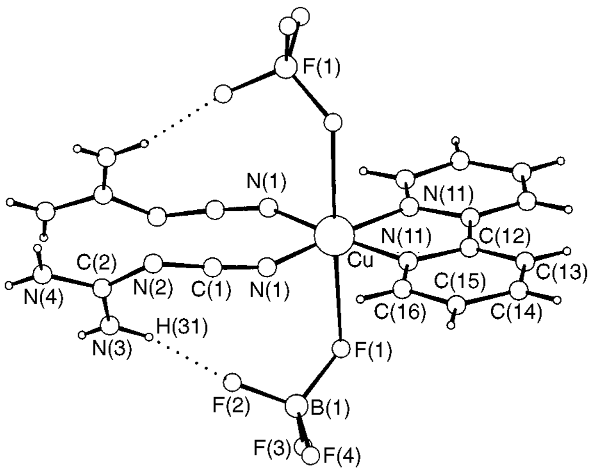


Fig. 1 Molecular structure of [Cu(bipy)(cnge)$_2$(FBF$_3$)$_2$] **1** showing the intramolecular hydrogen-bonding interaction between the co-ordinated cnge ligands and BF$_4^-$ anions

[Cu(bipy)(cnge)$_2$(FBF$_3$)$_2$] **1**, [Cu(bipy)(cnge)$_2$(NO$_3$)$_2$] **2**, [Cu(bipy)(cnge)Cl$_2$]·H$_2$O **3**, [Cu(bipy)(cnge)Br$_2$]·H$_2$O **4**, [Cu(bipy)$_2$(cnge)][BF$_4$]$_2$·H$_2$O **5**, describing structural data for **1**, **3** and **5**.

Results and Discussion

The complexes were crystallised from the mixtures obtained by combining aqueous solutions of the appropriate copper(II) salt [Cu(BF$_4$)$_2$·3.4H$_2$O, Cu(NO$_3$)$_2$·3H$_2$O, CuCl$_2$·2H$_2$O and CuBr$_2$] and cnge with an acetonitrile solution of bipy. Single products were formed in all systems studied except Cu(BF$_4$)$_2$·3.4H$_2$O–bipy–cnge which gave **1** and **5** and CuCl$_2$·2H$_2$O–bipy–cnge which yielded compounds which analysed for Cu(bipy)Cl$_2$ and Cu(bipy)$_2$Cl$_2$·2H$_2$O as well as **3**. The complexes were initially characterised by elemental analysis (C, H, N), IR and UV/VIS spectroscopy and fast atom bombardment (FAB) mass spectrometry. Although X-ray diffraction data were subsequently measured for **1**, **2**, **3** and **5**, it was only possible to solve the structures of **1**, **3** and **5**.

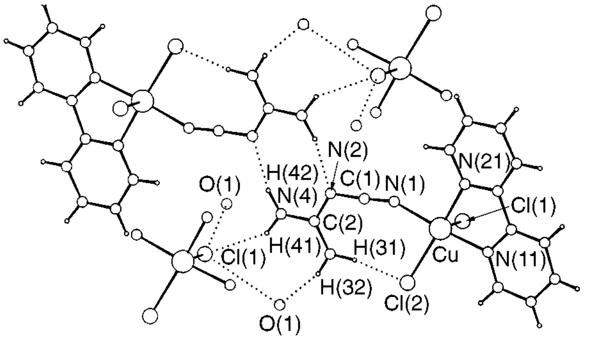


Fig. 2 Intra- and inter-molecular hydrogen-bonding interactions within the centrosymmetric dimeric unit of [Cu(bipy)(cnge)Cl$_2$]·H$_2$O **3**

Crystal and molecular structures of complexes 1, 3 and 5

Whereas the structures of **1** and **3** are based on the neutral complexes, [Cu(bipy)(cnge)$_2$(FBF$_3$)$_2$] and [Cu(bipy)(cnge)Cl$_2$] respectively, complex **5** comprises [Cu(bipy)$_2$(cnge)]$^{2+}$ cations and BF$_4^-$ anions. Both **3** and **5** also contain unco-ordinated water molecules. The structures of the copper(II) complexes are shown in Figs. 1–3. Selected interatomic distances and angles are collected in Table 1; hydrogen-bonding interactions are summarised in Table 2. Three different copper(II) co-ordination geometries are adopted; [Cu(bipy)(cnge)$_2$(FBF$_3$)$_2$] is *cis*-distorted tetragonally elongated octahedral, [Cu(bipy)(cnge)Cl$_2$] is square pyramidal and [Cu(bipy)$_2$(cnge)]$^{2+}$ is trigonal bipyramidal.

The copper atom in **1** (Fig. 1) is located on a crystallographic two-fold axis which bisects the bipy ligand. It is surrounded equatorially by a bidentate bipy ligand and two monodentate cnge molecules and axially by two BF$_4^-$ anions. The equatorial Cu–N bonds [Cu–N(bipy) 1.983; Cu–N(cnge) 1.931 Å] differ only by the difference of the N (sp^2) and N (sp) radii; the axial Cu–F bond (Cu–F 2.599 Å) can be classed as semi-co-ordinating.[14] The BF$_4^-$ anion, which exhibits no disorder, is locked in position by an intramolecular hydrogen bond [N(3)–H(31) · · · F(2); Table 2] to the amino group of the adjacent cnge molecule. The formation of this interaction is facilitated by the inclination (by 59.4°) of the planar (maximum deviation from

Table 2 Hydrogen bonding interactions (distances/Å and angles/°) in [Cu(bipy)(cnge)$_2$(FBF$_3$)$_2$] **1**, [Cu(bipy)(cnge)Cl$_2$]·H$_2$O **3** and [Cu(bipy)$_2$(cnge)][BF$_4$]$_2$·H$_2$O **5**

[Cu(bipy)(cnge)$_2$(FBF$_3$)$_2$] **1**

Interaction X–H···X′	Symmetry of X′	X–H/Å	X–X′/Å	H···X′/Å	XHX′/°
N(3)–H(31)···F(2)	(x, y, z)	0.87	2.99	2.13	167
N(4)–H(41)···F(4)	($0.5 - x, -0.5 + y, z$)	0.87	2.87	2.03	162
N(4)–H(42)···N(2)	($-x, -y, 2 - z$)	0.96	3.07	2.12	170

[Cu(bipy)(cnge)Cl$_2$]·H$_2$O **3**

Interaction X–H···X′	Symmetry of X′	X–H/Å	X–X′/Å	H···X′/Å	XHX′/°
N(3)–H(31)···Cl(2)	(x, y, z)	0.98	3.46	2.51	164
N(3)–H(32)···O(1)	($1 + x, y, -1 + z$)	0.97	3.03	2.08	163
N(4)–H(41)···Cl(1)	($1 + x, y, z$)	0.99	3.24	2.40	141
N(4)–H(42)···N(2)	($3 - x, 1 - y, 1 - z$)	0.97	2.98	2.03	167

Interaction X–H···X′	Symmetry of X′	X–X′/Å	X′XX′/°	
O(1)···Cl(1$^{\text{I}}$)	($x, y, 1 + z$)	3.30	Cl(1$^{\text{I}}$)–O(1)–Cl(1$^{\text{II}}$)	89
O(1)···Cl(1$^{\text{II}}$)	($1 - x, 1 - y, 1 - z$)	3.12	Cl(1$^{\text{I}}$)–O(1)–N(3)	95
			Cl(1$^{\text{II}}$)–O(1)–N(3)	84

[Cu(bipy)$_2$(cnge)][BF$_4$]$_2$·H$_2$O **5**

Interaction X–H···X′	Symmetry of X′	X–H/Å	X–X′/Å	H···X′/Å	XHX′/°
N(3)–H(31)···F(4)	($-x, -y, 1 - z$)	0.86	3.03	2.23	155
N(3)–H(32)···F(2)	($x, 1 + y, z$)	0.86	2.86	2.30	173
N(4)–H(41)···F(3)	($x, 1 + y, z$)	0.86	3.13	2.32	157
N(4)–H(42)···O(1A)*	($-x, 1 - y, 1 - z$)	0.86	2.77	1.95	175
N(4)–H(42)···O(1B)*	($-x, 1 - y, 1 - z$)	0.86	2.86	2.27	124

Interaction X···X′	Symmetry of X′	X–X′/Å	X′XX′/°	
O(1A)···F(7A)*,†	($x, 1 + y, z$)	2.74	F(7A)–O(1A)–F(8A)	137
O(1A)···F(8A)*,†	($-x, -y, 1 - z$)	2.53	F(7A)–O(1A)–N(8)	131
			F(8A)–O(1A)–N(8)	86
O(1B)···F(7B)*,†	(x, y, z)	2.68	O(1B$^{\text{III}}$)–O(1B)–F(7B)	72
O(1B) ···O(1B$^{\text{III}}$)*	($2 - x, 1 - y, 2 - z$)	2.94	F(7B)–O(1B)–N(8)	163
			O(1B$^{\text{III}}$)–O(1B)–N(8)	125

* Disordered water molecule, denoted O(1A) and O(1B), with 50% fractional occupancy. † BF$_4^-$ Anion in which three fluorine atoms are disordered about two positions, denoted A and B, each with 50% fractional occupancy.

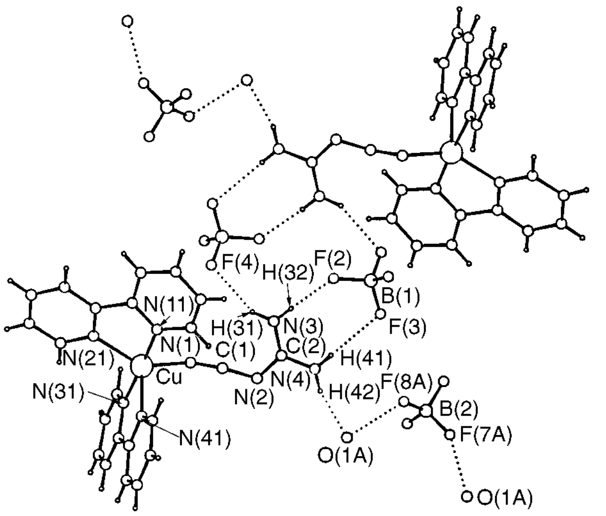


Fig. 3 Hydrogen-bonding interactions within the crystal structure of [Cu(bipy)$_2$(cnge)][BF$_4$]$_2$·H$_2$O **5**

the least-squares mean plane = 0.111 Å) cnge molecules to the copper(II) equatorial plane and results in a smaller cnge co-ordinate angle [Cu–N(1)–C(1) 151.0°] than that expected for a transition metal–nitrile interaction (180°). The cnge molecule is also involved in two intermolecular hydrogen bonds, one to an adjacent BF$_4^-$ anion [N(4)–H(41)···F(4); Table 2], the other to an adjacent cnge molecule [N(4)–H(42)···N(2); Table 2].

Semi-co-ordination of the BF$_4^-$ anion to the copper(II) centre and the intra- and inter-molecular hydrogen-bonding interactions result in loss of the T_d symmetry of the free anion. The B–F distances decrease in the logical sequence: B–F(1) 1.388(8) (co-ordination to copper), B–F(2) 1.379(8) (intramolecular hydrogen bond), B–F(4) 1.358(8) (intermolecular hydrogen bond), B–F(3) 1.336(8) Å (no interaction). The planar bipy ligand (maximum deviation from the least-squares mean plane, 0.027 Å) is coplanar with the equatorial plane of the copper(II) co-ordination sphere (dihedral angle, 0.7°).

The square-pyramidal copper in **3** (Fig. 2) is ligated equatorially by a bidentate bipy ligand, a monodentate cnge ligand and a chlorine atom, and axially by a second chlorine atom. As for **1**, the Cu–N distances to the sp^2 nitrogens of the bipy ligand are slightly longer than that to the sp nitrogen of the cnge ligand [average Cu–N(bipy) 2.015; Cu–N(cnge) 1.946 Å]. As is normal for square-pyramidal copper(II), the axial Cu–Cl distance (2.546) is longer than the equatorial Cu–Cl distance (2.300 Å). The co-ordinate angle of the cnge ligand [Cu–N(1)–C(1) 152.8°] is similar to that in **1**. It can be attributed to an intramolecular hydrogen-bonding interaction between a cnge amino moiety and the equatorially located chlorine [N(3)–H(31)···Cl(2); Table 2]. To promote this interaction the cnge molecule is effectively coplanar with the basal atoms of the square pyramidal co-ordination sphere. Indeed, with the exception of the axially located chlorine atom, the entire molecule is planar (Fig. 2) with maximum deviations from the least-squares best planes of 0.253 (basal plane), 0.029 (bipy) and 0.057 Å (cnge) and dihedral angles of 15.7 (basal plane–cnge), 5.6 (basal plane–bipy) and 16.4° (bipy–cnge). The copper atom is located 0.345 Å above the basal plane in the direction of the axial chlorine.

The trigonal-bipyramidal copper atom in **5** (Fig. 3) is surrounded by two chelating bipy molecules and a single monodentate cnge ligand. Each bipy occupies one axial and one equatorial position, the axial Cu–N distances being shorter (average 1.987) than the equatorial ones (average 2.093 Å). The equatorially located sp nitrogen of the cnge molecule is closer to the copper atom (2.014 Å) than the equatorially located sp^2 nitrogens of the bipy molecules. The three ligands are effectively planar with maximum displacements from the least-squares mean planes of 0.073 (bipy 1), 0.138 (bipy 2) and 0.122 Å (cnge). The copper atom is only marginally displaced (0.008 Å) from the equatorial plane and is equidistant from the two axial bipy nitrogens. The dihedral angles between the ligands and the equatorial plane are 87.63 (bipy 1), 79.59 (bipy 2) and 62.80° (cnge).

The co-ordinate angle of the cnge molecule is the smallest [Cu–N(1)–C(1) 146.0°] of all three complexes. It can be rationalised by the existence of strong hydrogen-bonding interactions between the cnge amino moieties and fluorines of two $B(1)F_4^-$ anions [N(3)–H(31) · · · F(4); N(3)–H(32) · · · F(2); N(4)–H(41) · · · F(3)]. Despite these interactions all four B–F distances in the $B(1)F_4^-$ anion are the same within experimental error [B–F(3) 1.360(8), B–F(2) 1.354(8), B–F(1) 1.343(8), B–F(4) 1.330(8) Å]. The detailed structure of the second $[B(2)F_4^-]$ anion in **5** cannot be similarly analysed owing to its disorder. The anions in **5** are, however, more symmetrical than those co-ordinated to the copper atom in **1**. This difference is manifest in the IR spectra of the two complexes, the reduction in symmetry from T_d (unco-ordinated) to C_s (co-ordinated) resulting in splitting of the triply degenerate ν(B–F) mode (T_2) centred at 1061 cm^{-1} in **5** into three singly degenerate modes (2A′ + A″) at 1089, 1035 and 906 cm^{-1} for **1**.[5]

Infrared spectroscopic diagnosis of cnge co-ordination

The ν_{asym}(NCN) 'doublet' in the IR spectrum of cnge is sensitive to co-ordination to transition metals.[3,7] For all but three examples, it moves to higher frequency, following a similar pattern to co-ordinated cyanide,[15] and shows a reversal in the relative intensities of the two bands. The three exceptions are the copper(II) complexes, **5**, $[Cu(dien)(cnge)(NO_2)_2]\cdot xH_2O$ **6** and $[Cu_2(\mu\text{-}O_2CMe)_4(cnge)_2]$ **7**. The band position moves to lower frequency for **5** and **6**,[6] and is virtually unchanged for **7**;[4] in all three cases, the relative intensities of the bands are the same as for free cnge[16] (the higher energy band has the greater intensity). The position of the ν_{asym}(NCN) doublet cannot be related to trends in the structural parameters (interatomic distances and angles) of co-ordinated cnge.[6] However, its co-ordination mode in **5** and **7** does differ considerably from that in all other structurally characterised copper(II)–cnge complexes. In **5** and **7**, cnge is located in weakly co-ordinating sites, trigonal-planar equatorial and square-pyramidal axial, respectively, with extended Cu–N distances (2.01, 2.14 Å) and low co-ordinate Cu–N(1)–C(1) angles (146, 136°). In the other complexes, including **1** and **3**, the cnge is strongly bound with shorter Cu–N distances (1.92–1.96 Å) and larger co-ordinate angles (151–176°). These results would suggest a five-co-ordinate structure, with weakly bound cnge, for **6**; structural data for **6** are not available owing to its extreme deliquescence.

The IR spectrum of **1** differs when recorded in a 'Nujol' mull and in a KBr disc, the latter being reminiscent of a mixture of **4**, free cnge and KBF_4. Whereas only two bands are observed in the 'Nujol' mull spectrum of **1** (2232 and 2198 cm^{-1}), the KBr disc spectrum of **1** contains four bands (2232, 2209, 2198 and 2164 cm^{-1}). Of these four, two are reminiscent of the 'doublet' in the spectrum of **4** (2237 and 2195 cm^{-1}) and two of the 'doublet' in the spectrum of free cnge (2209 and 2165 cm^{-1}). This conclusion implies the partial decomposition of **1** [equation (1)]: Since a similar problem does not occur for **5**

$$[Cu(bipy)(cnge)_2(FBF_3)_2] + 2KBr \longrightarrow [Cu(bipy)(cnge)Br_2] + cnge + 2KBF_4 \quad (1)$$

in which BF_4^- is unco-ordinated it is inferred that it is only co-ordinated BF_4^- which is highly labile. The KBr disc spectrum of **2**, which may have a comparable structure to **1**, also indicates decomposition, resembling a mixture of **4**, free cnge and KNO_3.

Hydrogen-bonding interactions involving co-ordinated cnge

Co-ordinate angles in copper(II)–acetonitrile systems with no potential for hydrogen bonding are close to linear [*e.g.*, 167, 170° in $\{[Cu(MeCN)_4(\mu\text{-pyz})]^{2+}\}_n$[8] (pyz = pyrazine)]. Strongly bound cnge molecules adopt angles ranging from 176.4 {in $[Cu(dien)(cnge)(ONO_2)_2]$[6] (dien = diethylenetriamine)} through 168.8 {in $[Cu(cnge)_2(H_2O)_2][NO_3]_2\cdot 2H_2O$[3]}, 164.9 {in $[Cu(cnge)_2Cl_2]\cdot 2H_2O$[2]}, and 152.8 (in **3**) to 151.0° (in **1**). The greatest distortions from linearity (in **3** and **1**) can be attributed to the presence of intramolecular [N–H · · · F (Fig. 1), N–H · · · Cl (Fig. 2)] hydrogen bonds. Weakly bound cnge molecules adopt even smaller angles ranging from 146 (in **5**) to 136° {in $[Cu_2(\mu\text{-}O_2CMe)_4(cnge)_2]$[4]}. Again, the greater distortion {in $[Cu_2(\mu\text{-}O_2CMe)_4(cnge)_2]$} corresponds to the presence of intramolecular (N–H · · · O) hydrogen bonds.

In addition to the intramolecular contacts in **1** and **3**, diverse intermolecular interactions exist in all three copper(II)–bipy–cnge complexes. Full details are given in Table 2. As well as forming regular hydrogen-bonding contacts in **1**, **3** and **5**, cnge molecules form, in **3**, centrosymmetric paired donor–acceptor interactions [Scheme 1(*iii*)] and, in **5**, double N–H donor contacts to BF_4^- fluorines [Scheme 1(*ii*)]. The extensive hydrogen-bonding network in **3** is shown in Fig. 2 which depicts two centrosymmetrically related asymmetric units joined by a pair of N(4)–H(42) · · · N(2) links, each cnge molecule acting as both donor and acceptor. The planar dimeric units are linked by N(3)–H(32) · · · O(1) and N(4)–H(41) · · · Cl(1) hydrogen bonds to coplanar water oxygens and axially located chlorines of adjacent dimers giving a two-dimensional sheet structure. The sheets are linked by Cl(1) · · · O(1) hydrogen bonds as well as the Cu–Cl(1) co-ordinate bond.

The asymmetric unit of **5** is depicted in Fig. 3. It shows the double contact [N(4)–H(41) · · · F(3); N(3)–H(32) · · · F(2)] between the cnge molecule and the $B(1)F_4^-$ anion. This anion, which is not disordered, is also hydrogen-bonded to a second cation [N(3)–H(31) · · · F(4)]. This contact is made possible by the low co-ordinate angle [Cu–N(1)–C(1) 146°]. With near-linear co-ordinate angles, the N(3)–H(31) vector necessarily points towards a *cis*-located co-ordination site and hence is not available for hydrogen-bonding interactions other than intramolecular (as in **3**). Decreasing the co-ordinate angle and increasing the dihedral angle between the equatorial plane and cnge permits access to H(31) for an acceptor atom [F(4) in **5**]. The fourth hydrogen on the cnge molecule is linked to a water oxygen [N(4)–H(42) · · · O(1)], which is disordered over two equally occupied sites. Full details of all four contacts are given in Table 2 together with those of a weaker hydrogen-bonding network involving the second $B(2)F_4^-$ anion and the water oxygen. This anion has two-fold rotational disorder about the F(5)–B(2) vector with 50% occupancy of the two possible sites, which coincides with the disorder of the water molecule.

Experimental

All reagents (Aldrich) were used as received, apart from cnge which was recrystallised from hot deionised water prior to use. Elemental analysis (C, H, N) and FAB mass spectra were determined using a Perkin-Elmer 240B elemental analyser and a VG70E micromass spectrometer by Mr. T. Spencer and Mr. T. Hollingworth, respectively, of the Nottingham University Chemistry Department Analytical Services Group. Chloride analysis was performed by precipitation of AgCl. Infrared spectra, in KBr discs or as Nujol mulls between KBr windows (protected by Polythene) and UV/VIS spectra, in aqueous solution $[(1–10) \times 10^{-4}\ mol\ dm^{-3}]$, were recorded using Perkin-Elmer 983G and Unicam UV2-100 spectrometers, respectively.

Table 3 Reaction stoichiometries and product analyses for complexes **1**–**5**

	Reagents											
	Copper salt[b]		Bipyridine		Cyanoguanidine		Yield			Elemental analysis (%)[a]		
Complex	g	mmol	g	mmol	g	mmol	g	mmol	%	C	H	N
1	2.40	7.99	0.32	2.05	1.01	12.00	0.50	0.89	43	29.90 (29.90)	2.85 (2.85)	24.70 (24.95)
2	0.80	3.31	0.52	3.31	0.56	6.62	1.31	2.56	77	33.05 (32.85)	3.15 (3.50)	32.85 (32.85)
3	1.28	7.48	1.17	7.48	0.63	7.48	0.50	1.30	17	36.80 (36.70)	3.55 (3.60)	21.55 (21.40)
4	1.07	4.78	0.75	4.78	0.40	4.78	0.75	1.56	33	30.20 (29.95)	2.85 (2.95)	17.25 (17.45)
5	2.40	8.00	1.87	12.00	0.39	4.70	2.78	4.27	71	40.65 (40.55)	3.25 (3.40)	18.10 (17.20)

[a] Calculated values in parentheses. [b] $Cu(BF_4)_2 \cdot 3.4H_2O$ for **1** and **5**, $Cu(NO_3)_2 \cdot 3H_2O$ for **2**, $CuCl_2 \cdot 2H_2O$ for **3**, $CuBr_2$ for **4**.

Table 4 Spectral data for complexes **1**–**5**

	IR*/cm^{-1}			UV/VIS		
Complex	cnge		anion	$\lambda_{max}(H_2O)$/nm	ε/mol^{-1} m^2	FAB Mass spectra *m*/*z*
1	2232m	2198s	1050s (br)	696	3.470	303 {[Cu(bipy)(cnge)]$^+$}; 231 {[Cu(cnge)$_2$]$^+$}, 219 {[Cu(bipy)]$^+$}; 147 {[Cu(cnge)]$^+$}
2	2232s	2189s	1383s	692	3.280	303 {[Cu(bipy)(cnge)]$^+$}; 231 {[Cu(cnge)$_2$]$^+$}; 219 {[Cu(bipy)]$^+$}; 147 {[Cu(cnge)]$^+$}
3	2233s	2197s		692	3.330	303 {[Cu(bipy)(cnge)]$^+$}; 254 {[Cu(cnge)Cl]$^+$}; 219 {[Cu(bipy)]$^+$}
4	2237s	2195s		688	3.470	
5	2198m	2158s	1035s (br)			

* In Nujol mulls.

Table 5 Crystallographic data for $[Cu(bipy)(cnge)_2(FBF_3)_2]$ **1**, $[Cu(bipy)(cnge)Cl_2] \cdot H_2O$ **3** and $[Cu(bipy)_2(cnge)][BF_4]_2 \cdot H_2O$ **5**

Complex	**1**	**3**	**5**
Formula	$C_{14}H_{16}B_2CuF_8N_{10}$	$C_{12}H_{14}Cl_2CuN_6O$	$C_{22}H_{22}B_2CuF_8N_8O$
M	561.53	392.73	651.63
Crystal system	Orthorhombic	Triclinic	Triclinic
Space group	*Pbcn* (no. 60)	$P\bar{1}$ (no. 2)	$P\bar{1}$ (no. 2)
a/Å	11.397(2)	9.406(4)	8.034(1)
b/Å	14.255(2)	10.980(4)	11.965(1)
c/Å	13.475(2)	9.205(4)	14.859(1)
α/°	90	97.09(3)	98.06(1)
β /°	90	115.61(3)	92.02(1)
γ/°	90	68.88(3)	105.03(1)
Z	4	2	2
U/Å^3	2189.2(6)	799.2(6)	1362.0(2)
μ_{calc}/cm^{-1}	22.64	17.16	19.13
D_c/g cm^{-3}	1.704	1.632	1.382
D_m/g cm^{-3} (bromoform–hexanes)	1.68	1.62	1.35
F(000)	1124	398	580
Crystal dimensions/mm	0.47 × 0.40 × 0.18	1.00 × 0.50 × 0.30	0.55 × 0.45 × 0.38
Radiation	Cu-Kα (1.541 84 Å)	Mo-Kα (0.710 73 Å)	Cu-Kα (1.541 84 Å)
Temperature/K	298	296	298
θ Range for data collection	4.97–49.97	25 (θ_{max})	3.01–54.98
Scan mode	2θ/ω	ω–2θ	2θ/ω
Index ranges	$-6 \leqslant h \leqslant 11$, $-14 \leqslant k \leqslant 0$, $0 \leqslant l \leqslant 13$	$0 \leqslant h \leqslant 10$, $-12 \leqslant k \leqslant 12$, $-10 \leqslant l \leqslant 9$	$-6 \leqslant h \leqslant 8$, $-12 \leqslant k \leqslant 12$, $-15 \leqslant l \leqslant 15$
Reflections collected	1299	2680	3423
Independent reflections	1132	2495	2725
Refinement method: full matrix least squares on	F^2	*F*	F^2
Data, restraints, parameters	1131, 0, 172	2362, 0, 199	2725, 87, 401
R, wR_2 (all data)	0.0607, 0.1235		0.0750, 0.1838
R, wR_2 [data with $I \geqslant 2\sigma(I)$ for **1** and **5**, $I \geqslant 3\sigma(I)$ for **3**]	0.0433, 0.111 2	0.032, 0.054	0.0578, 0.1526
ρ_{min}, ρ_{max}/e Å^{-3}	−0.281, 0.645	−0.30, 0.73	−0.385, 0.465

Preparation of complexes

The five complexes were prepared by similar protocols; quantitative details are given in Table 3. A copper(II)–bipy–cnge mixture, obtained by addition of an aqueous solution of the appropriate copper(II) salt to an acetonitrile solution of bipy and a hot aqueous solution of cnge, was heated gently on a steam bath for 30 min and set aside at room temperature for crystallisation. A single product was obtained for all systems except that involving $CuCl_2 \cdot 2H_2O$. In this case, three products which analysed for $Cu(bipy)Cl_2$ (30% yield), $[Cu(bipy)(cnge)Cl_2]$ (17% yield) and $Cu(bipy)_2Cl_2 \cdot 2H_2O$ (15% yield) crystallised consecutively from solution: $Cu(bipy)Cl_2$ {mint-green powder; $\lambda_{max}(H_2O)$ 692 nm, ε 3.280 m^2 mol^{-1} [Found (Calc. for $C_{10}H_8Cl_2CuN_2$): C, 40.95 (41.35); H, 2.70 (2.75); N, 10.25 (9.65); Cl, 24.55% (24.40)]}, $Cu(bipy)_2Cl_2 \cdot$

$2H_2O$ {blue crystals; $\lambda_{max}(H_2O)$ 736 nm, ε 8.235 m^2 mol^{-1} [Found (Calc. for $C_{20}H_{20}Cl_2CuN_4O_2$): C, 49.25 (49.75); H, 4.15 (4.15); N, 12.10% (11.60)], *m/z* 375, $[Cu(bipy)_2]^+$; 254, $[Cu(bipy)Cl]^+$; 219, $[Cu(bipy)]^+$]}. Analytical, IR and UV/VIS spectroscopic and FAB-mass spectrometric data for **1**–**5** are listed in full in Table 4.

Crystallography

Several crystals of **1**, **2**, **3** and **5** were mounted on glass fibres for preliminary study. Oscillation and Weissenberg photographs revealed orthorhombic parameters for **1** [space group *Pbcn* (no. 60)] and **2** [space group $P2_12_12_1$ (no. 18) or $P2_12_12$ (no. 19)] and triclinic parameters for **3** and **5** [space group *P*1 (no. 2)]. X-Ray diffraction data for the refinement of cell parameters and structure determination were collected using Enraf-Nonius CAD-4 (for **1** and **5**), and Rigaku AFC6S (for **3**) diffractometers with either Ni-filtered Cu-Kα radiation (for **1** and **5**; $\lambda = 1.541\ 84$ Å) or graphite-monochromated Mo-Kα radiation (for **3**; $\lambda = 0.710\ 73$ Å). For **1** and **5**, unique sets of data were collected in the range $5 < \theta < 50°$ and $3 < \theta < 55°$, respectively. Intensity control reflections were monitored periodically throughout the data collection and no significant decrease in intensity was observed. Lorentz and polarisation corrections were applied to the data. For **3**, a unique data set was collected from 2680 reflections ($\theta_{max} = 25°$). Intensity control reflections were monitored every 150 data and no significant decrease in intensity was observed. The data were corrected for Lorentz and polarisation effects. Crystal data for **1**, **3** and **5**, together with details of the diffraction experiments are listed in Table 5.

The structures of **1** and **5** were solved by Patterson and Fourier methods (SHELXS 86).[17] They were refined by full-matrix least-squares methods on F^2 using all data (SHELXL 93).[18] Non-hydrogen atoms were refined with anisotropic displacement parameters. Hydrogen atoms were located by Fourier-difference syntheses and their position refined {with U_{iso} fixed to $1.2U_{eq}$ of the carrying atom}. Absorption corrections were not applied. For **1**, refinement with two parameter Chebychev weighting scheme (0.0514, 6.13) converged to a conventional *R* index [$I \geqslant 2\sigma(I)$] of 0.0433. For **5**, refinement with unit weights converged to a conventional *R* index [$I \geqslant 2\sigma(I)$] of 0.0578. The structure of **3** was solved by Patterson[19] and Fourier[20] methods and refined by full-matrix least-squares methods on *F* using data with $I \geqslant 3\sigma(I)$ using the TEXSAN crystal structure package.[21] Non-hydrogen atoms were refined with anisotropic displacement parameters. All hydrogen atoms were located by Fourier-difference syntheses but not refined. Absorption corrections were applied (DIFABS).[22] Refinement converged to $R = 0.032$. Despite measuring three sets of diffraction data for **2** [proposed empirical formula, $C_{14}H_{16}CuN_{12}O_6$; proposed molecular mass, 511.9; orthorhombic, space group $P2_12_12_1$ or $P2_12_12$; $a = 7.222$, $b = 7.807$, $c = 41.63$ Å; $U = 2347$ Å^3; $Z = 4$; $D_c = 1.45$ kg m^{-3}, D_m (bromoform–hexanes) = 1.43 kg m^{-3}] and trying heavy-atom and diverse direct-methods programs, it was not possible to solve its structure.

Atomic coordinates, thermal parameters, and bond lengths and angles have been deposited at the Cambridge Crystallographic Data Centre (CCDC). See Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1997, Issue 1. Any request to the CCDC for this material should quote the full literature citation and the reference number 186/555.

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