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Discrete dinuclear and polymeric copper(I) cations bridged by 4,4′-bipyridine, *trans*-1,2-bis(4-pyridyl)ethene or bis(4-pyridyl) disulfide

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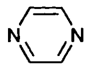
Treatment of an acetonitrile solution of copper(I) tetrafluoroborate and 4,4′-bipyridine (4,4′-bipy) with 2-cyanoguanidine (cnge) yielded [{Cu(cnge)$_2$}$_2$(μ-4,4′-bipy)][BF$_4$]$_2$·MeCN **1**. Structural analysis revealed a planar dinuclear cation containing two, three-co-ordinate T-shaped copper centres bridged by 4,4′-bipy and terminally co-ordinated by two cnge molecules. In the absence of cnge but with an excess of copper(I), the product was [Cu(4,4′-bipy)(MeCN)$_2$]BF$_4$ **2**, structural analysis of which revealed a one-dimensional polymeric cationic zigzag chain, based on tetrahedral copper(I) atoms bridged by 4,4′-bipy and terminally co-ordinated by two MeCN molecules. The same reaction mixture but with an excess of 4,4′-bipy gave [Cu(4,4′-bipy)$_2$]BF$_4$·MeCN **3**. The corresponding *trans*-1,2-bis(4-pyridyl)ethene (bpe) systems yielded the analogous [{Cu(cnge)$_2$}$_2$(μ-bpe)][BF$_4$]$_2$·6MeCN **4**, [Cu(bpe)(MeCN)$_2$]BF$_4$ **5** and [Cu(bpe)$_2$]BF$_4$ **6**, respectively. Only one product has been isolated from the corresponding bis(4-pyridyl) disulfide (bpds) systems, [Cu(bpds)(MeCN)$_2$]BF$_4$ **7**. Attempts to produce copper(I) derivatives of 3,6-bis(imidazolyl)pyridazine (bimpydz) were unsuccessful, the copper(II) product, Cu(bimpydz)(MeCN)$_2$(BF$_4$)$_2$ **8**, invariably being formed. Whereas the [{Cu(cnge)$_2$}$_2$(diimine)]$^{2+}$ and [Cu(diimine)(MeCN)$_2$]$^+$ cations reacted with NOBF$_4$ and NBu$^t_4$NO$_2$ forming copper(II) oxidation products, the [Cu(diimine)$_2$]$^+$ cations were unreactive.

To probe the redox chemistry of inorganic analogues of the active centre of the copper-containing nitrite reductase *Achromobacter cycloclastes* (A. C. NiR), which comprises two copper sites, one type 1 and one type 2, connected by a histidine–cysteine dipeptide link,[1] we have targetted discrete cationic complexes containing two co-ordinatively unsaturated copper(I) centres bridged by the planar bidentate diimines pyrazine (pyz), 4,4′-bipyridine (4,4′-bipy), *trans*-1,2-bis(4-pyridyl)ethene (bpe), bis(4-pyridyl) disulfide (bpds) and 3,6-bis(imidazolyl)pyridazine (bimpydz). To stabilise three-co-ordinate copper(I) geometries the reactions were undertaken in the presence of 2-cyanoguanidine (cnge).[2] The target molecules have proved to be elusive; thus far we have obtained two only, [{Cu(cnge)$_2$}$_2$(μ-diimine)]$^{2+}$ (diimine = 4,4′-bipy or bpe). With pyz the one-dimensional polymeric four-co-ordinate copper(I) complex [{Cu(μ-pyz)(cnge)(MeCN)}$_n$]$^{n+}$ was formed. With bpds, cnge was not incorporated in the product, [{Cu(μ-bpds)(MeCN)$_2$}$_n$]$^{n+}$. With bimpydz the only product was a copper(II) derivative, Cu(bimpydz)(MeCN)$_2$(BF$_4$)$_2$. In the absence of cnge, 4,4′-bipy and bpe afforded the polymeric products [{Cu(μ-diimine)(MeCN)$_2$}$_n$]$^{n+}$ or [{Cu(μ-diimine)$_2$}$_n$]$^{n+}$ depending on the reaction conditions. In a subsequent paper we will describe the chemistry of the copper(I)–pyz–cnge system.[3] We now report the syntheses and structures of [{Cu(cnge)$_2$}$_2$(μ-4,4′-bipy)][BF$_4$]$_2$·MeCN **1** and [{Cu(μ-4,4′-bipy)(MeCN)$_2$}$_n$][BF$_4$]$_n$ **2** and the preparation and characterisation of [Cu(4,4′-bipy)$_2$]BF$_4$·MeCN **3**, [{Cu(cnge)$_2$}$_2$(μ-bpe)][BF$_4$]$_2$·6MeCN **4**, [Cu(bpe)(MeCN)$_2$]BF$_4$ **5**, [Cu(bpe)$_2$]BF$_4$ **6**, [Cu(bpds)(MeCN)$_2$]BF$_4$ **7** and Cu(bimpydz)(MeCN)$_2$(BF$_4$)$_2$ **8**. We also describe the reaction chemistry of compounds **1**, **2**, **4** and **6** with NOBF$_4$ and with NBu$^t_4$NO$_2$.

Of the five diimines considered here, bimpydz is novel; the other four have been considered to differing extents as bridges in transition-metal complexes. Although the use of 4,4′-bipy to study electronic interaction between pairs of transition-metal cations in solution is well documented,[4] structurally characterised 4,4′-bipy-bridged dinuclear transition-metal complexes are extremely rare;[5,6] the majority are polymeric.[7] Structural data are only available for one copper(I) complex, [Cu(4,4′-bipy)$_2$]PF$_6$,[6] in which the cation exhibits a three-dimensional diamondoid network. A comprehensive literature search revealed only one other report on copper(I)–4,4′-bipy complexes; it describes the preparation and analysis of CuX(4,4′-bipy) and Cu$_2$X$_2$(4,4′-bipy) (X = Cl, Br or I).[8] The role of bpe as a bridging ligand is not well established. A very limited number of studies,[9] in which bpe has been used in the place of 4,4′-bipy to increase the distance between metal centres, has been published but none involves copper(I). The structure of the related copper(I) complex, [{Cu(dpm)}$_2$(μ-tpe)(μ-OH)][ClO$_4$]$_3$·2H$_2$O [tpe = tetrakis(2-pyridyl)ethene, dpm = dipyridylmethane], has, however, been reported.[10] Although the co-ordination of bpds to copper(I) has yet to be studied, its interaction with copper(II),[11] as well as with other later transition metals,[11,12] has been investigated. In the absence of structural data, the complexes CuX$_2$(bpds) (X = Cl or Br) have been inferred, from vibrational (IR and Raman) spectral data,[11] to have one-dimensional polymeric structures, bridged by bpds.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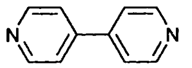
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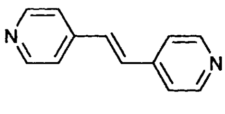
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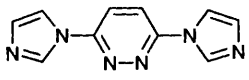
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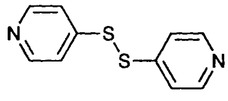
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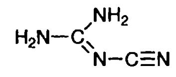

2-cyanoguanidine
(cnge)

Results and Discussion

(*i*) Synthesis and characterisation of discrete dinuclear and polymeric copper(I) cations bridged by 4,4′-bipyridine or *trans*-1,2-bis(4-pyridyl)ethene

The synthetic routes to the 4,4′-bipy and bpe complexes are summarised in Schemes 1 and 2, respectively, which also give their reaction chemistry with NOBF$_4$ and NBu$^t_4$NO$_2$. Reaction of [Cu(MeCN)$_4$]BF$_4$, 4,4′-bipy and cnge in a 2 : 1 : 4 molar ratio in MeCN gave bright yellow, air- and moisture-sensitive, needles of the discrete dinuclear complex [{Cu(cnge)$_2$}$_2$(μ-4,4′-bipy)][BF$_4$]$_2$·MeCN **1**. In the absence of cnge the identity of the product depended on the reactant molar ratio. With a 2 : 1 [Cu(MeCN)$_4$]BF$_4$: 4,4′-bipy molar ratio a MeCN solution gave bright yellow, air- and moisture-sensitive, needles of the one-dimensional polymeric complex [Cu(4,4′-bipy)(MeCN)$_2$]BF$_4$ **2**. With a 1 : 1 [Cu(MeCN)$_4$]BF$_4$: 4,4′-bipy molar ratio the orange, air-stable, microcrystalline product analysed for [Cu(4,4′-bipy)$_2$]BF$_4$·MeCN **3**. The stability of this compound is evidenced not only by its unreactivity towards air but also by the need to use an excess of copper(I) starting material to produce complex **2**. Attempts to form X-ray-quality crystals of **3** failed, orange glasses invariably being obtained. Its structure was inferred from that of [Cu(4,4′-bipy)$_2$]PF$_6$,[6] which comprises a three-dimensional [{Cu(μ-4,4′-bipy)$_2$}$_n$]$^{n+}$ cationic diamondoid network and PF$_6^-$ anions. Product **2** is readily converted into **3** by addition of 4,4′-bipy to MeCN solutions of the former.

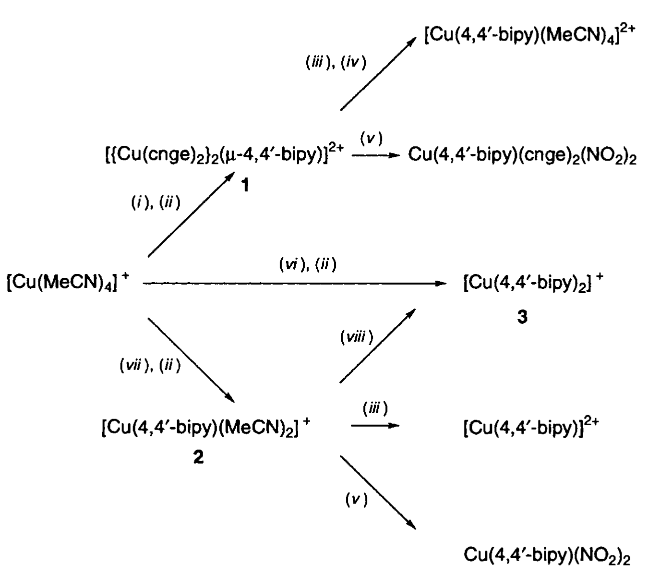
The chemistry of the corresponding bpe systems (Scheme 2) is very similar yielding [{Cu(cnge)$_2$}$_2$(μ-bpe)][BF$_4$]$_2$·6MeCN **4**, [Cu(bpe)(MeCN)$_2$]BF$_4$ **5** and [Cu(bpe)$_2$]BF$_4$ **6**. Product **6** could also be obtained by addition of bpe to a MeCN solution of **5**. As for the corresponding 4,4′-bipy complexes, compounds **4** and **5** are air- and moisture-sensitive but **6** is air stable. Attempts to grow X-ray-quality crystals of all three bpe products were unsuccessful; crystals were obtained but they comprised multiple overlapping platelets.

All products were characterised by chemical analysis (for C, H, N, Cu), IR spectroscopy, FAB mass spectrometry and cyclic voltammetry; structural data were also obtained for complexes **1** and **2**. Analytical and IR data are summarised in Table 1. The presence of 4,4′-bipy or bpe was confirmed by IR spectroscopy (Table 1). In the IR spectra of the cnge-containing complexes **1** and **4** the ν_{asym}(NCN) doublet of free cnge (2209, 2165 cm^{-1})[13] showed little shift. Small shifts are typical of copper(I)–cnge complexes in which the ligand is weakly co-ordinated to the metal centre; strongly co-ordinated cnge normally exhibits a shift to higher energy of $\approx$20 cm^{-1}.[13] The spectra of all the products contained a broad band at 1080–1030 cm^{-1} with little resolution which was assigned to ν_3(BF$_4$).[14] Mass spectrometry was of limited help. Complex **1** gave peaks for [Cu(4,4′-bipy)(cnge)$_2$]$^+$ (*m*/*z* 387), [Cu(cnge)$_2$]$^+$ (231) and [Cu(4,4′-bipy)]$^+$ (219) and **5** gave peaks for [Cu(bpe)]$^+$ (*m*/*z* 245) and [Cu(MeCN)]$^+$ (104). The spectra of complexes **4** and **6** only contained peaks for ligands and copper separately, [bpe]$^+$ (*m*/*z* 182), [cnge]$^+$ (84), [MeCN]$^+$ (41) and Cu$^+$ (63). Cyclic voltammetry of **1**, **2** and **6** showed irreversible oxidation.

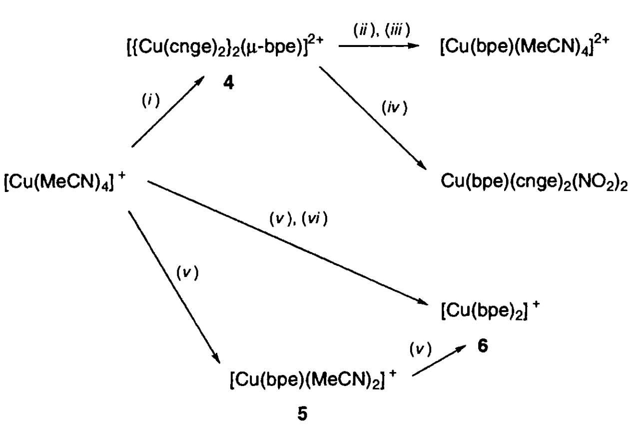
(*ii*) Reaction of copper(I) with bis(4-pyridyl) disulfide and 3,6-bis(imidazolyl)pyridazine in the presence of 2-cyanoguanidine

The reaction of [Cu(MeCN)$_4$]BF$_4$, bpds and cnge in a 2 : 1 : 4 molar ratio in MeCN gave a yellow product, which analysed for [Cu(bpds)(MeCN)$_2$]BF$_4$ **7**. Although it proved possible to crystallise compound **7**, individual crystals of suitable quality for an X-ray study could not be separated.

Whenever [Cu(MeCN)$_4$]BF$_4$, bimpydz and cnge were brought together in a 2 : 1 : 4 molar ratio in MeCN–dimethylformamide (dmf) mixtures (dmf was necessary to solubilise bimpydz; no reaction occurred in its absence) it proved impossible to isolate a copper(I) product, a green copper(II) material being formed which analysed for Cu(bimpydz)(MeCN)$_2$(BF$_4$)$_2$ **8**. The formation of this oxidised product could be attributed neither to disproportionation, there being no evidence for metallic copper formation, nor to decomposition of starting material, [Cu(MeCN)$_4$]BF$_4$ being stable in MeCN–dmf mixtures. It was concluded that bimpydz is necessary for oxidation of copper to occur, although a reduced product was never identified.



Scheme 1 Counter ion is BF$_4^-$. (*i*) 4,4′-bipy, cnge, MeCN; (*ii*) C$_6$H$_5$Me; (*iii*) NOBF$_4$, CH$_2$Cl$_2$; (*iv*) recrystallisation from MeCN; (*v*) NBu$^t_4$NO$_2$, MeCN or CH$_2$Cl$_2$; (*vi*) 4,4′-bipy (1 : 1), MeCN; (*vii*) 4,4′-bipy (1 : 2), MeCN; (*viii*) 4,4′-bipy, MeCN



Scheme 2 Counter ion is BF$_4^-$. (*i*) bpe, cnge, MeCN; (*ii*) NOBF$_4$, CH$_2$Cl$_2$; (*iii*) recrystallisation from MeCN; (*iv*) NBu$^t_4$NO$_2$, MeCN or CH$_2$Cl$_2$; (*v*) bpe, MeCN; (*vi*) C$_6$H$_5$Me

The two products **7** and **8** were characterised by elemental analysis (for C, H, N, Cu); IR spectroscopy provided evidence for bpds in **7** and bimpydz in **8**. The presence of BF$_4^-$ in the two products was confirmed by a broad band at 1085–1035 cm^{-1} and the absence of cnge by the lack of the diagnostic ν_{asym}(NCN) doublet.[13]

(*iii*) Reaction of discrete dinuclear and polymeric copper(I) cations bridged by 4,4′-bipy or bpe

With NOBF$_4$. The chemistry of the 4,4′-bipy and bpe complexes with NOBF$_4$ is summarised in Schemes 1 and 2, respectively. Analytical and IR spectroscopic data for the identified products are given in Table 1. The discrete dinuclear complexes **1** and **4** reacted similarly, treatment with NOBF$_4$ under a static vacuum yielding nitric oxide and blue solids.

Table 1 Analytical and spectroscopic data for the products containing 4,4′-bipy and bpe

Complex	Analysis (%)[a] C	H	N	Cu	IR data/cm^{-1} 4,4′-bipy[b] or bpe[c]	ν_{asym}(NCN) (cnge)	ν_3(BF_4)	ν_{asym}(NO_2)
1 [{Cu(cnge)$_2$}$_2$(μ-4,4′-bipy)][BF_4]$_2$·MeCN	28.90	3.50	31.60	16.05	1644s, *d*, 1412s, 807m	2207s, 2163s	1080–1030 (br)	
	(28.80)	(3.25)	(31.90)	(15.25)				
2 [Cu(4,4′-bipy)(MeCN)$_2$]BF_4	42.55	3.70	15.00	16.25	1634s, 1606s, 1416s, 805m		1080–1035 (br)	
	(43.25)	(3.65)	(14.40)	(16.35)				
3 [Cu(4,4′-bipy)$_2$]BF_4·MeCN	52.30	3.80	13.85	12.85	1638s, 1599s, 1410s, 802m		1085–1030 (br)	
	(52.45)	(3.80)	(13.90)	(12.60)				
[Cu(4,4′-bipy)(MeCN)$_4$][BF_4]$_2$	38.50	3.00	15.15	11.75	1637s, 1606s, —, 783s		1080–1035 (br)	
	(38.80)	(3.60)	(15.05)	(11.40)				
Cu(4,4′-bipy)(BF_4)$_2$	30.60	3.05	7.55	15.45	1637s, 1603s, 1410s, 803s		1070–1035 (br)	
	(30.55)	(2.05)	(7.10)	(16.15)				
Cu(4,4′-bipy)(cnge)$_2$(NO_2)$_2$	34.65	3.25	34.85	12.95	1633s, *d*, 1410s, 809s	2228s, 2184s		1262s
	(35.05)	(3.35)	(35.00)	(13.25)				
Cu(4,4′-bipy)(NO_2)$_2$	38.15	2.55	18.15	19.00	1635s, 1601s, 1413s, 805s			1267s
	(38.55)	(2.60)	(17.95)	(20.40)				
4 [{Cu(cnge)$_2$}$_2$(μ-bpe)][BF_4]$_2$·6MeCN	36.60	4.00	31.55	11.80	*d*, 1412s, 819w	2206s, 2164s	1075–1035 (br)	
	(36.05)	(4.15)	(31.55)	(11.95)				
5 [Cu(bpe)(MeCN)$_2$]BF_4	45.70	3.55	13.95	16.00	1612s, —, 824w		1060–1030 (br)	
	(46.35)	(3.90)	(13.50)	(15.30)				
6 [Cu(bpe)$_2$]BF_4	55.85	4.15	10.90	11.90	1602s, 1421w, 825m		1060–1030 (br)	
	(56.00)	(3.90)	(10.90)	(12.35)				
[Cu(bpe)(MeCN)$_4$][BF_4]$_2$	40.80	4.00	13.50	10.65	1611s, 1388w, 833s		1085–1035 (br)	
	(41.15)	(3.80)	(14.40)	(10.90)				
Cu(bpe)(cnge)$_2$(NO_2)$_2$	37.20	3.95	33.80	13.00	*d*, 1429w, 832w	2227s, 2173s		1254s
	(38.00)	(3.60)	(33.20)	(12.55)				

[a] Calculated values in parentheses. [b] Free 4,4′-bipy: 1633m, 1588s, 1403s and 806s. [c] Free bpe: 1593s, 1412s and 820w. [d] Masked by cnge vibrations.

Infrared spectroscopy of the product from **1** indicated the presence of 4,4′-bipy (1642, 1415, 806 cm^{-1}), cnge [ν_{asym}(NCN) 2212, 2169 cm^{-1}] and BF_4^- [ν_3(BF_4) 1080–1035 cm^{-1}]. The FAB mass spectrum gave only one copper-containing peak at *m/z* 219 {[Cu(4,4′-bipy)]$^+$}. The IR spectrum of the product from compound **4** indicated the presence of bpe (1412, 824 cm^{-1}), cnge [ν_{asym}(NCN) 2210, 2163 cm^{-1}] and BF_4^- [ν_3(BF_4) 1085–1035 cm^{-1}]. Recrystallisation of both solids from MeCN (the only organic solvent in which they were moderately soluble) gave different blue products, the analytical data for which (Table 1) were consistent with Cu(diimine)(MeCN)$_4$(BF_4)$_2$. Corroboration of these formulations came from their IR spectra which contained bands attributable to 4,4′-bipy or bpe and BF_4^- but not cnge (Table 1). The spectra did not give any evidence for MeCN. This was not surprising, however, as in our experience, co-ordinated MeCN is very difficult to detect by IR methods, the ν(CN) band of free MeCN (2292, 2253 cm^{-1}) being too weak to be observed when complexed. Clearly recrystallisation resulted in the replacement of cnge by MeCN, probably giving a polymeric structure, similar to that of [Cu(pyz)(MeCN)$_4$][BF_4]$_2$, in which Cu(MeCN)$_4$ moieties are bridged by pyz.[3]

The only other complexes treated with $NOBF_4$ were **2** and **6**. The former (**2**) gave an insoluble blue powder, the analytical and spectroscopic data for which were consistent with the formulation Cu(4,4′-bipy)(BF_4)$_2$ (Table 1). Purification and further characterisation was not possible owing to its insolubility in organic solvents. The latter (**6**) did not react with $NOBF_4$ even after stirring for 72 h at 298 K; starting material was recovered unchanged.

Our failure to generate a copper–nitrosyl product by this route is consistent with earlier observations. Thus far, the use of NO^+ as a nitrosyl ligand source has only been successful for the synthesis of dinuclear copper(I)–nitrosyl species in which the NO acts as a μ-η^1:η^1-bridging ligand;[15] reaction of mononuclear copper(I) species, [Cu(tmpa)(MeCN)]$^+$ [tmpa = tris(2-pyridylmethyl)amine], with $NOPF_6$ results in oxidation to the copper(II) species, [Cu(tmpa)(MeCN)]$^{2+}$, without nitrosyl co-ordination.[15] Mononuclear copper nitrosyl complexes, [Cu{HB(pz)$_3$}(NO)] (pz = 3-*tert*-butyl- or 3,5-diphenyl-pyrazolyl), have only been obtained using NO gas as the nitrosyl ligand source and then only with substituted tris(pyrazolyl)borate ligands to stabilise the copper(I).[16]

With $NBu^t_4NO_2$. The chemistry of the 4,4′-bipy and bpe complexes with $NBu^t_4NO_2$ is summarised in Schemes 1 and 2, respectively. Analytical and IR spectroscopic data for the identified products are given in Table 1. The discrete dinuclear complexes **1** and **4** reacted similarly, giving in each case two solid products. A white powder, which could be purified by crystallisation from CH_2Cl_2–Et_2O, was identified as $NBu^t_4BF_4$. A green product, insoluble in organic solvents, was tentatively characterised as Cu(diimine)(cnge)$_2$(NO_2)$_2$ on the basis of analytical and spectroscopic data.

Infrared spectroscopy can be useful in determining the co-ordination mode of NO_2^-.[14] However, the presence of the organic ligands in these products results in very complex spectra in the range (1500–1000 cm^{-1}) which contains the bands due to the ν(N–O) stretching vibrations, thereby precluding unambiguous assignment. The spectra do exhibit a broad band close to 1266 cm^{-1} (Table 1) which is typical of the ν_{asym}(NO_2) stretch of bidentate chelating nitrite.[14] This co-ordination mode also occurs in the A. C. NiR models, [Cu(tepa)(NO_2)]PF_6 {tepa = tris[2-(2-pyridyl)ethyl]amine}[17] and [Cu{HB(bpz)$_3$}(NO_2)] (bpz = 3-*tert*-butylpyrazolyl).[18]

The only other complexes treated with $NBu^t_4NO_2$ were compounds **2** and **6**; **2** reacted similarly to **1** and **4** giving two isolable products, the analytical and spectroscopic data for which were consistent with $NBu^t_4BF_4$ and Cu(4,4′-bipy)(NO_2)$_2$ (Table 1). Although the former could be purified by crystallisation from CH_2Cl_2–Et_2O, this was not possible for the latter owing to its insolubility in organic solvents. Clearly, in all these reactions, $NBu^t_4NO_2$ acted as both oxidising agent and nitrite source.

Compound **6** did not react with $NBu^t_4NO_2$ even after stirring for 72 h at 298 K; starting material was recovered unchanged. The lack of reactivity of **6** towards air, $NOBF_4$ and $NBu^t_4NO_2$ is supportive of a three-dimensional diamondoid network structure,[6] in which the four-co-ordinate copper(I) atoms are ligated solely by 4,4′-bipy or bpe bridging molecules. Such structures are normally quite unreactive. The reactivity of the other substrates can be related to the fact they contain either co-ordinatively unsaturated copper(I) (**1** and **4**) or copper(I) centres co-ordinated by substitution labile MeCN ligands (**2**).

(*iv*) Crystal and molecular structures of complexes 1 and 2

Selected interatomic distances and angles are in Table 2. Complex **1** comprises discrete dinuclear [{Cu(cnge)$_2$}$_2$(μ-4,4′-bipy)]$^{2+}$ cations, BF_4^- anions and MeCN molecules. The dinuclear cation (Fig. 1) contains two crystallographically independent three-co-ordinate (T-shaped) copper(I) centres (Cu ⋯ Cu 11.23 Å) bridged by 4,4′-bipy and terminally co-ordinated by two cnge molecules; the shorter Cu–N (cnge) distances (average 1.872 Å) compared to the Cu–N (4,4′-bipy) distances (average 2.075 Å) are consistent with the hybridisation of the ligating nitrogen atoms (sp for cnge, sp^2 for 4,4′-bipy). The cation is effectively planar, the maximum deviation from the best-fit least-squares plane is 0.302 Å [N(33)]. The dihedral angle between the two pyridine rings is 4.3°, those between the bipy and cnge molecules range from 3.1 to 14.7° and those between the cnge molecules range from 5.3 to 17.5°.

The four cnge molecules have very similar geometries (Table

Table 2 Interatomic distances (Å) and angles (°) in the copper co-ordination spheres of [{Cu(cnge)$_2$}$_2$(μ-4,4′-bipy)][BF_4]$_2$·MeCN **1** and [Cu(4,4′-bipy)(MeCN)$_2$]BF_4 **2**

Complex **1**			
Cu(1)–N(1)	2.059(7)	Cu(2)–N(2)	2.091(7)
Cu(1)–N(11)	1.864(7)	Cu(2)–N(31)	1.881(7)
Cu(1)–N(21)	1.872(7)	Cu(2)–N(41)	1.871(7)
N(1)–Cu(1)–N(11)	107.6(3)	N(2)–Cu(2)–N(31)	106.0(3)
N(1)–Cu(1)–N(21)	106.9(3)	N(2)–Cu(2)–N(41)	105.1(3)
N(11)–Cu(1)–N(21)	145.5(4)	N(31)–Cu(2)–N(41)	148.8(3)
Cu(1)–N(1)–C(1)	122.2(8)	Cu(1)–N(11)–C(11)	170.3(8)
Cu(1)–N(1)–C(5)	122.4(8)	Cu(1)–N(21)–C(21)	166.5(8)
Cu(2)–N(2)–C(6)	121.2(8)	Cu(2)–N(31)–C(31)	171.9(8)
Cu(2)–N(2)–C(10)	122.8(8)	Cu(2)–N(41)–C(41)	169.9(8)
Complex **2**			
Cu(1)–N(1)	1.961(10)	Cu(2)–N(3)	1.928(10)
Cu(1)–N(2)	1.986(10)	Cu(2)–N(4)	2.019(10)
Cu(1)–N(11)	2.053(9)	Cu(2)–N(21)	2.067(8)
Cu(1)–N(31)	2.090(8)	Cu(2)–N(41)	2.079(8)
N(1)–Cu(1)–N(2)	121.3(4)	N(3)–Cu(2)–N(4)	122.8(4)
N(1)–Cu(1)–N(11)	114.1(3)	N(3)–Cu(2)–N(21)	111.9(3)
N(1)–Cu(1)–N(31)	117.0(3)	N(3)–Cu(2)–N(41′)	112.3(3)
N(2)–Cu(1)–N(11)	102.1(3)	N(4)–Cu(2)–N(21)	102.6(3)
N(2)–Cu(1)–N(31)	100.6(3)	N(4)–Cu(2)–N(41′)	103.5(3)
N(11)–Cu(1)–N(31)	98.2(3)	N(21)–Cu(2)–N(41′)	101.1(3)
Cu(1)–N(11)–C(12)	125.0(7)	Cu(1)–N(31)–C(32)	122.9(8)
Cu(1)–N(11)–C(16)	120.0(8)	Cu(1)–N(31)–C(36)	119.7(8)
Cu(2)–N(21)–C(22)	122.4(7)	Cu(2)–N(41′)–C(42′)	118.2(7)
Cu(2)–N(21)–C(26)	122.2(7)	Cu(2)–N(41′)–C(46′)	123.4(7)
Cu(1)–N(1)–C(1)	172.7(10)		
Cu(1)–N(2)–C(2)	163.0(11)		
Cu(2)–N(3)–C(3)	175.4(10)		
Cu(2)–N(4)–C(4)	167.2(9)		

Table 3 Comparison of interatomic distances (Å) and angles (°) in the cnge molecules[a] in complex **1** with those of free cnge[b] and those of the terminal cnge molecules in $[\{Cu(cnge)\}_2(\mu\text{-}cnge)_2][S_2O_6]$ **9**[c] and $[\{Cu(cnge)\}_2(\mu\text{-}pydz)_2][BF_4]_2$ **10**[d]

	cnge 1	cnge 2	cnge 3	cnge 4	**9**	**10**	Free cnge
N(1)–C(1)	1.163(10)	1.158(10)	1.132(9)	1.142(9)	1.15(2)	1.15(1)	1.169
C(1)–N(2)	1.306(10)	1.328(10)	1.308(10)	1.311(10)	1.31(2)	1.33(1)	1.305
N(2)–C(2)	1.331(10)	1.331(10)	1.312(10)	1.331(10)	1.37(2)	1.33(1)	1.341
C(2)–N(3)	1.310(11)	1.312(10)	1.319(11)	1.324(10)	1.29(2)	1.30(1)	1.339
C(2)–N(4)	1.324(10)	1.326(10)	1.328(10)	1.342(10)	1.34(2)	1.34(1)	1.333
N(1)–C(1)–N(2)	175.1(9)	174.6(10)	175.1(10)	174.3(9)	173(1)	172(1)	175.1
C(1)–N(2)–C(2)	119.5(8)	117.3(7)	118.1(8)	118.5(8)	117(1)	117.6(9)	118.4
N(2)–C(2)–N(3)	123.7(8)	125.3(8)	124.2(8)	124.0(8)	125(1)	126(1)	123.8
N(2)–C(2)–N(4)	116.5(8)	115.9(7)	117.2(8)	117.3(8)	115(1)	115.8(9)	117.5
N(3)–C(2)–N(4)	119.9(8)	118.7(8)	118.7(8)	118.7(8)	121(1)	119(1)	118.7
Cu–N(1)–C(1)	170.3(8)	166.5(8)	171.9(8)	169.9(8)	173(1)	174.7(9)	

[a] The cnge molecules are identified by the numbering in Table 6; thus molecule 1 comprises N(11), C(11), N(12), C(12), N(13), N(14), 2 comprises N(21), C(21), N(22), C(22), N(23), N(24), *etc.* [b] Ref. 21. [c] Refs. 13 and 20. [d] Ref. 19.

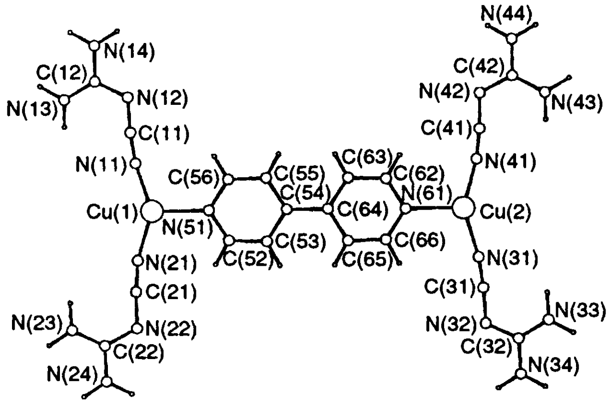


Fig. 1 Molecular structure of the $[\{Cu(cnge)_2\}_2(\mu\text{-}4,4'\text{-}bipy)]^{2+}$ dication

3); hence the observation of only two bands in the $\nu_{asym}(NCN)$ stretching region of the IR spectrum of compound **1** (Table 1). They are comparable to those of terminal cnge molecules in other three-co-ordinate copper(I)–cnge complexes (Table 3), the only significant difference being the smaller Cu–N–C angles in **1** (average 169.7°) compared to those (average 173.9°) in the other complexes. This is associated with the T-shaped copper(I) co-ordination geometry in **1** as discussed later.

The packing diagram for compound **1** (Fig. 2) reveals a two-dimensional sheet structure held together by an extensive hydrogen-bonding network, details of which are given in Table 4. Both BF_4^- anions are involved in the hydrogen bonding. For each anion, three of the fluorine atoms are sited within the two-dimensional sheets; the fourth bridges the sheets (Fig. 2). The MeCN molecule, which is hydrogen bonded to a cnge amino hydrogen through its nitrile nitrogen, is located in a hole in the sheet.

Complex **2** comprises polymeric zigzag $[Cu(4,4'\text{-}bipy)(MeCN)_2]^+$ cationic chains (Fig. 3) and BF_4^- anions. The chains, which lie parallel to the *a* axis (Fig. 4), contain two crystallographically independent copper(I) atoms [Cu(1)···Cu(2) 11.18, 11.22 Å] each of which is tetrahedrally co-ordinated to two bridging 4,4'-bipy molecules and two terminal MeCN molecules. As for complex **1**, the distances to the sp-hybridised nitrogens are shorter [average Cu–N (MeCN) 1.9735 Å] than those to the sp^2-hybridised nitrogens [average Cu–N (4,4'-bipy) 2.0723 Å]. The Cu–N (cnge) distances in **1** (average 1.872 Å) are considerably shorter than the Cu–N (MeCN) distances in **2**. They are, however, typical of Cu–N (cnge) distances for co-ordinatively unsaturated copper(I) (1.811 in $[Cu(\mu\text{-}Cl)(\mu\text{-}cnge)CuCl]$,[2] 1.901 in $[Cu(\mu\text{-}Br)(\mu\text{-}cnge)CuBr]$,[2] 1.885 in $[\{Cu(cnge)\}_2(\mu\text{-}pydz)_2][BF_4]_2$ (pydz = pyridazine),[19] 1.851, 1.874 Å in $[\{Cu(cnge)\}_2(\mu\text{-}cnge)_2][S_2O_6]$[13,20]). Only two complexes are known in which cnge is co-ordinated to four-co-ordinate copper(I). In these, the Cu–N distances are considerably longer (1.965 in $[Cu(\mu\text{-}pyz)(cnge)(MeCN)]BF_4$[3] and 1.928, 1.941 Å in $[Cu(\mu\text{-}bbppydz)_2\{Cu(cnge)(MeCN)\}_2][BF_4]_3\cdot MeCN$ {bbppydz = 3,6-bis[*N*-(3-*tert*-butylpyrazolyl)]-pyridazine[22]}) suggesting that the very short Cu–N distances in complex **1** must be attributed to a combination of the sp hybridisation of the cnge nitrogen and the co-ordinative unsaturation of the copper(I).

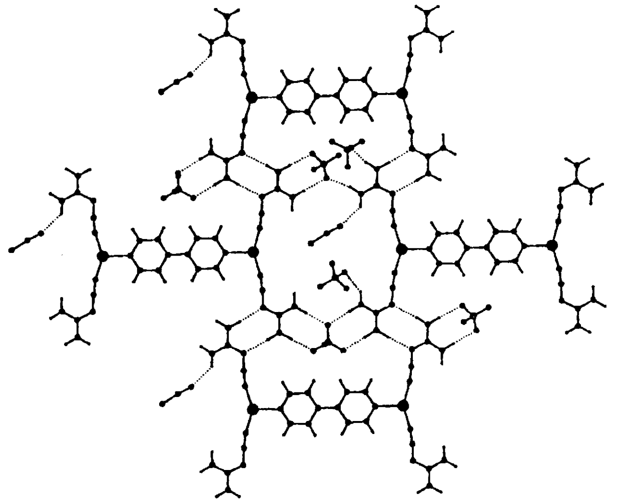


Fig. 2 View of the two-dimensional sheet structure of $[\{Cu(cnge)_2\}_2(\mu\text{-}4,4'\text{-}bipy)][BF_4]_2\cdot MeCN$

The structure of compound **2** is much more flexible than that of **1**. The 4,4'-bipy molecules in **2** are not planar, the dihedral angles between the two pyridine rings being 28.0(4) and 30.0(4)°. Despite this, there are no major differences between the interatomic distances and angles in the 4,4'-bipy molecules in compounds **1** and **2**; even the C–C bonds between the pyridine rings are similar, being 1.479(11) in **1** and 1.444(11) and 1.458(12) Å in **2**. The BF_4^- anions are located in gaps between the cationic chains (Fig. 4). Unlike the BF_4^- anions in the crystal structure of **1**, they are not held in place by hydrogen-bonding interactions. The fluorine atoms exhibit very high displacement parameters, which may imply some static disorder, which was impossible to rationalise.

(*v*) Three-co-ordinate copper(I)

The co-ordinatively unsaturated copper(I) centre (Fig. 1) is

Table 4 Hydrogen-bond contacts in complex **1**

Interaction X–H ··· X′	Symmetry properties of X′	r(X ··· X′)/Å	r(X ··· H)/Å	X–H–X′/°
N(13)–H(131) ··· F(23)	$x, -1 + y, -1 + z$	2.969	2.199	133.3
N(13)–H(132) ··· F(12)	$1 + x, -1 + y, -1 + z$	2.935	1.947	165.9
N(14)–H(141) ··· F(11)	$1 + x, -1 + y, -1 + z$	2.915	1.912	170.4
N(14)–H(142) ··· N(32)	$1 + x, y, -1 + z$	3.029	2.033	176.9
N(23)–H(231) ··· N(1)	x, y, z	2.948	2.143	136.6
N(23)–H(232) ··· F(21)	$-x, 1 - y, 1 - z$	2.940	1.974	161.4
N(24)–H(241) ··· F(14)	$-x, 1 - y, 1 - z$	2.808	1.998	136.8
N(24)–H(242) ··· N(42)	$-1 + x, -1 + y, z$	3.034	2.031	174.6
N(33)–H(331)				
N(33)–H(332) ··· F(21)	$-x, 2 - y, 2 - z$	2.953	1.963	171.9
N(34)–H(341) ··· F(22)	$-x, 2 - y, 2 - z$	2.994	2.002	173.9
N(34)–H(342) ··· N(12)	$-1 + x, y, 1 + z$	3.076	2.092	167.0
N(43)–H(431)				
N(43)–H(432) ··· F(12)	$1 + x, y, z$	2.938	1.970	161.7
N(44)–H(441) ··· F(13)	$1 + x, y, z$	2.891	1.891	175.3
N(44)–H(442) ··· N(22)	$1 + x, 1 + y, z$	3.082	2.093	171.6

Contact		Distance/Å	Angle/°
Intercnge N–H ··· N	Average	3.055	172.5
	Range	3.029–3.082	167.0–176.9
Intraplane N–H ··· F	Average	2.938	168.6
	Range	2.891–2.994	161.4–175.3
Interplane N–H ··· F	Average	2.889	135.1
	Range	2.808–2.969	133.3–136.8
cnge ··· MeCN N–H ··· N		2.948	136.6

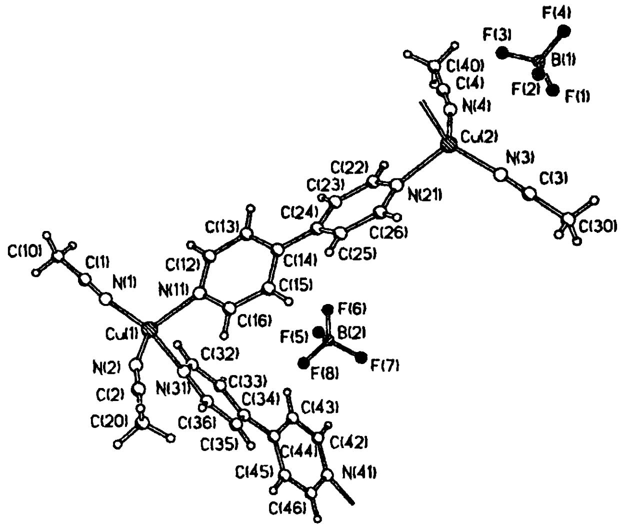


Fig. 3 Molecular structure of the asymmetric unit of [Cu(4,4′-bipy)(MeCN)$_2$]BF$_4$

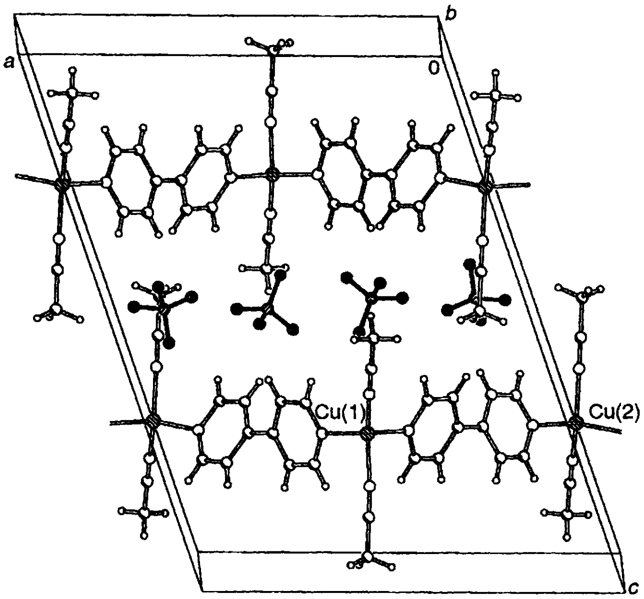
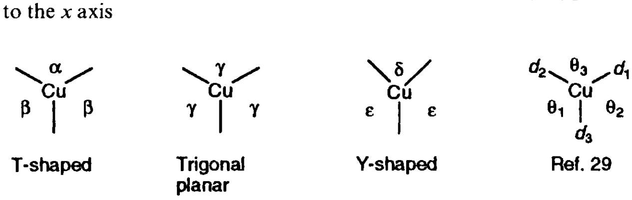


Fig. 4 View of the unit cell of [Cu(4,4′-bipy)(MeCN)$_2$]BF$_4$ perpendicular to the (010) plane showing the cation chains lying parallel to the x axis

noteworthy; in the absence of cnge, distorted-tetrahedral copper(I) occurs as in the polymeric cations $[\{Cu(\mu\text{-}4,4'\text{-}bipy)(MeCN)_2\}_n]^{n+}$ and $[\{Cu(\mu\text{-}4,4'\text{-}bipy)_2\}_n]^{n+}$. Its stability is attributed to the two terminal cnge molecules, which have been shown to stabilise three-co-ordinate copper(I) in $[\{Cu(\mu\text{-}X)(\mu\text{-}cnge)CuX\}_n]$ (X = Cl or Br),[2] $[\{Cu(cnge)\}_2(\mu\text{-}cnge)_2]^{2+}$ [13,20] and $[\{Cu(cnge)\}_2(\mu\text{-}pydz)_2]^{2+}$.[19]

The T-shaped geometry of the copper centre [N–Cu(1)–N 106.9, 107.6, 145.5°; N–Cu(2)–N 106.0, 105.1, 148.8°] in complex **1** is, to our knowledge, the most severely distorted trigonal copper(I) co-ordination sphere yet described for three effectively monodentate ligands. With three identical ligands [three-co-ordinate copper(I) prefers soft bases, particularly S-donor thiolates and thioureas,[23–25] N-donor nitriles and azines[26] and P-donor phosphines[27]], maximum distortion was previously reported for the $[Cu(2\text{-}MeC_5H_4N)_3]^{2+}$ cation (N–Cu–N 113–139°).[26]

Although distorted trigonal-planar geometries resulting from the steric demands of bi- and tri-dentate ligands[28,29] and from the constraints imposed by dibridged dimeric species[13,19,20] are not unexpected, those arising with three effectively monodentate ligands are noteworthy as they should exhibit minimum distortion from local D_{3h} symmetry. Theoretical calculations, however, show the computed energy cost for distortion to be small;[30] to reach T-shaped geometry with $\beta = 160°$ (Scheme 3) it is only 6.7 kJ mol^{-1}, to reach Y-shaped geometry with $\delta = 80°$ it is 41.4 kJ mol^{-1}. This is confirmed in practice by the $[Cu(SPh)_3]^-$ anion, the geometry of which depends on the cation;[23,24] with $[NEt_4]^+$ it is almost symmetrical (S–Cu–S



Scheme 3 $\gamma = 120$; $\alpha, \varepsilon > 120$; $\beta, \delta < 120°$

118.2–121.3°),[23] with $[PPh_4]^+$ it is significantly distorted (S–Cu–S 111.7–135.4°).[24] The distortion is attributed to strong interactions between the anion phenyl rings and the hydrogens of the cation phenyl rings.

Munakata *et al.*[29] have noted a simple correlation between the bond distances $\{\Delta d = [(d_1 + d_2)/2] - d_3\}$ and angles $\{\Delta\theta = [(\theta_1 + \theta_2)/2] - \theta_3\}$ for three-co-ordinate copper(I) complexes (Scheme 3). By far the greater proportion are T-shaped, the Y-shaped copper centres being restricted to systems with one mono- and one bi-dentate ligand, the latter dictating the shape of the copper(I) co-ordination sphere. The two copper centres in compound **1** have very similar Δd and $\Delta\theta$ values [Cu(1), $\Delta d = -0.191$ Å, $\Delta\theta = -38.2°$; Cu(2), $\Delta d = -0.215$ Å, $\Delta\theta = -43.2°$] and fall close to the T-shaped extreme of the relationship.

For compound **1** a detailed packing diagram (Fig. 5) clearly shows that hydrogen-bonding interactions contribute to the T-shaped copper(I) co-ordination geometry (Fig. 1); the contacts between the amino moieties of cnge molecules of adjacent cations and the fluorine atoms of the BF_4^- anions effectively pull together the *cis*-located cnge molecules on a discrete cation, thus decreasing not only the N (4,4′-bipy)–Cu–N (cnge) angles but also the Cu–N–C (cnge) angles (Table 3). The formation of these hydrogen bonds must be sufficiently exothermic to overcome the energy loss associated with T-shaped geometry [$\approx$6.7 kJ mol^{-1} for an N (4,4′-bipy)–Cu–N (cnge) angle of 100°].[30] Despite the fact that the hydrogen atoms were placed in calculated positions, the hydrogen bonds have very regular geometries (Table 4), with average N–H–N and N–H–F angles of 173 and 169° and average N $\cdots$ N and N $\cdots$ F distances of 3.06 and 2.94 Å, respectively.

Conclusion

The formation of the planar dinuclear cations $[\{Cu(cnge)_2\}_2(\mu\text{-diimine})]^{2+}$ provides a further example of the remarkable ability of cnge to stabilise co-ordinatively unsaturated copper(I), as in $[\{Cu(cnge)\}_2(\mu\text{-pydz})_2]^{2+}$,[19] $[\{Cu(cnge)\}_2(\mu\text{-cnge})_2]^{2+}$ [13,20] and $[Cu(\mu\text{-}X)(\mu\text{-cnge})CuX]^{2+}$ (X = Cl or Br).[2] In the absence of cnge, the more typical four-co-ordinate tetrahedral copper(I) geometry is formed in the polymeric cations $[Cu(diimine)(MeCN)_2]^+$ and $[Cu(diimine)_2]^+$. The three-co-ordinate copper(I) atoms in $[\{Cu(cnge)_2\}_2(\mu\text{-}4,4'\text{-bipy})]^{2+}$ are severely distorted adopting a T-shaped geometry. The relatively small amount of energy required for this distortion may originate from a hydrogen-bonded two-dimensional network involving the cnge ligands and BF_4^- anions.

The complexes exhibit differing reactivity towards air, moisture, $NOBF_4$ and $NBu^t{}_4NO_2$. Those containing three-co-ordinate copper(I), $[\{Cu(cnge)_2\}_2(\mu\text{-diimine})]^{2+}$, or four-co-ordinate copper(I) with substitution-labile MeCN ligands, $[Cu(diimine)(MeCN)_2]^+$, are reactive; those containing four-co-ordinate copper(I) ligated solely by bridging ligands to form a three-dimensional diamondoid network, $[Cu(diimine)_2]^+$ are unreactive. Reaction with $NOBF_4$ leads solely to oxidation, with $NBu^t{}_4NO_2$ to both oxidation and nitrite substitution.

Experimental

All reactions were carried out under an argon or nitrogen atmosphere unless otherwise noted. Infrared and mass spectra and elemental analyses were consistent with the proposed structures. Infrared spectra were obtained on a Perkin-Elmer PE983G spectrometer as KBr pressed pellets. Carbon, nitrogen and hydrogen (microanalysis) and copper analyses (atomic absorption spectroscopy) were carried out in the University of Nottingham Chemistry Department by Mr. T. J. Spencer and Mr. M. Guyler, respectively. Analytical and spectroscopic data for the 4,4′-bipy and bpe complexes are collated in Table 1.

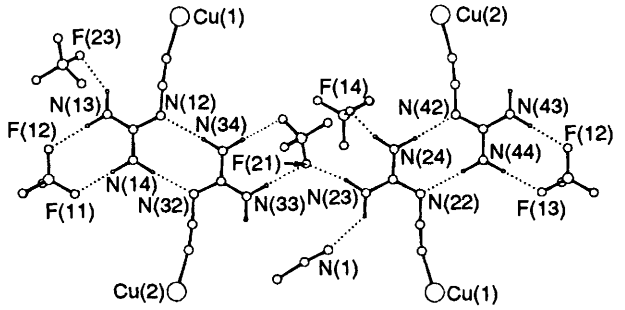


Fig. 5 Detail of the two-dimensional sheet structure of $[\{Cu(cnge)_2\}_2(\mu\text{-}4,4'\text{-bipy})][BF_4]_2\cdot MeCN$ showing the hydrogen-bonding interactions which generate the T-shaped copper(I) co-ordination geometry

Acetonitrile, CH_2Cl_2 and toluene were distilled from CaH_2 prior to use.[31] Dimethylformamide was dried over freshly regenerated Linde type 4A molecular sieves before distillation under reduced pressure.[31]

The complex $[Cu(MeCN)_4]BF_4$ was prepared either by oxidation of copper foil suspended in dry MeCN with $NOBF_4$[32] or by reduction of aquated copper(II) tetrafluoroborate with copper powder suspended in MeCN.[33] The compounds $NOBF_4$, $NBu^t{}_4NO_2$, 4,4′-bipy, bpe and cnge were obtained from Aldrich Chemical Company Ltd. Bis(4-pyridyl) disulfide was prepared by oxidation of pyridine-4-thiol with bromine in CH_2Cl_2 in the presence of K_2CO_3.[34] 2-Cyanoguanidine was purified by recrystallisation from water, 4,4′-bipy from MeCN and bpe from MeCN–toluene mixtures. All recrystallised materials were dried at room temperature *in vacuo* prior to use; $NOBF_4$ and $NBu^t{}_4NO_2$ were used without further purification.

The compound bimpydz was prepared by addition of 3,6-dichloropyridazine (3.0 g, 20 mmol), dissolved in the minimum volume of dmf, to a mixture of potassium carbonate (6.0 g, 43.2 mmol) and imidazole (2.8 g, 41 mmol) previously stirred at 80 °C for 20 min in dmf (60 cm^3). After refluxing for 180 min, the reaction mixture was cooled to room temperature and added to iced water. The resulting light brown product was isolated by vacuum filtration and recrystallised from dmf. Yield 1.65 g (39%), m.p. 264–268 °C [Found (Calc. for $C_{10}H_8N_6$): C, 56.55 (56.60); H, 3.80 (3.80); N, 39.45 (39.60)%]. Electron impact mass spectrum: *m*/*z* 212 $[bimpydz]^+$, 145 $[bimpydz - C_3H_3N_2]^+$, 78 $[bimpydz - 2C_3H_3N_2]^+$ and 67 $[C_3H_3N_2]^+$. IR: 3145w, 3107m, 1576s, 1516m, 1487s, 1455m, 1371w, 1322s, 1305m, 1239w, 1109m, 1067m, 1055m, 1035s, 967m, 908m, 860m, 824m, 768m, 749w, 648s, 617w and 506w cm^{-1}.

Preparation of complexes

$[\{Cu(cnge)_2\}_2(\mu\text{-}4,4'\text{-bipy})][BF_4]_2\cdot MeCN$ 1. The complex $[Cu(MeCN)_4]BF_4$ (0.40 g, 1.27 mmol) in MeCN (25 cm^3) was added to 4,4′-bipy (0.10 g, 0.64 mmol) in MeCN (25 cm^3) in the presence of cnge (0.21 g, 2.50 mmol) giving a yellow solution. After stirring for 16 h the solvent volume was reduced, excess of cnge was filtered off and a yellow product precipitated by addition of toluene (0.24 g, 0.29 mmol, 45% yield). Vapour-phase diffusion of toluene into an MeCN solution of the product gave an air- and moisture-sensitive bright yellow crystalline material.

$[Cu(4,4'\text{-bipy})(MeCN)_2]BF_4$ 2. The complex $[Cu(MeCN)_4]BF_4$ (0.40 g, 1.27 mmol) in MeCN (25 cm^3) was added to 4,4′-bipy (0.10 g, 0.64 mmol) in MeCN (25 cm^3) giving a yellow solution. After stirring for 16 h the solvent volume was reduced and a mixture of yellow and white powders precipitated by addition of toluene. The white product was identified as starting complex and the yellow product as [Cu(4,4′-bipy)(Me-

Table 5 Data collection parameters for complexes **1** and **2**

	1	**2**
Formula	$C_{20}H_{27}B_2Cu_2F_8N_{19}$	$C_{14}H_{14}BCuF_4N_4$
M	834.27	388.64
Crystal system	Triclinic	Monoclinic
Space group	$P\bar{1}$ (no. 2)	$P2_1/c$ (no. 14)
a/Å	7.613(2)	15.253(2)
b/Å	14.157(2)	11.594(1)
c/Å	16.330(4)	20.752(2)
α/°	86.19(2)	
β/°	77.62(2)	108.53(1)
γ/°	89.20(2)	
Z	2	8
U/Å^3	1715(1)	3480(1)
μ_{calc}/cm^{-1}	13.3	21.76
D_c/g cm^{-3}	1.615	1.484
F(000)	840	1568
Crystal dimensions/mm	0.08 × 0.15 × 0.35	0.40 × 0.25 × 0.18
Radiation (λ/Å)	Mo-Kα (0.710 73)	Cu-Kα (1.541 84)
θ range for data collection/°	0–22	4.4–49.9
Scan mode	ω–2θ	θ–2θ
hkl Ranges	−7 to 7, −14 to 14, 0–17	−1 to 14, −1 to 11, −20 to 19
Reflections collected	4186	4480
Independent reflections	2614	3463
Refinement method[a] (full-matrix least squares on)	F	F^2
Final R,R'[b]	0.068, 0.046	0.0599, 0.1283
Data, restraints, parameters	2614, 0, 441	1361, 42, 264
Largest difference peak and hole/e Å^{-3}	0.719, −0.690	0.304, −0.301

[a] The data set for complex **2** was very weak; refinement was carried out using (*a*) all data {3358 reflections; $R(F)$ 0.2399; $wR(F^2)$ 0.1895; conventional R [$I > 2\sigma(I)$, 1361 reflections] 0.0591, R' 0.1247} and (*b*) all low-angle ($\theta < 25°$) and non-zero high-angle ($\theta > 25°$) data {2595 reflections, $R(F)$ 0.1633; $wR(F^2)$ 0.1508; conventional R [$I > 2\sigma(I)$, 1361 reflections] 0.0599, R' 0.1283}. [b] Data with $I > 3\sigma(I)$ for complex **1** and $I > 2\sigma(I)$ for **2**.

CN)$_2$]BF$_4$ **2** (0.22 g, 0.57 mmol, 45% yield). Vapour-phase diffusion of toluene into an MeCN solution of the latter gave an air- and moisture-sensitive, bright yellow, crystalline material. A pure sample could only be obtained by repeated recrystallisation from MeCN by addition of toluene since an increase in the amount of 4,4′-bipy in the reaction mixture gave the alternative product [Cu(4,4′-bipy)$_2$]BF$_4$·MeCN **3**.

[Cu(4,4′-bipy)$_2$]BF$_4$·MeCN 3. The complex [Cu(MeCN)$_4$]BF$_4$ (0.40 g, 1.27 mmol) in MeCN (25 cm^3) was added to 4,4′-bipy (0.20 g, 1.28 mmol) in MeCN (35 cm^3) giving a bright yellow solution. After stirring for 16 h the solvent volume was reduced and an orange powder precipitated by addition of toluene (0.35 g, 0.70 mmol, 55% yield). Vapour-phase diffusion of toluene into an MeCN solution of the product gave an orange microcrystalline solid.

[{Cu(cnge)$_2$}$_2$(μ-bpe)][BF$_4$]$_2$·6MeCN 4. The complex [Cu(MeCN)$_4$]BF$_4$ (3.87 g, 12.3 mmol) in MeCN (125 cm^3) was added to bpe (1.21 g, 6.6 mmol) in MeCN (125 cm^3) in the presence of cnge (2.07 g, 2.46 mmol) giving a yellow solution. After stirring for 16 h the solvent volume was reduced, excess of cnge was filtered off and an air- and moisture-sensitive yellow product precipitated by addition of toluene. It was characterised as [{Cu(cnge)$_2$}$_2$(μ-bpe)][BF$_4$]$_2$·6MeCN **4** (3.75 g, 3.52 mmol, 57% yield).

[Cu(bpe)(MeCN)$_2$]BF$_4$ 5 and [Cu(bpe)$_2$]BF$_4$ 6. The complex [Cu(MeCN)$_4$]BF$_4$ (1.47 g, 4.67 mmol) in MeCN (60 cm^3) was added to bpe (0.43 g, 2.36 mmol) in MeCN (60 cm^3). During the addition the mixture changed from colourless through yellow to red. After stirring for 16 h a bright red solid was filtered off to yield a yellow solution. After reduction in the solvent volume a second crop of red solid was formed and filtered off. Addition of toluene to the remaining solution gave a yellow precipitate. Both products were crystallised from MeCN by addition of toluene. The air-stable red solid was identified as [Cu(bpe)$_2$]BF$_4$ **6** (0.83 g, 1.49 mmol, 32% yield) and the air- and moisture-sensitive yellow solid as [Cu(bpe)(MeCN)$_2$]BF$_4$ **5** (0.27 g, 0.65 mmol, 14% yield). Compound **5** could be obtained in greater amounts, but only in impure form, by using higher [Cu(MeCN)$_4$]BF$_4$: bpe molar ratios.

[Cu(bpds)(MeCN)$_2$]BF$_4$ 7. The complex [Cu(MeCN)$_4$]BF$_4$ (1.5 g, 4.90 mmol) in MeCN (100 cm^3) was added to bpds (0.56 g, 2.54 mmol) in MeCN (125 cm^3) in the presence of cnge (0.85 g, 1.01 mmol) forming a yellow solution. After stirring for 16 h the solvent volume was reduced. A white powder, subsequently shown to be cnge (0.8 g, 0.95 mmol), was filtered off. After further reduction in the solvent volume yellow product was precipitated by addition of toluene. Recrystallisation from an MeCN–toluene mixture yielded an air- and moisture-sensitive yellow microcrystalline solid which was characterised as [Cu(bpds)(MeCN)$_2$]BF$_4$ **7** (0.93 g, 2.06 mmol, 42% yield) [Found (Calc. for $C_{14}H_{14}BCuF_4N_4S_2$): C, 37.30 (37.15); H, 3.10 (3.10); Cu 13.95 (14.05); N, 12.30 (12.35)%]. IR: 3431s, 1582s, 1540w, 1474w, 1410s, 1085–1035s (br), 804s, 707m and 505m cm^{-1}.

Cu(bimpydz)(MeCN)$_2$(BF$_4$)$_2$ 8. The compound bimpydz (0.37 g, 1.76 mmol) in dmf (30 cm^3) was added to MeCN (30 cm^3) containing cnge (0.60 g, 7.14 mmol) followed by [Cu(MeCN)$_4$]BF$_4$ (1.12 g, 3.56 mmol) in MeCN (60 cm^3). On mixing, the solution slowly became yellow-green. After stirring for 16 h the solvent volume was reduced yielding an air-stable green solid, which after recrystallisation from MeCN and diethyl ether was identified as Cu(bimpydz)(MeCN)$_2$(BF$_4$)$_2$ **8** (0.36 g, 0.68 mmol, 38% yield) [Found (Calc. for $C_{14}H_{14}B_2CuF_8N_8$): C, 31.25 (31.65); H, 3.10 (2.65); Cu, 12.05 (11.95); N, 20.85 (21.10)%]. IR: 3135w, 3097m, 1575m, 1527w, 1487s, 1450s, 1383w, 1319m, 1304s, 1130–1020s (br), 967m, 840w (br), 820m, 759w, 743w, 650m, 620w and 500w cm^{-1}.

Reactions of NOBF$_4$

With complex 1. Solid NOBF$_4$ (0.11 g, 0.94 mmol) was placed

Table 6 Fractional atomic co-ordinates for the non-hydrogen atoms in complex **1**

Atom	*X/a*	*Y/b*	*Z/c*	Occupancy
Cu(1)	0.377 0(2)	0.280 32(8)	0.173 52(7)	1.0
Cu(2)	0.357 3(2)	0.787 26(8)	0.675 99(7)	1.0
N(1)	0.358(1)	0.379 1(5)	0.262 0(4)	1.0
C(1)	0.262(1)	0.364 0(6)	0.339 4(6)	1.0
C(2)	0.253(1)	0.424 1(6)	0.402 1(6)	1.0
C(3)	0.349(1)	0.507 7(5)	0.386 7(5)	1.0
C(4)	0.445(1)	0.526 2(6)	0.305 1(6)	1.0
C(5)	0.451(1)	0.460 4(7)	0.246 8(5)	1.0
C(6)	0.448(1)	0.712 9(6)	0.504 4(6)	1.0
C(7)	0.451(1)	0.654 5(6)	0.440 3(5)	1.0
C(8)	0.347(1)	0.574 2(6)	0.453 0(5)	1.0
C(9)	0.244(1)	0.557 2(6)	0.532 5(5)	1.0
C(10)	0.248(1)	0.618 9(7)	0.593 4(6)	1.0
N(2)	0.347 6(9)	0.697 1(5)	0.580 7(4)	1.0
N(11)	0.531(1)	0.329 2(6)	0.075 7(4)	1.0
C(11)	0.624(1)	0.371 7(6)	0.020 1(5)	1.0
N(12)	0.731(1)	0.424 6(5)	−0.037 7(4)	1.0
C(12)	0.802(1)	0.389 7(7)	−0.111 3(5)	1.0
N(13)	0.766(1)	0.304 9(6)	−0.131 1(5)	1.0
N(14)	0.916(1)	0.445 1(5)	−0.165 5(4)	1.0
N(21)	0.226(1)	0.179 6(5)	0.223 2(4)	1.0
C(21)	0.120(1)	0.129 9(6)	0.265 5(5)	1.0
N(22)	0.003(1)	0.075 6(5)	0.320 3(4)	1.0
C(22)	−0.057(1)	−0.001 0(6)	0.292 3(5)	1.0
N(23)	−0.009(1)	−0.028 3(5)	0.215 5(5)	1.0
N(24)	−0.178(1)	−0.052 0(5)	0.347 6(4)	1.0
N(31)	0.205(1)	0.733 0(5)	0.773 5(4)	1.0
C(31)	0.110(1)	0.692 4(6)	0.826 5(5)	1.0
N(32)	0.000(1)	0.639 6(5)	0.883 3(4)	1.0
C(32)	−0.070(1)	0.675 7(7)	0.954 9(5)	1.0
N(33)	−0.050(1)	0.764 5(6)	0.970 9(5)	1.0
N(34)	−0.173(1)	0.619 2(5)	1.013 7(4)	1.0
N(41)	0.514(1)	0.884 7(5)	0.624 5(4)	1.0
C(41)	0.604(1)	0.940 4(6)	0.582 3(5)	1.0
N(42)	0.715(1)	0.997 4(5)	0.529 5(4)	1.0
C(42)	0.766(1)	1.076 8(6)	0.557 1(5)	1.0
N(43)	0.703(1)	1.105 1(5)	0.633 5(4)	1.0
N(44)	0.890(1)	1.130 1(4)	0.503 7(4)	1.0
N(51)	0.200(2)	0.004(1)	0.041 9(8)	1.0
C(51)	0.278(2)	−0.031(1)	−0.020(1)	1.0
C(52)	0.381(2)	−0.066(1)	−0.097(1)	1.0
B(1)	0.036(2)	1.301 5(8)	0.645 6(7)	1.0
F(11)	0.054 6(9)	1.390 9(4)	0.663 5(4)	0.6
F(12)	−0.108(1)	1.256 5(5)	0.694 1(5)	0.6
F(13)	0.028(1)	1.297 1(5)	0.560 9(4)	0.6
F(14)	0.189(1)	1.250 4(6)	0.649 2(6)	0.6
F(31)	0.140	1.262	0.579	0.40
F(32)	−0.176	1.294	0.671	0.25
F(33)	0.157	1.261	0.700	0.25
F(34)	−0.045	1.408	0.650	0.25
F(41)	−0.015	1.228	0.718	0.15
F(42)	0.156	1.379	0.680	0.15
F(43)	−0.058	1.319	0.590	0.15
B(2)	0.368(2)	1.201 4(8)	0.835 6(9)	1.0
F(21)	0.186(1)	1.174 7(5)	0.857 5(5)	0.65
F(22)	0.357(1)	1.299 6(6)	0.825 5(5)	1.0
F(23)	0.442(1)	1.182 2(6)	0.901 9(6)	0.65
F(24)	0.439(1)	1.173 4(7)	0.760 1(6)	0.65
F(51)	0.537	1.149	0.862	0.25
F(52)	0.397	1.110	0.791	0.25
F(53)	0.261	1.133	0.884	0.25
F(61)	0.504	1.231	0.764	0.10
F(62)	0.238	1.133	0.820	0.10
F(63)	0.385	1.226	0.922	0.10

in the side arm of a reaction vessel containing complex **1** (0.4 g, 0.48 mmol) in CH_2Cl_2 (60 cm^3). The solution was cooled until frozen and the vessel evacuated. The system was allowed to warm to room temperature under a static vacuum and the $NOBF_4$ added. A change from yellow to lime green was accompanied by effervescence, a blue-green solid finally being precipitated. After stirring for 16 h the initial product was filtered off. Crystallisation from hot MeCN gave the final product, which was characterised as [Cu(4,4′-bipy)-$(MeCN)_4][BF_4]_2$ (0.34 g, 0.60 mmol, 64% yield). This material could not have formed in the original reaction mixture since it did not contain sufficient MeCN; the product must have changed identity on recrystallisation.

With complex 2. This reaction was carried out as for complex **1** but involved treatment of **2** (0.28 g, 0.72 mmol) with $NOBF_4$ (0.08 g, 0.68 mmol). The initial blue product was characterised as Cu(4,4′-bipy)$(BF_4)_2$ (0.14 g, 0.38 mmol, 56% yield). Attempts to purify it were unsuccessful owing to insolubility in all organic solvents.

With complex 4. This reaction was carried out as for complex **1** but involved treatment of **4** (1.00 g, 0.94 mmol) with $NOBF_4$ (0.22 g, 1.88 mmol). The final blue product was characterised as [Cu(bpe)$(MeCN)_4][BF_4]_2$ (0.52 g, 0.89 mmol, 47% yield).

With complex 6. This reaction was carried out as for complex **1** but involved treatment of **6** (0.67 g, 1.21 mmol) with $NOBF_4$ (0.13 g, 1.11 mmol). Neither effervescence nor a colour change occurred. After stirring for 48 h the solvent volume was reduced, producing a red solid which was crystallised from MeCN and toluene. It analysed as the starting complex [Found (Calc. for $C_{24}H_{20}BCuF_4N_4$): C, 55.35 (56.00); H, 4.15 (3.90); N, 11.00 (10.90)%].

Reactions of $NBu^t_4NO_2$

With complex 1. Solid $NBu^t_4NO_2$ (0.70 g, 2.43 mmol) was placed in the side arm of a reaction vessel containing a solution of complex **1** (0.4 g, 0.48 mmol) in CH_2Cl_2 (60 cm^3). The solution was cooled until frozen and the vessel evacuated. The system was allowed to warm to room temperature under a static vacuum and the $NBu^t_4NO_2$ added. A change from yellow to green was accompanied by effervescence, a blue-green solid finally being precipitated.

After stirring for 16 h a gum was deposited on the surfaces of the reaction vessel. Repeated washing of the gum with Et_2O gave a dark green solid, which owing to its insolubility in organic solvents, could not be recrystallised. Addition of Et_2O to the filtrate gave a light green solid, which when recrystallised from CH_2Cl_2 and Et_2O gave an off-white solid. The green solid was identified as Cu(4,4′-bipy)(cnge)$_2(NO_2)_2$ (0.12 g, 0.25 mmol, 26% yield), and the white solid as $NBu^t_4BF_4$ (0.22 g, 0.66 mmol, 35% yield) [Found (Calc. for $C_{16}H_{36}BF_4N$): C, 57.90 (58.35); H, 10.85 (11.00); N, 5.05 (4.25)]. FAB mass spectrum: *m/z* 242 $[Bu^t_4N]^+$, 185 $[Bu^t_3N]^+$, 128 $[Bu^t_2N]^+$, 71 $[Bu^tN]^+$ and 57 Bu^+. IR: 2693m, 2872m, 2132s, 1487s, 1385s, 1080–1055s (br) and 801m cm^{-1}.

With complex 2. This reaction was carried out as for complex **1** but involved treatment of **2** (0.51 g, 1.31 mmol) with $NBu^t_4NO_2$ (0.76 g, 2.63 mmol). The green product was identified as Cu(4,4′-bipy)$(NO_2)_2$ (0.16 g, 0.51 mmol, 39%

Table 7 Fractional atomic coordinates for the non-hydrogen atoms in complex **2**

Atom	*X*/*a*	*Y*/*b*	*Z*/*c*
Cu(1)	0.4830(1)	0.1039(2)	0.7119(1)
Cu(2)	−0.0052(1)	0.8090(1)	0.7434(1)
N(11)	0.3859(6)	0.2244(7)	0.7153(4)
C(12)	0.3172(8)	0.2619(10)	0.6615(6)
C(13)	0.2579(7)	0.3531(9)	0.6639(5)
C(14)	0.2703(6)	0.4132(8)	0.7231(5)
C(15)	0.3414(7)	0.3760(9)	0.7779(5)
C(16)	0.3958(7)	0.2826(9)	0.7713(5)
N(21)	0.0973(5)	0.6951(7)	0.7396(4)
C(22)	0.1135(7)	0.6702(9)	0.6827(5)
C(23)	0.1684(6)	0.5802(8)	0.6745(5)
C(24)	0.2126(6)	0.5090(9)	0.7286(5)
C(25)	0.1970(7)	0.5349(9)	0.7885(5)
C(26)	0.1420(7)	0.6285(9)	0.7924(5)
N(31)	0.5935(5)	0.2161(7)	0.7210(4)
C(32)	0.6095(7)	0.2637(9)	0.6683(6)
C(33)	0.6694(7)	0.3561(9)	0.6726(5)
C(34)	0.7140(6)	0.4062(8)	0.7351(5)
C(35)	0.6995(7)	0.3545(9)	0.7905(5)
C(36)	0.6384(7)	0.2628(10)	0.7813(6)
N(41)	0.8930(5)	0.6957(7)	0.7512(4)
C(42)	0.8193(7)	0.6786(10)	0.6962(5)
C(43)	0.7592(7)	0.5868(8)	0.6906(5)
C(44)	0.7742(7)	0.5064(9)	0.7421(5)
C(45)	0.8496(7)	0.5260(9)	0.7990(5)
C(46)	0.9061(7)	0.6194(9)	0.8010(5)
N(1)	0.4449(6)	0.0047(8)	0.6312(5)
C(1)	0.4191(8)	−0.0423(11)	0.5810(7)
C(10)	0.3875(9)	−0.1041(12)	0.5194(6)
N(2)	0.5194(6)	0.0379(8)	0.8049(5)
C(2)	0.5457(8)	0.0279(11)	0.8611(8)
C(20)	0.5809(10)	0.0158(14)	0.9349(6)
N(3)	0.0360(6)	0.9114(8)	0.8203(5)
C(3)	0.0622(8)	0.9643(10)	0.8673(6)
C(30)	0.0961(8)	1.0315(11)	0.9304(5)
N(4)	−0.0545(6)	0.8660(7)	0.6466(5)
C(4)	−0.0833(7)	0.8769(9)	0.5891(7)
C(40)	−0.1183(8)	0.8910(10)	0.5162(5)
B(1)	−0.1332(12)	1.2279(14)	0.4915(8)
F(1)	−0.0621(6)	1.2970(8)	0.4928(4)
F(2)	−0.1188(7)	1.1825(8)	0.5512(3)
F(3)	−0.1389(7)	1.1473(7)	0.4447(4)
F(4)	−0.2065(6)	1.2941(9)	0.4735(5)
B(2)	0.6334(11)	0.7625(14)	0.5296(8)
F(5)	0.5889(5)	0.6993(8)	0.5636(4)
F(6)	0.5770(5)	0.7817(7)	0.4680(3)
F(7)	0.6674(7)	0.8577(7)	0.5651(4)
F(8)	0.7052(6)	0.7002(8)	0.5258(4)

yield) and the white product as $NBu^t_4BF_4$ (0.42 g, 1.27 mmol, 49% yield) (Found: C, 58.85; H, 10.60; N, 4.30%).

With complex 4. This reaction was carried out as for complex **1** but involved treatment of **4** (0.23 g, 0.22 mmol) with $NBu^t_4NO_2$ (0.32 g, 1.11 mmol). The green solid was identified as $Cu(bpe)(cnge)_2(NO_2)_2$ (0.10 g, 0.20 mmol, 45% yield) and the white solid as $NBu^t_4BF_4$ (0.11 g, 0.33 mmol, 38% yield) (Found: C, 58.40; H, 10.90; N, 4.30%).

With complex 6. This reaction was carried out as for complex **1** but involved treatment of **6** (0.97 g, 1.75 mmol) with $NBu^t_4NO_2$ (1.00 g, 3.47 mmol). Neither effervescence nor a colour change occurred. After stirring for 48 h the solvent volume was reduced, producing a red solid which was crystallised from MeCN and toluene. It analysed as the starting complex [Found (Calc. for $C_{24}H_{20}BCuF_4N_4$): C, 55.25 (56.00); H, 3.80 (3.90); N, 11.20 (10.90)%].

Crystallography

Several crystals of each product were mounted in Lindemann tubes under dry nitrogen for preliminary study. Oscillation and Weissenberg photographs revealed triclinic cell parameters for $[\{Cu(cnge)_2\}_2(\mu\text{-}4,4'\text{-bipy})][BF_4]_2\cdot MeCN$ **1** and monoclinic cell parameters with space group either $P2/c$ (no. 13) or $P2_1/c$ (no. 14) for $[Cu(4,4'\text{-bipy})(MeCN)_2]BF_4$ **2**. X-Ray diffraction data for the refinement of cell parameters and structure determination were collected for suitable crystals at 293 K using a Hilger and Watts Y290 (for **1**) or Enraf-Nonius CAD4 (for **2**) four-circle diffractometer. Details of the data collection and structure solution are collated in Table 5.

For complex **1** one unique set of data was collected in the range $1 < \theta < 22°$ using graphite-monochromated Mo-Kα radiation. Standard reflections were constant throughout the course of the data collection indicating that the crystals were stable. Data were corrected for Lorentz and polarisation effects; absorption corrections were not applied. The positions of the copper atoms and of the ligating nitrogen atoms were determined by direct methods using the MULTAN 80 suite of programs.[35] The positions of the remaining atoms were obtained by Fourier-difference syntheses using the CRYSTALS programs.[36] Both tetrafluoroborate anions were disordered with fluorine occupancies of 60, 25 and 15% for $B(1)F_4^-$ and 65, 25 and 10% for $B(2)F_4^-$. Copper, carbon, nitrogen, boron and the 60%-occupancy fluorine atoms were refined with anisotropic displacement parameters. The 65%-occupancy fluorine atoms were refined with isotropic displacement parameters. The remaining fluorine atoms (located by Fourier-difference syntheses; U_{iso} 0.10 Å^2) and the hydrogen atoms [placed, d(X–H) 1.00 Å, U_{iso} 0.05 Å^2] were not refined. Full-matrix least-squares refinement against F with a five-parameter Chebyshev weighting scheme (−3.07, −12.1, −6.28, −4.97, −1.78) converged to $R = 0.068$ and $R' = 0.046$ for data with $I > 3\sigma(I)$ in space group $P\bar{1}$. Final atomic coordinates are given in Table 6.

For complex **2** the structure was solved by direct methods (SHELXS 86)[37] and refined by full-matrix least squares against F^2, using a Chebyshev weighting scheme (SHELXL 93 software[38]). No absorption corrections were applied, the ψ-scan curves showing insignificant variations. Copper, fluorine and methyl carbon atoms were refined with anisotropic displacement parameters, the other non-hydrogen atoms with isotropic displacement parameters. The hydrogen atoms were allowed to 'ride' on the corresponding carbon atoms and the BF_4^- anions were restricted to tetrahedral geometry. Full-matrix least-squares refinement converged to $R = 0.060$ and $R' = 0.128$ for 1361 'observed' data with $I > 2\sigma(I)$ in space group $P2_1/c$. Very high displacement parameters for fluorine atoms may imply some static disorder, which was impossible to rationalise. Final atomic coordinates are given in Table 7.

Complete atomic coordinates, thermal parameters and bond lengths and angles have been deposited at the Cambridge Crystallographic Data Centre. See Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1996, Issue 1.

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