

Copper(I) chelated by 2,9-dimethyl-1,10-phenanthroline and bridged by 4,4'-bipyridine or *trans*-1,2-bis(pyridin-4-yl)ethene to give discrete dinuclear and polymeric cations

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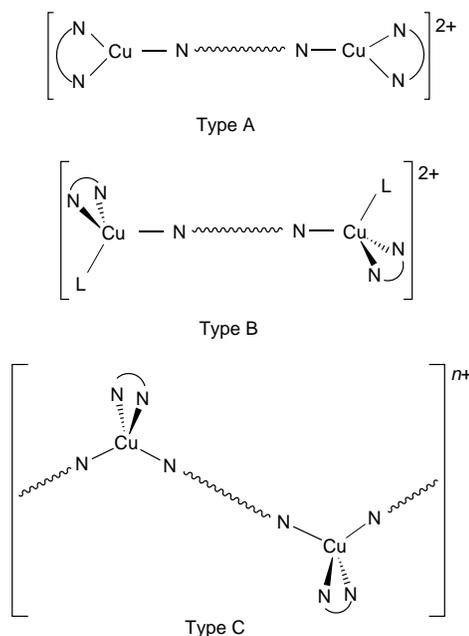
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Treatment of $[\text{Cu}(\text{MeCN})_4][\text{BF}_4]$ with 2,9-dimethyl-1,10-phenanthroline (dmp) and either pyrazine (pyz), 4,4'-bipyridine (4,4'-bipy) or *trans*-1,2-bis(pyridin-4-yl)ethene (bpe) gave, depending on conditions, the copper(I) species $[\{\text{Cu}(\text{dmp})(\text{NCMe})\}_2(\mu\text{-diimine})]^{2+}$, $\{\text{Cu}(\text{dmp})(\mu\text{-diimine})\}_n^{n+}$ (diimine = 4,4'-bipy or bpe) or $[\text{Cu}(\text{dmp})_2]\text{BF}_4 \cdot x\text{solv}$ ($x = 0.5$, solv = CH_2Cl_2 ; $x = 1$, solv = C_7H_8). The discrete dinuclear cation $[\{\text{Cu}(\text{dmp})(\text{NCMe})\}_2(\mu\text{-4,4'-bipy})]^{2+}$ comprises two distorted tetrahedral copper(I) centres ($\text{Cu} \cdots \text{Cu}$ 11.23 Å), each ligated by a bidentate dmp ligand (mean Cu–N 2.059 Å), an acetonitrile molecule (Cu–N 1.943 Å), and bridged by a 4,4'-bipyridine molecule (Cu–N 2.070 Å). The polymeric species $\{\text{Cu}(\text{dmp})(\mu\text{-diimine})\}_n^{n+}$ both comprise 1-D polymeric zig-zag chains, based on distorted tetrahedral copper(I) co-ordination geometries, each copper atom being ligated by the dmp ligand and two pyridine N-atoms [diimine = 4,4'-bipy: $\text{Cu} \cdots \text{Cu}$ 11.11, mean Cu–N (dmp) 2.073, mean Cu–N (py) 2.011 Å; diimine = bpe: mean $\text{Cu} \cdots \text{Cu}$ 13.375, mean Cu–N (dmp) 2.061, mean Cu–N (py) 1.996 Å]. π - π Stacking interactions between dmp molecules in the 4,4'-bipy bridged polymer leads to the formation of large elliptical channels which host two chains of alternating tetrafluoroborate anions and acetonitrile solvent molecules. The mononuclear species $[\text{Cu}(\text{dmp})_2]\text{BF}_4 \cdot x\text{solv}$ ($x = 0.5$, solv = CH_2Cl_2 ; $x = 1$, solv = C_7H_8) are also based on tetrahedral copper(I); that in $[\text{Cu}(\text{dmp})_2]\text{BF}_4 \cdot 0.5\text{CH}_2\text{Cl}_2$ is highly distorted with three short (2.006–2.074 Å) and one longer Cu–N distance (2.139 Å), that in $[\text{Cu}(\text{dmp})_2]\text{BF}_4 \cdot \text{C}_7\text{H}_8$ is much more regular with four similar Cu–N distances (2.022–2.025 Å).

Interest in the design and synthesis of discrete multinuclear copper complexes has been stimulated recently by the structural elucidation of several di-, tri- and tetra-nuclear copper centres in biologically active molecules.¹ Polynuclear copper complexes are also the subject of intensive study owing to their formation of diverse innovative structural networks, including chains, sheets and matrices.² Using a variety of diimines [pyridazine and its 3,6-bis(pyrazol-1-yl) substituted derivatives, pyrazine (pyz), 4,4'-bipyridine (4,4'-bipy) or *trans*-1,2-bis(pyridin-4-yl)ethene (bpe)] as bridging ligands and nitriles [2-cyanoguanidine (cng), benzonitrile or acetonitrile] as terminal ligands, we have generated not only a variety of discrete di- and tri-nuclear copper(I) systems reminiscent of the multinuclear copper proteins such as the nitrite reductases, ascorbate oxidases and haemocyanins,³ but also diverse polynuclear copper(I) cationic chains and matrices.^{3a,4}

In order to extend our knowledge of these systems we have targeted dinuclear cationic species of types A and B and polynuclear species of type C (Scheme 1), bridged by pyz, 4,4'-bipy and bpe and terminally ligated by 2,9-dimethyl-1,10-phenanthroline (dmp). Our rationale was based on the unsaturated trigonal-planar geometry of the complexes $[\text{Cu}(\text{dmp})(\text{NCMe})\text{X}]$, (X = ClO_4 or PF_6).⁵ Substitution of the acetonitrile ligand by a bridging diimine gives type A; expansion of the copper co-ordination sphere to accommodate a bridging diimine results in type B; substitution of the acetonitrile and expansion of the copper co-ordination sphere by bridging diimines results in type C.

For the three bridging diimines considered, Cu^{I} -pyz and -substituted pyz complexes are by far the most extensively studied.^{4a,6–12} Diverse polymeric structural types, ranging from one-dimensional chains^{6–9} through two-dimensional sheets^{9–11} to three-dimensional matrices,¹² have been reported. No discrete dinuclear copper(I) cations have been structurally



Scheme 1 Three- and four-co-ordinate diimine bridged dinuclear (types A and B) and polynuclear (type C) copper(I) targets

characterised. Copper(I)-4,4'-bipy complexes are rare: only one dinuclear species and just three polymeric systems have been structurally characterised. In $[\{\text{Cu}(\text{cng})_2\}_2(\mu\text{-4,4'-bipy})][\text{BF}_4]_2 \cdot \text{MeCN}$ the cation adopts a planar three-co-ordinate T-shaped geometry.^{3a} In $[\text{Cu}(\mu\text{-4,4'-bipy})(\text{MeCN})_2]\text{BF}_4$ a 1-D polymeric cationic zig-zag chain is formed,^{3a} while in $[\text{Cu}(4,4'\text{-bipy})_2]\text{PF}_6$, the copper atoms in both structures adopting a tetrahedral geometry. The only other reported Cu^{I} -4,4'-bipy complexes are of general formula $\text{Cu}(4,4'\text{-bipy})\text{X}$ and $\text{Cu}_2(4,4'\text{-bipy})\text{X}_2$, however structural data are only available

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for the former.¹⁴ The complex Cu(4,4'-bipy)Cl forms interpenetrated sheets, based around a Cu₂Cl₂ core. Just one Cu^I-bpe complex has thus far been reported in the literature, [Cu(bpe)₂]BF₄,^{4b} it has a polymeric diamondoid structure similar to [Cu(4,4'-bipy)₂]PF₆.

Both three- and four-co-ordinate Cu^I-dmp complexes have been structurally characterised.^{5,15-18} In [Cu(dmp)(MeCN)]X (X = ClO₄ or PF₆), the copper atom is three-co-ordinate, and has a Y-shaped geometry,⁵ while the complexes [Cu(dmp)₂]X·nH₂O (X = Br, n = 1; X = NO₃, n = 0 or 2; X = ClO₄, n = 0)¹⁵⁻¹⁸ exhibit tetrahedral geometry at copper, distorted due to the small 'bite-angle' of the chelating diimine ligands.

We now report the synthesis of the discrete dinuclear species [{Cu(dmp)(NCMe)}₂(μ-4,4'-bipy)] [BF₄]₂ **1** and its toluene solvate **1A**, [{Cu(dmp)(NCMe)}₂(μ-bpe)] [BF₄]₂ **2**, the polymeric species [Cu(dmp)(μ-4,4'-bipy)]BF₄·MeCN **3** and [Cu(dmp)(μ-bpe)]BF₄ **4**, and the monomeric species [Cu(dmp)₂]BF₄·C₇H₈ **5**, [Cu(dmp)₂]BF₄·0.5CH₂Cl₂ **6**, and [Cu(dmp)(NCMe)]BF₄ **7**. Of these, the structures of **1A** and **3-6** have been determined and the unit cell parameters of **7** have been measured by oscillation and Weissenberg photographs.

Results and Discussion

The bridging diimines 4,4'-bipy and bpe can be used with dmp and [Cu(MeCN)₄]BF₄ to isolate discrete dinuclear cations of the form [{Cu(dmp)(NCMe)}₂(μ-diimine)]²⁺ or polymeric species of the form {[Cu(dmp)(μ-diimine)]_n}ⁿ⁺. With pyz the only products obtained were [Cu(dmp)₂]BF₄·xsolv and [Cu(dmp)(NCMe)]BF₄, regardless of the ratio of the reactants.

The compounds were initially identified by elemental analysis (C, H, N) and IR spectroscopy. Preliminary electrochemical (cyclic voltammetry) studies were consistent with irreversible redox processes, presumably owing to the rearrangement of the co-ordination sphere on interconversion between copper(I) and copper(II). Crystals suitable for X-ray diffraction were obtained for **1A** and **3-7**. The structure of **7** was not determined after oscillation and Weissenberg photographs indicated that the cell parameters were similar to those of [Cu(dmp)(NCMe)]ClO₄, which has been studied previously.⁵

Crystal and molecular structure of compound 1A

The structure of **1A** (Fig. 1) comprises discrete, dimeric, centrosymmetric [{Cu(dmp)(NCMe)}₂(μ-4,4'-bipy)]²⁺ cations [Cu...Cu 11.23(3) Å], BF₄⁻ anions and toluene solvent molecules. Each copper atom has distorted tetrahedral geometry and is ligated by the bidentate dmp ligand, the bridging 4,4'-bipy and an acetonitrile molecule (Table 1). The nitrile nitrogen is much closer to the copper atom [Cu-N 1.943(5) Å] than the other nitrogens [Cu-N 2.043(4), 2.075(4) Å] owing to sp compared to sp² hybridisation. The anions and toluene molecules are located in channels running throughout the structure. The BF₄⁻ anion exhibits disorder about the B(1)-F(11) three-fold axis. The modelling of the disorder has been only partially successful. The toluene solvent molecule also exhibits disorder; it is positioned on an inversion centre, such that the methyl group coincides with the *p*-carbon atom.

Crystal and molecular structures of compounds 3 and 4

Complexes **3** and **4** both exist as {[Cu(dmp)(μ-diimine)]_n}ⁿ⁺ polymeric cations [Cu...Cu 11.111(1) in **3**; 13.382(2) and 13.368(2) Å in **4**], with discrete BF₄⁻ anions. Complex **3** also has unco-ordinated acetonitrile solvent molecules. The cations form 1-D zig-zag polymeric structures (Figs. 2 and 3). Each copper atom has a distorted tetrahedral geometry and is ligated by the dmp ligand and the two bridging diimine ligands (Table 1).

In compound **3** the 4,4'-bipy bridges are related by symmetry. In **4**, there are two crystallographically distinct bpe bridges,

Table 1 Interatomic distances (Å) and angles (°) in the copper co-ordination spheres of [{Cu(dmp)(MeCN)}₂(μ-4,4'-bipy)] [BF₄]₂·C₇H₈ **1A**, [Cu(dmp)(μ-4,4'-bipy)]BF₄·MeCN **3** and [Cu(dmp)(μ-bpe)]BF₄ **4**

	1A	3	4
Cu-N(1)	2.075(4)	2.064(4)	2.072(6)
Cu-N(2)	2.043(4)	2.085(4)	2.049(6)
Cu-N(21)	2.070(4)	2.005(4)	2.012(7)
Cu-N(31)	1.943(5)	2.018(4)	1.980(7)
N(1)-Cu-N(2)	81.5(2)	80.8(1)	81.8(2)
N(1)-Cu-N(21)	113.1(2)	117.1(2)	110.1(3)
N(1)-Cu-N(31)	117.9(2)	110.3(2)	116.8(3)
N(2)-Cu-N(21)	109.7(2)	112.1(2)	112.0(3)
N(2)-Cu-N(31)	132.0(2)	114.3(2)	120.3(3)
N(21)-Cu-N(31)	102.0(2)	116.9(2)	112.3(3)

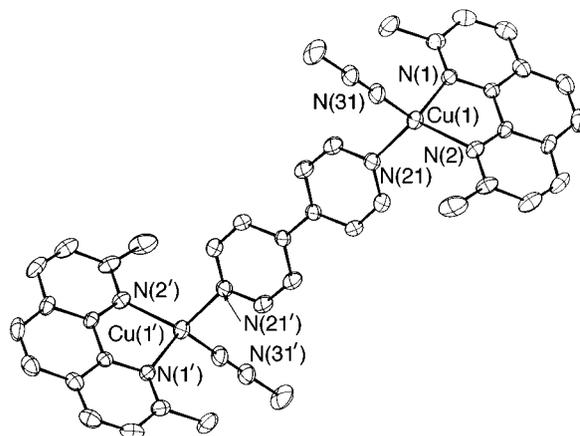


Fig. 1 Molecular structure of the [{Cu(dmp)(MeCN)}₂(μ-4,4'-bipy)]²⁺ cation in compound **1A**

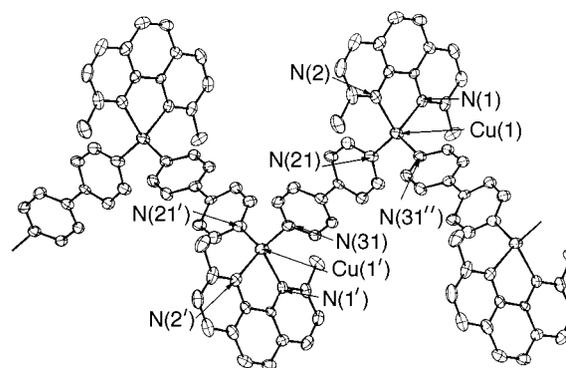


Fig. 2 Molecular structure of the {[Cu(dmp)(μ-4,4'-bipy)]_n}ⁿ⁺ polymeric cation in compound **2**, showing the one-dimensional zig-zag polymeric motif

with the centres of the ethene moieties situated on inversion centres. The two pyridine rings of the 4,4'-bipy molecule in **3** are twisted relative to each other (dihedral angle 17.02°), whereas those of the bpe molecules in **4** are constrained by symmetry to be coplanar. One bpe molecule [N(31) *etc.*, Fig. 3] is disordered (50:50) about a two-fold axis passing through the nitrogens and the centre of the ethene bridging moiety. For clarity only one is shown in Fig. 3. The bridging ligands are approximately perpendicular to the chelating ligands, the dihedral angles between the planes of the co-ordinated pyridine molecules and the dmp ligands ranging from 75.7 to 77.7° in **3** and from 76.7 to 85.4° in **4**.

The cationic chains in **3** lie along the [201] directions. Those in **4** lie along the [131] and [1 - 31] directions. In **3**, the packing of the chains is dominated by π-π interactions between dmp ligands which lie perpendicular to the chain direction [Fig.

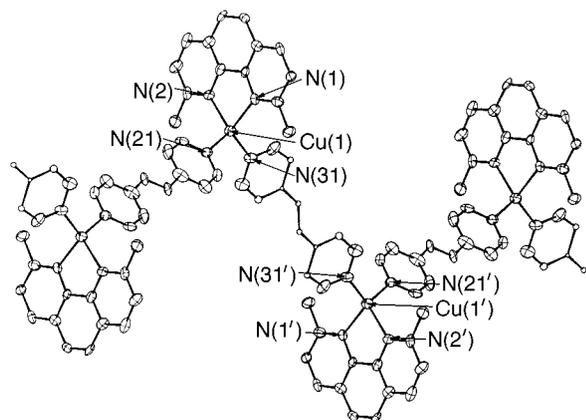


Fig. 3 Molecular structure of the $\{[\text{Cu}(\text{dmp})(\mu\text{-bpe})]_n\}^{1+n+}$ polymeric cation in compound **4**, showing the one-dimensional zig-zag polymeric motif

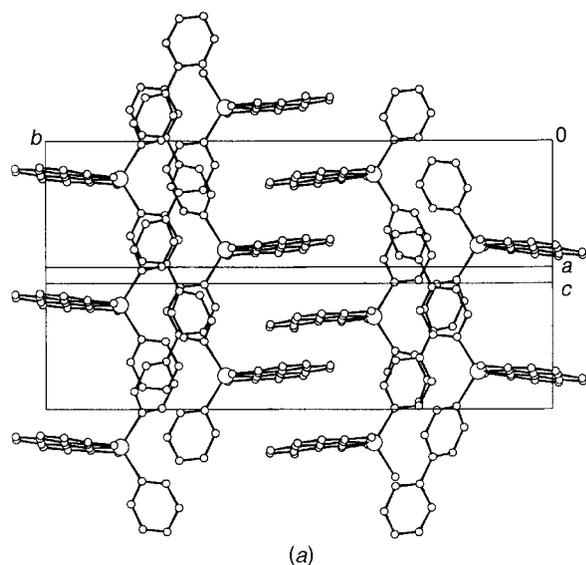


Fig. 4 Predominant π - π stacking interactions observed in compounds **2** [(a) the zip-like motif formed due to stacking interactions between dmp molecules] and **4** [(b) the sandwiching of a bridging bpe molecule between two parallel dmp molecules]

4(a)]. Overlap between the dmp molecules, which are constrained to be parallel by their centrosymmetric relationship, extends over two aromatic rings with a separation of 3.28 Å.

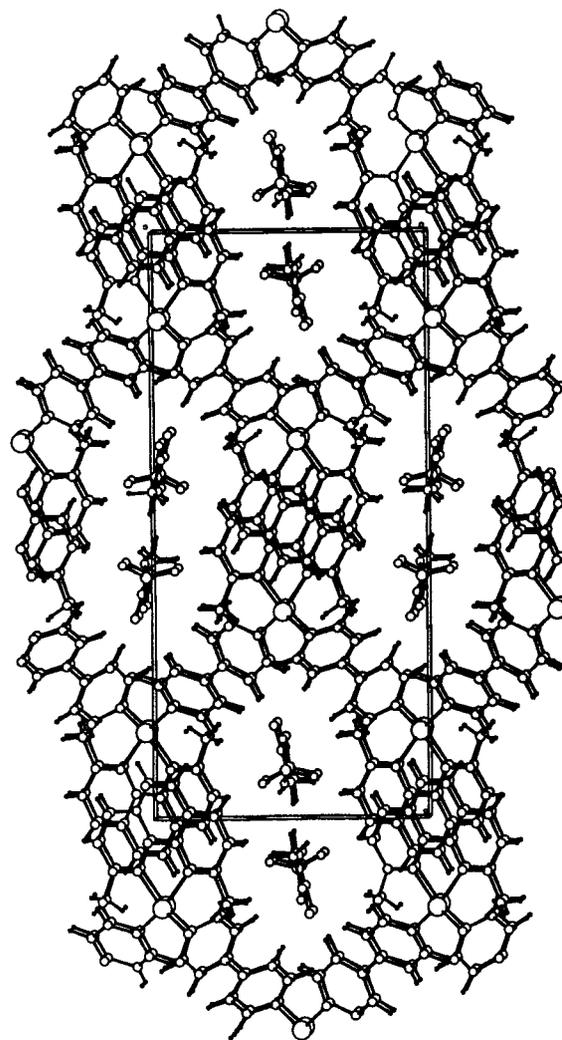


Fig. 5 Packing diagram of compound **2**, showing the formation of large ($\approx 5 \times 11.5$ Å) elliptical shaped channels, containing BF_4^- anions and MeCN molecules

The pyridine rings of the 4,4'-bipy molecules are not involved in π - π interactions. π - π Stacking interactions also occur in **4** but differ significantly from those in **3**. The overlap in **4** involves the ethene group of the ordered bpe molecule [N(21) *etc.*, Figs. 3, 4(b)] which is sandwiched between the pyridine rings of two parallel dmp molecules of separate chains with a separation of 3.38 Å. The disordered bpe molecule is not involved in π - π interactions. The packing of the dmp and 4,4'-bipy ligands in **3** gives rise to a 3-D structure with large elliptical ($\approx 5 \times 11.5$ Å) channels parallel to the *a* axis (Fig. 5). Each channel, the surface of which is exclusively hydrophobic, contains two chains of alternating tetrafluoroborate anions and acetonitrile molecules.

Crystal and molecular structures of compounds **5** and **6**

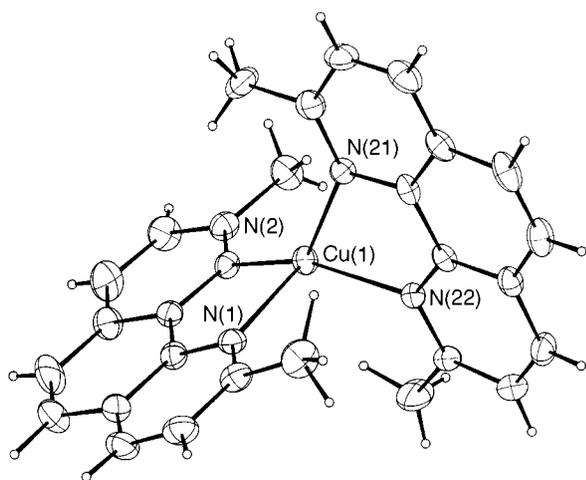
The monomeric species, $[\text{Cu}(\text{dmp})_2]\text{BF}_4 \cdot \text{C}_7\text{H}_8$ **5** and $[\text{Cu}(\text{dmp})_2]\text{BF}_4 \cdot 0.5\text{CH}_2\text{Cl}_2$ **6**, both contain discrete distorted tetrahedral $[\text{Cu}(\text{dmp})_2]^+$ copper(I) cations, BF_4^- anions and solvent molecules. In **5**, the copper atom is situated on a two-fold axis making it similar to that in $[\text{Cu}(\text{dmp})_2]\text{NO}_3$, with crystallographically related dmp ligands.¹⁵ The $[\text{Cu}(\text{dmp})_2]^+$ cation in **6** (Fig. 6) is unsymmetrical as are the majority of those described previously.¹⁶⁻¹⁸

Key interatomic distances and angles of the copper coordination spheres in compounds **5** and **6** are compared with previously characterised $[\text{Cu}(\text{dmp})_2]^+$ complexes in Table 2. The only consistent data are the bite angles of the dmp ligands which vary over a small range (81.3–83.0°). A comparison of the data shows that both **5** and **6** clearly have no precedents.

Table 2 Comparison of copper co-ordination sphere interatomic distances (Å) and angles (°) in [Cu(dmp)₂]X·xsolv

X xsolv	BF ₄ C ₇ H ₈ 5	BF ₄ 0.5CH ₂ Cl ₂ 6	Br H ₂ O	NO ₃ 2H ₂ O	NO ₃ —	ClO ₄ —
Cu–N(1)	2.022(2)	2.139(2)	2.053(5)	2.049(7)	2.084(7)	2.077(6)
Cu–N(2)	2.025(2)	2.006(2)	2.041(5)	2.040(4)	2.058(8)	2.020(5)
Cu–N(21)	—	2.063(2)	2.053(5)	2.042(4)	—	2.060(6)
Cu–N(22)	—	2.051(2)	2.027(5)	2.027(4)	—	2.053(6)
N(1)–Cu–N(2)	82.8(1)	81.6(1)	82.4(2)	82.7(2)	82.7(3)	81.3(3)
N(1)–Cu–N(21)*	128.7(1)	118.6(1)	124.3(2)	122.3(2)	121.3(3)	126.9(2)
N(1)–Cu–N(22)*	121.7(1)	108.0(1)	122.9(2)	123.8(2)	133.7(3)	114.9(2)
N(2)–Cu–N(21)*	121.7(1)	130.8(1)	114.7(2)	119.3(2)	133.7(3)	127.0(2)
N(2)–Cu–N(22)*	124.8(1)	137.9(1)	135.2(2)	131.2(2)	109.9(3)	130.8(2)
N(21)–Cu–N(22)*	82.8(1)	81.5(1)	82.9(2)	83.0(2)	82.7(3)	81.7(2)

* In compound **5**, for N(21) read N(1'), for N(22) read N(2'); symmetry relationship $2 - x, y, 1.5 - z$. In [Cu(dmp)₂]NO₃, for N(21) read N(1'), for N(22) read N(2'); symmetry relationship $1 - x, y, 0.5 - z$.

**Fig. 6** Molecular structure of the [Cu(dmp)₂]⁺ cation in compound **6**

The cation in **5** is the most symmetrical, not only in the copper lying on a two-fold axis, but also in the limited range of Cu–N distances [2.022(2)–2.025(2) Å] and interligand N–Cu–N angles [121.7(1)–128.7(1)°]. That in **6** is the most severely distorted, with the greatest range of Cu–N distances [2.006(2)–2.139(2) Å] and interligand N–Cu–N angles [108.0(1)–137.9(1)°]. The cause of this distortion, which results in one side of the copper co-ordination sphere being more open, is unclear, as neither the anion nor the solvent molecule lies close to this area.

Conclusion

Introduction of the bridging diimine ligands 4,4'-bipy and bpe into systems which normally yield co-ordinatively unsaturated three-co-ordinate Cu^I complexes has led to novel dinuclear Cu^I complexes of type B (**1**, **1A** and **2**) but not type A and to 1-D polymeric chains of type C (**3** and **4**).

We attribute the absence of type A products to the difficulty of stabilising three-co-ordinate copper. The only previous example of a three-co-ordinate dinuclear copper(I) complex is [Cu(cnge)₂]₂(μ-4,4'-bipy)[BF₄]₂·MeCN.^{3a} In this complex, the planar T-shaped copper(I) co-ordination geometry is stabilised by the parallel stacking of planar 2-D sheets, generated by extensive hydrogen-bonding interactions between cnge and BF₄⁻. It is clear from the structures of **1A**, **3** and **4** that it is not possible to generate planar molecular structures using dmp and pyridine donors, unlike those found using dmp and nitrile donors in [Cu(dmp)(NCMe)]X, (X = ClO₄ or PF₆).⁵ Steric hindrance between the dmp methyl groups and the pyridine *ortho* protons, enforces dihedral angles between dmp and pyridine in the region of 80°. The loss of ligand coplanarity destroys the

Table 3 Key interatomic angles^a (°) in the polymeric diimine bridged copper(I) species, [Cu(dmp)(μ-4,4'-bipy)]BF₄·MeCN **3**, [Cu(dmp)(μ-bpe)]BF₄ **4** and [Cu(MeCN)₂(μ-4,4'-bipy)]BF₄ **8**

	3	4	8(a)^b	8(b)^b
N–Cu–N (A)	81	82	121	122
N–Cu–N (B)	117	112	98	101
N–Cu–N (C)	113.5	114.8	108.3	107.6

^a Angle N–Cu–N (A) is either the dmp bite angle (**3**, **4**) or the angle between MeCN molecules (**8**); angle N–Cu–N (B) is the angle between pyridine molecules (**3**, **4**, **8**); angle N–Cu–N (C) is the average of the angles between the pyridine molecules and either the dmp (**3**, **4**) or MeCN molecules (**8**). ^b Complex **8** has two crystallographically independent copper atoms.

packing forces which promote trigonal planar copper(I), giving rise to the more common tetrahedral (albeit distorted) geometry. Since the methyl groups of the dmp chelate play a significant role in hindering the planar approach of a pyridine group, the use of unsubstituted phenanthroline (phen) or 2,2'-bipy ligands may be one way around this problem. Few such complexes are known {examples include [Cu(2,2'-bipy)₂]ClO₄ and [Cu(phen)₂]X, X = ClO₄ or CuBr₂},¹⁹ but tetrahedral geometries are again observed.

The Cu···Cu separation in **1A** (11.23 Å), which is very similar to those in the 4,4'-bipy bridged dication [Cu(cnge)₂]₂(μ-4,4'-bipy)²⁺ (11.23 Å) and the 4,4'-bipy bridged polymeric species [Cu(μ-4,4'-bipy)(NCMe)₂]BF₄ **8** (11.18, 11.22 Å), is somewhat shorter than that in *Achromobacter cycloclastes* nitrate reductase (12.5 Å).²⁰ Comparison of Cu···Cu contacts in the 4,4'-bipy (11.11 Å) and bpe (13.37, 13.38 Å) bridged polymeric cations suggests that the Cu···Cu separation in the bpe bridged cation would be closer to that in the enzyme.

The polynuclear cations in compounds **3** and **4**, have been synthesised and structurally characterised. These have zig-zag chain structures similar to that of **8**,^{3a} the pair of MeCN molecules being replaced by the dmp ligand. Selected structural data for **3** and **4** are compared with those of the crystallographically independent copper atoms in **8** in Table 3. The bite angle of the dmp ligand is much smaller than the angle between the MeCN ligands [N–Cu–N (A); Table 3]. This results in a widening of all the other tetrahedral angles, especially that between the pyridine ligands [N–Cu–N (B); Table 3]. Hence the 'wavelength' of the 4,4'-bipy chain in **3** (19.65 Å) is much longer than that in **8** (15.23 Å). However, it does not follow that the difference in 'wavelength' is due to the effect of the small bite angle of the dmp ligand. It is undoubtedly due to the π–π stacking interactions between dmp molecules which dictate a periodicity which is some multiple of their separation ($6 \times 3.28 = 19.68$ cf. 19.65 Å).

Experimental

The salt $[\text{Cu}(\text{MeCN})_4]\text{BF}_4$ was prepared by literature methods,²¹ dmp (neocuproin), 4,4'-bipy, bpe and pyz (Aldrich) were used without further purification. All solvents were freshly distilled, degassed and dried by literature procedures.²²

Complexes **1–7** were characterised using elemental analyses and IR spectroscopy. Carbon, hydrogen and nitrogen analyses (microanalyses) were carried out by Mr. T. J. Spencer in the University of Nottingham Chemistry Department. The dimers gave consistently low nitrogen data; these were attributed to the difficulty of ensuring complete combustion of compounds with high nitrogen content. The IR spectra were measured using a Perkin-Elmer PE1600C spectrometer, as KBr pressed pellets.

Synthesis of $[\{\text{Cu}(\text{dmp})(\text{NCMe})\}_2(\mu\text{-}4,4'\text{-bipy})][\text{BF}_4]_2$ **1**

The salt $[\text{Cu}(\text{MeCN})_4]\text{BF}_4$ (0.200 g, 0.636 mmol), dmp (0.132 g, 0.636 mmol) and 4,4'-bipy (0.05 g, 0.318 mmol), were dissolved in acetonitrile (40 ml) and the resulting red solution was stirred for several hours. The solution was then reduced in volume and filtered *via* cannula. Diethyl ether (40 ml) was then added and the resulting red-orange precipitate was obtained by cannula filtration, and was identified as $[\{\text{Cu}(\text{dmp})(\text{MeCN})\}_2(\mu\text{-}4,4'\text{-bipy})][\text{BF}_4]_2 \cdot \text{MeCN}$ (Found: C, 52.75; H, 3.75; N, 10.55. Calc. for $\text{C}_{42}\text{H}_{38}\text{B}_2\text{Cu}_2\text{F}_8\text{N}_8$: C, 52.80; H, 4.00; N, 11.75%). IR $\tilde{\nu}/\text{cm}^{-1}$: 1602m (4,4'-bipy), 1591s (dmp), 1508m (dmp), 1409m (dmp or 4,4'-bipy), 1381m (dmp), 1059 (br) (BF_4^-), 867m, (4,4'-bipy), 851s (dmp), 817m (4,4'-bipy), 799m (4,4'-bipy), 725m (dmp), 549w (dmp). The precipitate was redissolved in acetonitrile and orange-red crystals of **1A** were grown by the vapour-phase diffusion of toluene into the mother-liquor.

Synthesis of $[\text{Cu}(\text{dmp})(\mu\text{-}4,4'\text{-bipy})]\text{BF}_4 \cdot \text{MeCN}$ **3**

The salt $[\text{Cu}(\text{MeCN})_4]\text{BF}_4$ (0.314 g, 1.00 mmol), dmp (0.208 g, 1.00 mmol) and 4,4'-bipy (0.156 g, 1.00 mmol), were dissolved in a 4:1 dichloromethane–acetonitrile mixture (50 ml) and the resulting red solution was stirred overnight. The solution was then reduced in volume and filtered *via* cannula. Diethyl ether (40 ml) was then added and the resulting red-orange precipitate was obtained by cannula filtration, and was identified as $[\text{Cu}(\text{dmp})(\mu\text{-}4,4'\text{-bipy})]\text{BF}_4 \cdot \text{MeCN}$ (Found: C, 56.50; H, 4.25; N, 12.75. Calc. for $\text{C}_{24}\text{H}_{20}\text{BCuF}_4\text{N}_4 \cdot \text{CH}_3\text{CN}$: C, 56.20; H, 4.15; N, 12.60%). IR $\tilde{\nu}/\text{cm}^{-1}$: 1603s (4,4'-bipy), 1593s (dmp), 1510s (dmp), 1415s (dmp or 4,4'-bipy), 1379m (4,4'-bipy), 1063 (br) (BF_4^-), 868m (4,4'-bipy), 850s (dmp), 817m (4,4'-bipy), 798m (4,4'-bipy), 721s (dmp), 549m (dmp). The precipitate was redissolved in acetonitrile and red crystals of **3** suitable for X-ray diffraction were grown by the vapour-phase diffusion of ether into the mother-liquor.

Synthesis of $[\{\text{Cu}(\text{dmp})(\text{NCMe})\}_2(\mu\text{-bpe})][\text{BF}_4]_2$ **2** and $[\text{Cu}(\text{dmp})(\mu\text{-bpe})]\text{BF}_4$ **4**

The salt $[\text{Cu}(\text{MeCN})_4]\text{BF}_4$ (0.314 g, 1.00 mmol), dmp (0.198 g, 0.95 mmol) and bpe (0.219 g, 1.20 mmol), were dissolved in a 2:1 dichloromethane–acetonitrile mixture (45 ml) and the resulting orange solution was stirred overnight. The solution was then reduced in volume to yield a red precipitate which was removed by cannula filtration. This was identified as $[\{\text{Cu}(\text{dmp})(\text{NCMe})\}_2(\mu\text{-bpe})][\text{BF}_4]_2$ **2** (Found: C, 53.65; H, 3.85; N, 9.60. Calc. for $\text{C}_{44}\text{H}_{40}\text{B}_2\text{Cu}_2\text{F}_8\text{N}_8$: C, 53.85; H, 4.10; N, 11.40%). IR $\tilde{\nu}/\text{cm}^{-1}$: 1604s (bpe), 1592s (dmp), 1561m (dmp), 1508s (dmp), 1495m (dmp), 1423m (bpe), 1381s (dmp), 1059 (br) (BF_4^-), 851s (dmp), 825m (bpe), 724s (dmp), 547m (bpe). The remaining solution was reduced in volume further to yield an orange precipitate. This was removed by cannula filtration and identified as $[\text{Cu}(\text{dmp})(\mu\text{-bpe})]\text{BF}_4$ **4** (Found: C, 57.10; H, 4.10; N, 10.35. Calc. for $\text{C}_{26}\text{H}_{22}\text{BCuF}_4\text{N}_4$: C, 57.75; H, 4.10; N, 10.35%). IR $\tilde{\nu}/\text{cm}^{-1}$: 1604s (bpe), 1587s (dmp), 1498s (dmp),

1358m (dmp), 1154m (dmp), 1054 (br) (BF_4^-), 988s (bpe), 858s (dmp), 828s (bpe), 730m, (dmp), 550s (bpe or dmp). Orange crystals of **4** suitable for X-ray diffraction studies were grown by the vapour-phase diffusion of ether into the mother-liquor.

Attempted synthesis of $[\text{Cu}(\text{dmp})(\mu\text{-pyz})]\text{BF}_4$. Synthesis of $[\text{Cu}(\text{dmp})_2]\text{BF}_4 \cdot \text{C}_7\text{H}_8$ **5** and $[\text{Cu}(\text{dmp})_2]\text{BF}_4 \cdot 0.5\text{CH}_2\text{Cl}_2$ **6**

The salt $[\text{Cu}(\text{MeCN})_4]\text{BF}_4$ (0.314 g, 1.00 mmol), dmp (0.198 g, 0.95 mmol) and pyz (0.096 g, 1.20 mmol), were dissolved in a 2:1 dichloromethane–acetonitrile mixture (45 ml) and the resulting orange solution was stirred overnight. The solution was then reduced in volume. Addition of ether caused the precipitation of a red solid, identified as $[\text{Cu}(\text{dmp})_2]\text{BF}_4$ (Found: C, 58.95; H, 4.25; N, 10.15. Calc. for $\text{C}_{28}\text{H}_{24}\text{BCuF}_4\text{N}_4$: C, 59.35; H, 4.25; N, 9.90%). IR $\tilde{\nu}/\text{cm}^{-1}$ (all bands due to dmp unless stated otherwise): 1590m, 1560w, 1509m, 1359m, 1260w, 1149m, 1055 (br) (BF_4^-), 860s, 732m, 550w. Orange-red crystals of **5** and **6** suitable for X-ray diffraction studies, were grown by the vapour-phase diffusion of toluene and ether, respectively, into the mother-liquor. The vapour-phase diffusion of ether also afforded yellow crystals of **7**.

Synthesis of $[\text{Cu}(\text{dmp})(\text{NCMe})]\text{BF}_4$ **7**

The salt $[\text{Cu}(\text{MeCN})_4]\text{BF}_4$ (0.314 g, 1.00 mmol) and dmp (0.208 g, 1.00 mmol) were dissolved in dichloromethane (40 ml), and the resulting red solution was stirred for 90 min, after which a yellow precipitate of **7** had formed. This was removed by cannula filtration and dried under vacuum (0.289 g, 0.72 mmol, 72%) (Found: C, 47.55; H, 3.65; N, 10.70. Calc. for $\text{C}_{16}\text{H}_{15}\text{BCuF}_4\text{N}_3$: C, 48.10; H, 3.80; N, 10.50%). IR $\tilde{\nu}/\text{cm}^{-1}$ (all bands due to dmp unless stated otherwise): 1592s, 1560m, 1496m, 1422m, 1381m, 1361m, 1142s, 1054 (br) (BF_4^-), 851s, 725m, 548m. Yellow crystals of **7** were prepared by the vapour-phase diffusion of ether into a solution of **7** in acetonitrile. Oscillation and Weissenberg photographs of a suitable crystal of **7** (monoclinic, space group $P2_1/c$, $a = 11.83$, $b = 19.77$, $c = 7.52$ Å, $\beta = 106.3^\circ$), showed it to be isostructural with the perchlorate analogue [monoclinic, space group $P2_1/c$, $a = 11.9101(9)$, $b = 19.987(1)$, $c = 7.636(1)$ Å, $\beta = 108.159(9)^\circ$].⁵

Crystallography

Suitable crystals were mounted in sealed Lindemann tubes. Oscillation and Weissenberg photographs were carried out to determine preliminary cell dimensions, symmetry and space group. A second crystal of each complex was selected and mounted on a two-stage fibre, before being transferred to a Stoe Stadi-4 four-circle diffractometer equipped with an Oxford Cryosystems open flow cryostat.²³ Data were collected for all crystals except **1A** at 150 K. Attempts were made to collect data for **1A** at 150 K, but this led to a more serious degradation of the crystal and a new crystal was selected for collection at 220 K. Data were collected using graphite-monochromated Mo-K α radiation ($\lambda = 0.71073$ Å) and ω - θ scans. The data were collected for Lorentz and polarisation effects. Absorption corrections were applied using Ψ scans. Intensity-control reflections were monitored periodically throughout data collection, and no significant decrease in intensity was observed.

The structure of **1A** was solved by direct methods (SIR 92).²⁴ Full-matrix least-squares refinement on F^2 was carried out (SHELXL).²⁵ The BF_4^- anion was disordered by rotation around one B–F axis: the three affected F atoms were each disordered over three equally-occupied sites. Similarity restraints were applied to the B–F distances. The toluene solvent molecule was found to be disordered about a crystallographic inversion centre. All ordered non-hydrogen atoms were refined with anisotropic displacement parameters. Methyl hydrogen atoms were found by Fourier-difference synthesis (SHELXL),²⁵ and thereafter refined as part of rigid groups allowed to rotate

Table 4 Data collection parameters for [$\text{Cu}(\text{dmp})(\text{MeCN})_2(\mu\text{-}4,4'\text{-bipy})$][BF_4] $\cdot\text{C}_7\text{H}_8$ **1A**, [$\text{Cu}(\text{dmp})(\mu\text{-}4,4'\text{-bipy})$] $\text{BF}_4\cdot\text{MeCN}$ **3**, [$\text{Cu}(\text{dmp})(\mu\text{-bpe})$] BF_4 **4**, [$\text{Cu}(\text{dmp})_2$] $\text{BF}_4\cdot\text{C}_7\text{H}_8$ **5** and [$\text{Cu}(\text{dmp})_2$] $\text{BF}_4\cdot 0.5\text{CH}_2\text{Cl}_2$ **6**

	1A	3	4	5	6
Empirical formula	$\text{C}_{42}\text{H}_{38}\text{B}_2\text{Cu}_2\text{F}_8\text{N}_8\cdot\text{C}_7\text{H}_8$	$\text{C}_{24}\text{H}_{20}\text{BCuF}_4\text{N}_4\cdot\text{MeCN}$	$\text{C}_{26}\text{H}_{22}\text{BCuF}_4\text{N}_4$	$\text{C}_{28}\text{H}_{24}\text{BCuF}_4\text{N}_4\cdot\text{C}_7\text{H}_8$	$\text{C}_{28}\text{H}_{24}\text{BCuF}_4\text{N}_4\cdot 0.5\text{CH}_2\text{Cl}_2$
<i>M</i>	1047.6	555.86	541.84	658.0	608.33
Crystal shape and colour	Orange-red taper	Red rhomboid tablet	Orange tablet	Orange-red column	Orange-red column
Crystal system	Triclinic	Monoclinic	Monoclinic	Monoclinic	Triclinic
Space group	$P\bar{1}$ (no. 1)	$P2_1/c$ (no. 14)	$I2/a$ (alt. $C2/c$ no. 15)	$C2/c$ (no. 15)	$P\bar{1}$ (no. 2)
<i>a</i> /Å	7.920(14)	8.399(2)	18.767(4)	15.875(4)	10.514(2)
<i>b</i> /Å	12.18(2)	25.186(5)	12.903(4)	15.493(4)	11.119(2)
<i>c</i> /Å	13.914(7)	11.874(2)	20.117(7)	13.296(3)	12.889(2)
α /°	68.46(6)	—	—	—	67.27(2)
β /°	75.30(9)	95.32(3)	95.32(3)	106.71(2)	74.00(2)
γ /°	88.61(13)	—	—	—	73.17(2)
<i>U</i> /Å ³	1204(2)	2501.1(8)	4850.36(19)	3132.14(10)	1307.25(3)
<i>Z</i>	2	4	8	4	2
<i>D</i> _c /g cm ⁻³	1.445	1.48	1.48	1.40	1.55
Crystal dimensions/mm	0.96 × 0.62 × 0.35	0.34 × 0.29 × 0.19	0.31 × 0.21 × 0.12	0.15 × 0.17 × 0.58	0.50 × 0.19 × 0.19
<i>F</i> (000)	536	1137	2218	1357	621
μ /mm ⁻¹	0.958	0.926	0.95	0.75	0.99
2 θ _{max} /°	55.3	50.04	50	50	50
Index ranges	−9 ≤ <i>h</i> ≤ 10, −15 ≤ <i>k</i> ≤ 14, −16 ≤ <i>l</i> ≤ 16	−9 ≤ <i>h</i> ≤ 9, 0 ≤ <i>k</i> ≤ 29, −12 ≤ <i>l</i> ≤ 14	−20 ≤ <i>h</i> ≤ 20, 0 ≤ <i>k</i> ≤ 13, 0 ≤ <i>l</i> ≤ 21	−18 ≤ <i>h</i> ≤ 18, 0 ≤ <i>k</i> ≤ 18, −7 ≤ <i>l</i> ≤ 15	−11 ≤ <i>h</i> ≤ 12, −11 ≤ <i>k</i> ≤ 13, −12 ≤ <i>l</i> ≤ 15
Reflections collected	6272	5103	5214	4514	5611
Independent reflections	4966 (<i>R</i> _{int} = 0.022)	4033 (<i>R</i> _{int} = 0.042)	2711 (<i>R</i> _{int} = 0.056)	2631 (<i>R</i> _{int} = 0.025)	5279
Number of parameters	316	414	322	271	409
$\Delta\rho_{\text{min}}, \Delta\rho_{\text{max}}$ (Δ/σ) _{max}	−0.99, 0.95 0.15	−0.79, 0.61 0.063	−0.76, 1.21 0.10	−0.56, 0.67 0.07	−0.98, 1.06 0.11
Goodness of fit	1.0830	1.1372	1.0002	1.2502	1.1329
Final <i>R</i> indices (all data)	<i>R</i> 1 = 0.0732, <i>wR</i> 2 = 0.1908	<i>R</i> = 0.0871, <i>R</i> ' = 0.0936	<i>R</i> = 0.1090, <i>R</i> ' = 0.1400	<i>R</i> = 0.0669, <i>R</i> ' = 0.0626	<i>R</i> = 0.0645, <i>R</i> ' = 0.0695
Final <i>R</i> indices [<i>I</i> > 2 σ (<i>I</i>)]	<i>R</i> 1 = 0.0640, <i>wR</i> 2 = 0.1758	<i>R</i> = 0.0649, <i>R</i> ' = 0.0756	<i>R</i> = 0.0815, <i>R</i> ' = 0.1167	<i>R</i> = 0.0534, <i>R</i> ' = 0.0556	<i>R</i> = 0.0566, <i>R</i> ' = 0.0646

about their local C–C axis. Other hydrogen atoms were introduced at geometrically calculated positions and thereafter allowed to ride on their parent C atoms.

The structures of complexes **3–6** were also solved by direct methods (SIR 92).²⁴ Iterative Fourier-difference syntheses (CRYSTALS)²⁶ revealed disorder in **4** and **6** but not in **3**. In **4**, one of the bpe molecules [N(31) *etc.*] adopts one of two positions (50:50) related by a two-fold axis passing through the two nitrogen atoms N(31) and the centre of the ethene moiety. In **5**, B(1) and F(1) of the BF_4^- anion lie on a two-fold axis resulting in disorder of the other three fluorine atoms (50:50); the toluene solvent molecule is located on an inversion centre disordering the methyl group equally about the two centrosymmetrically related positions. In **6**, the dichloromethane solvate molecule is located at an inversion centre such that the chlorine atoms have 100% occupancy and the carbon and hydrogen atoms 50% occupancy of the centrosymmetrically related sites.

All hydrogen atoms were found in **3**, except those attached to C(32), C(36) and C(43); in **5**, except toluene protons; and in **6**, except the methyl protons of the dmp ligand. All hydrogens in **4** were placed (C–H 1.00 Å; $U_{\text{iso}} = 0.05 \text{ \AA}^2$), as were those not found in **3**, **5** and **6**.

Full-matrix least-squares refinement on F^2 were carried out (CRYSTALS)²⁶ using all positive data. Non-hydrogen atoms were refined anisotropically except for the disordered bpe atoms in **4**, which were refined isotropically. Those hydrogen atoms which were found were refined isotropically; those which were placed were all allowed to ride on the corresponding carbon atom in the calculated position. All diagrams were generated using the CAMERON suite of programs.²⁷

Full details of the diffraction experiments are given in Table 4. Pertinent interatomic distances and angles are summarised in Tables 1 and 2.

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See <http://www.rsc.org/suppdata/dt/1998/909/> for crystallographic files in .cif format.

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