DALTON

Nitrate- and nitrite-ligated 3,6-bis(imidazolyl)pyridazine-bridged dinuclear copper(II) cations with copper–copper separations similar to that in *Achromobacter cycloclastes* nitrite reductase†

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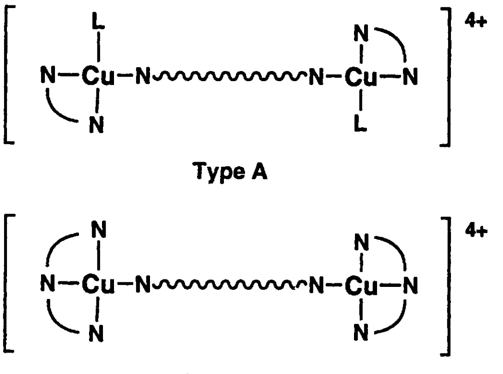
The 4,4′-bipyridine (4,4′-bipy) and 3,6-bis(imidazolyl)pyridazine (bimpydz) bridged dinuclear copper(II)–diethylenetriamine (dien) complexes, $[\{Cu(dien)\}_2(\mu\text{-diimine})][NO_3]_4{\cdot}xH_2O$ (diimine = 4,4′-bipy, $x = 2$ **1**; diimine = bimpydz, $x = 0$ **5**), $[\{Cu(dien)\}_2(\mu\text{-diimine})][BF_4]_4{\cdot}4MeCN$ (diimine = 4,4′-bipy **2** or bimpydz **6**) and $[\{Cu(dien)\}_2(\mu\text{-bimpydz})]Cl_4{\cdot}4H_2O$ **4**, have been synthesised and characterised. Reaction of the tetrafluoroborates, **2** and **6**, with $NaNO_2$ yields the nitrites $[\{Cu(dien)\}_2(\mu\text{-diimine})][NO_2][BF_4]_3{\cdot}xMeCN$ (diimine = 4,4′-bipy, $x = 0$ **3**; diimine = bimpydz, $x = 0.5$ **7**). Neither the chloride nor the nitrates react with $NaNO_2$. Structural analysis of complexes **5** and **7** has shown that although they are both based on the dinuclear cationic unit, $[\{Cu(dien)\}_2(\mu\text{-bimpydz})]^{4+}$, in **5** the bimpydz bridge adopts a transoid arrangement of imidazole molecules, whereas in **7** it adopts a cisoid arrangement, giving Cu $\cdots$ Cu separations of 13.28 and 12.88 Å, respectively. In **5**, the dications are linked by two axially co-ordinated nitrate anions, one strongly bound, the other very weakly bound, to give chains with a ladder-type motif. In **7**, the dications are bridged by μ-nitrito-κ*O*:κ*N* moieties to form a chain with helical geometry. The copper(II)–nitrite interaction is novel; the anion bridges the weakly binding axial positions of two square-pyramidal copper atoms using the nitrogen lone pair and the *syn* lone pair of an oxygen.

The copper-containing nitrite reductase from *Achromobacter cycloclastes* has recently been shown[1] to contain a dinuclear copper centre bridged by a histidine–cysteine section of the protein chain. As part of our attempts to generate[2] discrete dinuclear copper complexes with similar Cu $\cdots$ Cu separations to that in the enzyme (12.5 Å) we have recently described the synthesis and structural characterisation of a series of dicopper(I) complexes, bridged by the diimines 4,4′-bipyridine (4,4′-bipy) or 1,2-bis(4′-pyridyl)ethene (bpe) and terminally co-ordinated by 2-cyanoguanidine (cnge), *viz.* $[\{Cu(cnge)_2\}_2(\mu\text{-diimine})][BF_4]_2$. Their reaction with nitrite ($NBu^t_4NO_2$) led to a product tentatively formulated as $Cu(diimine)(cnge)(MeCN)(NO_2)_2$.[2] We now wish to report the results of our studies of dicopper(II)–nitrite systems bridged by the neutral, N-donor bidentate bridging ligands, 4,4′-bipy or 3,6-bis(imidazolyl)pyridazine (bimpydz). Both bidentate [2,2′-bipyridine (2,2′-bipy) or ethane-1,2-diamine (en)] and tridentate [diethylenetriamine (dien) or 2,6-bis(pyrazolyl)pyridine (bppy)] chelating ligands were used in an attempt to target dinuclear copper(II) complexes of the types A and B (Scheme 1) as substrates for reaction with $NaNO_2$. Success was achieved with dien and bppy only.



Scheme 1 Bridging bidentate ligand: 4,4′-bipy, bpe or bimpydz. Chelating bidentate ligand: 2,2′-bipy or en. Chelating tridentate ligand: dien or bppy

Reports of bis[copper(II)–dien] complexes containing neutral bridges are sparse,[3–5] the only structurally characterised ones being $[\{Cu(dien)\}_2(\mu\text{-diimine})][ClO_4]_4$ {diimine = 4,4′-bipy,[3] pyrazine[4] or 2,5-bis[(dimethylamino)methyl]pyrazine[5]}. They include discrete molecular units with four anions in the axial positions of the two copper(II) 4 + 2 co-ordination spheres of the $[(dien)Cu(\mu\text{-diimine})Cu(dien)]^{4+}$ dinuclear cation[4] and cationic chains comprising dinuclear cations bridged by two similarly located anions.[3] There are, however, several well characterised dinuclear $[\{Cu(dien)\}_2(\mu\text{-L})]^{n+}$ systems with anionic [bromide,[6] hydroxide,[7] oxalate,[8,9] phthalate,[10] terephthalate,[11] pyrazolate,[12] biimidazolate,[9] bibenzimidazolate,[9] hexacyanoferrate(III)[13] and dicyanamidobenzene dianion[14]] bridges. A number of complexes containing alkyl substituted diethylenetriamines with anionic (azide,[15] oxalate,[9,15–17] oxamide,[17] oxamate,[17] squarate,[18] terephthalate,[19] imidazolate,[20] methylimidazolate,[20,21] benzimidazolate,[20,21] biimidazolate,[9,22] and bibenzimidazolate[9]) bridges are also known. No examples of bis[copper(II)–bppy] complexes have been described previously.

Results and Discussion

(*i*) Copper(II)–en or 2,2′-bipy–diimine systems

Treatment of hydrated copper(II) tetrafluoroborate with a bridging diimine [4,4′-bipy, bimpydz or 3,6-bis(2-isopropylimidazolyl)pyridazine (biimpydz)] and a bidentate chelating ligand (en or 2,2′-bipy) in 2:1:2 molar ratios in dimethylformamide (dmf)–MeCN mixtures was unsuccessful. Instead of the target molecules (Type A, Scheme 1), mixtures of bis(bidentate) chelate complexes, $[CuL_2(FBF_3)_2]$ (L = en or 2,2′-bipy) and bridge containing complexes, $[\{Cu(2,2'\text{-bipy})\}(\mu\text{-}4,4'\text{-bipy})][BF_4]_2$, $[Cu(4,4'\text{-bipy})_2][BF_4]_2$ or

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† *Non-SI unit employed:* $\mu_B \approx 9.27 \times 10^{-24}$ J T^{-1}.

Table 1 Analytical and spectroscopic data for the products of the reaction of 4,4'-bipy or bimpydz with copper(II) salts in the presence of dien or bppy

	Analysis (%)[a]				IR spectra/cm^{-1}						
Complex	C	H	N	Cu	(4,4'-bipy or bimpydz; dien or bppy)[b]						Anion[c]
1	28.05 (27.95)	4.60 (4.95)	21.55 (21.75)	16.05 (16.45)	1611s	1422s	1228s	816s	—	—	1383s (br)
					3220m	2920m	1603w	—	1144w	—	—
2	30.65 (31.20)	5.20 (4.65)	16.00 (16.80)	11.90 (12.70)	1612s	1423s	1230s	817s	—	—	1060s (br)
					3215m	2920m	—	—	—	—	—
3	26.80 (27.15)	4.90 (4.30)	16.05 (15.85)	14.95 (15.95)	1610s	1423m	—	816m	—	—	1273s
					3219m	2933m	—	—	—	—	1060s (br)
4	28.95 (28.45)	5.10 (5.55)	22.25 (22.15)	15.95 (16.75)	3136m	1579m	1503s	1326m	1030m	650w	—
					3215m	2920m	1605w	1463m	1145w	—	—
5	27.55 (27.25)	4.25 (4.30)	28.00 (28.25)	15.00 (16.00)	3133m	1581m	1493m	1329w	1040m	660m	1384s (br)
					3220m	2920m	—	1458w	1147w		—
6	29.55 (29.55)	4.00 (4.40)	21.30 (21.20)	12.00 (12.00)	3112m	1577s	1505s	1310m	—	650w	1055s (br)
					3210m	2910m	—	1460m	1135w		—
7	26.15 (26.30)	4.35 (4.10)	21.05 (21.75)	13.80 (14.50)	3110m	1577s	1498m	—	—	651m	1272s
					3219m	2959m	—	—	—	—	1055s (br)
8	35.50 (35.55)	2.80 (3.15)	25.90 (25.90)	11.60 (11.75)	3112s	1591m	1500 (sh)	1358 (sh)	1045w	644w	1384s (br)
					2923s	1625s	1483m	1069m	780m	—	—

[a] Calculated values in parentheses. [b] Principal ligand IR vibrations: 4,4'-bipy 1590s, 1406s, 1218m, 988m, 806s, 608s, 498m; bimpydz 3109m, 1579m, 1490s, 1323s, 1036s, 649s; dien 3280m (br), 2930s (br), 1598w, 1458w, 1130w, 904m (br); bppy 2919m, 1607s, 1482s, 1392m, 1036s, 760s cm^{-1}. [c] Anion IR vibrations:[27] NO_3^- 1390, BF_4^- 1070, NO_2^- 1244 cm^{-1}

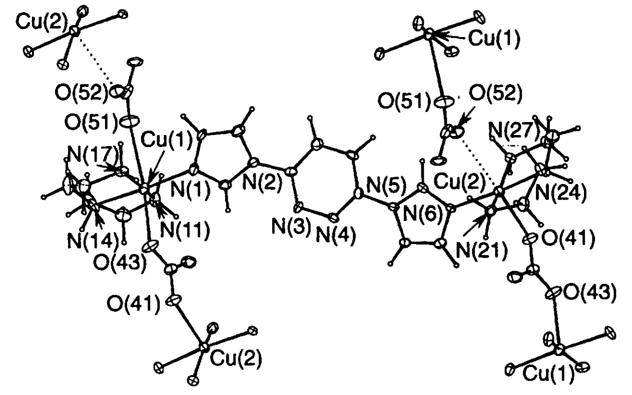


Fig. 1 Molecular structure of the dinuclear cation of **5** showing the co-ordination of the bridging nitrates

$[CuL][BF_4]_2$ (L = bimpydz or biimpydz), were obtained. Although the first two complexes are well known,[23,24] and the perchlorate analogue of $[\{Cu(2,2'\text{-bipy})(\mu\text{-}4,4'\text{-bipy})\}_n][BF_4]_{2n}$ has been structurally characterised,[25] the remainder are novel; unfortunately, insolubility in non-polar solvents prevented their purification and full characterisation.

(*ii*) Copper(II)–dien or bppy–diimine systems

The chemistries of the copper(II)–dien–diimine (diimine = 4,4'-bipy or bimpydz) systems in dmf–MeCN differed with counter anion. The target dinuclear cations, $[\{Cu(dien)\}_2(\mu\text{-diimine})]^{4+}$ (Type B, Scheme 1) were obtained for both 4,4'-bipy and bimpydz starting with hydrated copper(II) nitrate and tetrafluoroborate. Hydrated copper(II) chloride yielded the desired product with bimpydz only; with 4,4'-bipy, the sole identified product was $[CuCl_2(dien)]$.[26] The five complexes, $[\{Cu(dien)\}_2(\mu\text{-}4,4'\text{-bipy})][NO_3]_4\cdot 2H_2O$ **1**, $[\{Cu(dien)\}_2(\mu\text{-}4,4'\text{-bipy})][BF_4]_4\cdot 4MeCN$ **2**, $[\{Cu(dien)\}_2(\mu\text{-bimpydz})]Cl_4\cdot 4H_2O$ **4**, $[\{Cu(dien)\}_2(\mu\text{-bimpydz})][NO_3]_4$ **5** and $[\{Cu(dien)\}_2(\mu\text{-bimpydz})][BF_4]_4\cdot 4MeCN$ **6** were initially characterised from analytical and spectroscopic data (Table 1); subsequently, structural data were obtained from single crystals of **5**. They had very similar (royal blue) chromophores, their electronic absorption spectra comprising a single broad absorption band ($\lambda_{max} \approx 620$ nm) and they exhibited similar magnetic properties characteristic of a d^9 system ($\mu_{eff} \approx 1.7$ μ_B).

A similar complex, $[\{Cu(bppy)\}_2(\mu\text{-bimpydz})][NO_3]_4\cdot 4H_2O$ **8** was isolated from the corresponding copper(II) nitrate–bppy–bimpydz system. Although it had a different (emerald green) chromophore ($\lambda_{max} \approx 700$ nm), its magnetic properties were similar ($\mu_{eff} = 1.75$ μ_B) to those of the copper(II)–dien complexes. Analytical and IR spectroscopic data for this complex are included in Table 1. Although single crystals were grown and diffraction data collected for this complex, which crystallised in orthorhombic *Abam* space group, it was not possible to solve the structure.

(*iii*) Reaction of copper(II)–dien–diimine systems with $NaNO_2$

The reaction of copper(II)–dien–diimine systems with $NaNO_2$ in MeOH–MeCN (5:1) mixtures produced nitrite-containing complexes from tetrafluoroborate (**2** and **6**) substrates only; chloride (**4**) and nitrate (**1** and **5**) substrates yielded starting materials. The products, $[\{Cu(dien)\}_2(\mu\text{-}4,4'\text{-bipy})][NO_2][BF_4]_3$ **3**, and $[\{Cu(dien)\}_2(\mu\text{-bimpydz})][NO_2][BF_4]_3\cdot 0.5MeCN$ **7**, were initially characterised from analytical and spectroscopic data (Table 1); subsequently, single crystals of **7** suitable for X-ray diffraction structural analysis, were grown from MeOH–MeCN (5:1) by Et_2O vapour diffusion. They had chromophores (royal blue, $\lambda_{max} \approx 620$ nm) and magnetic properties ($\mu_{eff} \approx 1.7$ μ_B) very similar to those of the other copper(II)–dien complexes.

(*iv*) Crystal and molecular structure of complex 5

The structure of $[\{Cu(dien)\}_2(\mu\text{-bimpydz})][NO_3]_4$ **5** is based on the dinuclear cationic unit, $[\{Cu(dien)\}_2(\mu\text{-bimpydz})]^{4+}$ (Fig. 1) with two nitrate anions co-ordinated to each copper atom. The crystallographically independent copper atoms, bridged by a bimpydz molecule with a transoid arrangement of imidazoles, are separated by 13.28 Å; their co-ordination spheres comprise four equatorial nitrogens provided by the bridging (bimpydz) and chelating (dien) ligands and two apical oxygens provided by the co-ordinated nitrates. The Cu–N interatomic distances (Table 2) are typical of sp^2-hydridised nitrogens in equatorial positions. The Cu–O interatomic distances (Table 2) vary from 2.31 to 3.00 Å, reflecting the strength of the co-ordinate interaction. The description of the copper(II) co-

Table 2 Interatomic distances (Å) and angles (°) in the copper co-ordination spheres of complexes **5** and **7**

Complex **5**			
Cu(1)–N(1)	2.01(1)	Cu(2)–N(6)	2.01(1)
Cu(1)–N(11)	2.01(1)	Cu(2)–N(21)	2.01(1)
Cu(1)–N(14)	2.01(1)	Cu(2)–N(24)	2.00(1)
Cu(1)–N(17)	2.01(1)	Cu(2)–N(27)	2.02(1)
Cu(1)–O(43)	2.43(1)	Cu(2)–O(41$^{\text{II}}$)	2.31(1)
Cu(1)–O(51$^{\text{I}}$)	2.69(1)	Cu(2)–O(52)	3.00(1)
N(1)–Cu(1)–N(11)	95.0(4)	N(6)–Cu(2)–N(21)	94.3(4)
N(1)–Cu(1)–N(14)	176.5(4)	N(6)–Cu(2)–N(24)	174.8(4)
N(1)–Cu(1)–N(17)	95.1(4)	N(6)–Cu(2)–N(27)	95.7(4)
N(11)–Cu(1)–N(14)	83.9(4)	N(21)–Cu(2)–N(24)	84.3(4)
N(11)–Cu(1)–N(17)	164.6(4)	N(21)–Cu(2)–N(27)	163.1(4)
N(14)–Cu(1)–N(17)	85.4(4)	N(24)–Cu(2)–N(27)	84.5(4)
N(1)–Cu(1)–O(43)	97.3(4)	N(6)–Cu(2)–O(41$^{\text{II}}$)	93.0(3)
N(11)–Cu(1)–O(43)	106.8(4)	N(21)–Cu(2)–O(41$^{\text{II}}$)	102.6(3)
N(14)–Cu(1)–O(43)	86.2(4)	N(24)–Cu(2)–O(41$^{\text{II}}$)	92.2(3)
N(17)–Cu(1)–O(43)	83.5(4)	N(27)–Cu(2)–O(41$^{\text{II}}$)	90.4(3)
N(1)–Cu(1)–O(51$^{\text{I}}$)	86.1(4)	N(6)–Cu(2)–O(52)	85.2(3)
N(11)–Cu(1)–O(51$^{\text{I}}$)	83.5(4)	N(21)–Cu(2)–O(52)	75.8(3)
N(14)–Cu(1)–O(51$^{\text{I}}$)	90.5(4)	N(24)–Cu(2)–O(52)	89.7(3)
N(17)–Cu(1)–O(51$^{\text{I}}$)	85.5(4)	N(27)–Cu(2)–O(52)	91.5(3)
Complex **7**			
Cu(1)–N(1)	1.982(8)	Cu(1)–N(17)	2.001(8)
Cu(1)–N(11)	2.005(8)	Cu(1)–N(21)	2.484(15)
Cu(1)–N(14)	1.989(9)	Cu(1)–O(22$^{\text{III}}$)	2.328(16)
N(1)–Cu(1)–N(11)	94.6(4)	N(11)–Cu(1)–N(21)	91.6(4)
N(1)–Cu(1)–N(14)	176.4(4)	N(14)–Cu(1)–N(21)	87.7(3)
N(1)–Cu(1)–N(17)	94.9(4)	N(17)–Cu(1)–N(21)	104.2(4)
N(11)–Cu(1)–N(14)	85.4(4)	N(1)–Cu(1)–O(22$^{\text{III}}$)	93.8(4)
N(11)–Cu(1)–N(17)	160.7(4)	N(11)–Cu(1)–O(22$^{\text{III}}$)	110.2(5)
N(14)–Cu(1)–N(17)	84.1(4)	N(14)–Cu(1)–O(22$^{\text{III}}$)	89.6(5)
N(1)–Cu(1)–N(21)	95.9(3)	N(17)–Cu(1)–O(22$^{\text{III}}$)	86.0(5)

Symmetry relationships: I $2 - x, 1 - y, 1 - z$; II $2 - x, -y, 1 - z$; III $2 - x, y, 1.5 - z$.

ordination geometries is subjective; they may be considered to be either square-based pyramidal or tetragonally elongated distorted octahedral. The nitrate anions bridge dications to build 'ladder type' one-dimensional chains, which lie along the *b* axis (Fig. 1). One nitrate anion [N(41)O_3^-] binds strongly [Cu(1)–O(43) 2.43, Cu(2)–O(41) 2.31 Å], the other [N(51)O_3^-] binds weakly [Cu(1)–O(51) 2.69, Cu(2)–O(52) 3.00 Å]. The more effective ligation by N(41)O_3^- is confirmed by the fact that the copper atoms lie slightly above the mean basal planes generated by the four equatorial nitrogens [0.13 Å for Cu(1); 0.16 Å for Cu(2)] and by the nitrate bridged Cu ··· Cu interatomic distances [6.23 Å through N(41)O_3^- and 6.69 Å through N(51)O_3^-]. The other two nitrate anions [N(61)O_3^-, N(71)O_3^-] are unco-ordinated. They are held in position by hydrogen-bonding interactions to the dien ligands; full details are given in Table 3. The N–O interatomic distances [1.22(1)–1.28(1) Å] and angles [119.1(10)–120.5(10)°] within the anions are not influenced by either co-ordination or hydrogen-bonding interactions.

A very similar arrangement is found in the centrosymmetric structure of [{Cu(dien)}$_2$(μ-4,4′-bipy)][ClO_4]$_4$,[3] in which the dinuclear cations are bridged by two symmetry related perchlorate anions [Cu–O 2.66, 2.88 Å]; the other, crystallographically independent perchlorate anion is non-co-ordinated.

The bimpydz bridge is not planar, the dihedral angles between the pyridazine and imidazole rings being 24.5 and 18.6°. Similarly, the co-ordinating imidazole rings do not lie in the same plane as the mean basal planes, the dihedral angles being 48.7 [Cu(1)] and 71.2° [Cu(2)]. The overall twist in the dinuclear cation is given by the dihedral angle (43.1°) between the two basal planes. The structure thus differs from that of [{Cu(dien)}$_2$(μ-4,4′-bipy)][ClO_4]$_4$,[3] in which coplanarity of the 4,4′-bipy aromatic rings is imposed by the inversion centre, although the dihedral angle between the mean basal plane and the 4,4′-bipy bridge is similar at 56.4°. The interatomic distances and angles in the bimpydz and dien ligands are unremarkable.

(*v*) Crystal and molecular structure of complex 7

The structure of [{Cu(dien)}$_2$(μ-bimpydz)][NO_2][BF_4]$_3$·0.5MeCN **7** comprises dinuclear cationic units, [{Cu(dien)}$_2$(μ-bimpydz)]$^{4+}$ bridged by μ-nitrito-κ*O*:κ*N* moieties to form a one-dimensional chain (Fig. 2), non-co-ordinated tetrafluoroborate anions and acetonitrile molecules. Both the bimpydz ligands and the nitrite anions straddle two-fold axes of symmetry giving a helical geometry to the chains, which lie along the *a* axis. The tetrafluoroborate anions, one in a general position [B(1)F_4^-], the other on a two-fold axis of symmetry [B(2)F_4^-], are located by hydrogen-bonding interactions with the dien amino groups (Table 3), both inside and outside the helix. Their geometries are unremarkable. The acetonitrile molecules, which are somewhat disordered, lie along a two-fold axis of symmetry.

The two copper atoms of the dinuclear cation (Fig. 3) are symmetry related by a two-fold rotation axis, which dictates the cisoid arrangement of the imidazoles (Cu ··· Cu 12.88 Å) of the bridging bimpydz molecules; their square-pyramidal co-ordination spheres comprise four equatorial nitrogens provided by the bimpydz and dien ligands and a single apical atom provided by the co-ordinated nitrite. This location for the anion is novel, nitrite binding by copper(II) normally involving one short interaction to an equatorial co-ordination site.[28]

Since the nitrite anion straddles a two-fold axis of symmetry, it is disordered among two equally populated sites giving either N- or O-ligation to the copper(II) atom (Fig. 3). The nitrite bridging mode, involving metal co-ordination to the *syn* oxygen lone pair (Fig. 3), instead of the more normal *anti* oxygen lone pair,[28,29] is unusual for copper(II). It has been noted previously for copper(I) in [{Cu(Pr^i_3[9]aneN_3)}$_2$(NO_2)][PF_6], (Pr^i_3[9]aneN_3 = 1,4,7-triisopropyl-1,4,7-triazacyclononane)[30] for cobalt(II) in [Co(NO)$_2$(NO_2)][31] and for nickel in [{Ni(en)}$_2$(NO_2)]X_3 (X = ClO_4[32] or BF_4[33]). Structural details for the μ-nitrito-κ*O*:κ*N* moieties in the five complexes are compared in Table 4. The most significant difference lies in the M–O and M–N interatomic distances, those for copper(II) being greatest. These extended axial bonds, which result from the copper(II) d^9 electronic configuration, give a relatively long Cu ··· Cu separation (5.55 Å). The weak copper–nitrite binding is probably responsible for the minimal change in ν_{asym}(ONO) from that for free nitrite (Table 1).[27]

The bimpydz bridge is not planar, the dihedral angle between the pyridazine and imidazole rings being 10.1°. Similarly, the co-ordinating imidazole ring does not lie in the same plane as the mean basal plane, the dihedral angle being 77.3°. The overall twist in the dinuclear cation is given by the dihedral angle (81.0°) between the two basal planes. The interatomic distances in the bimpydz and dien molecules are similar to those in complex **5** and hence are unremarkable.

Conclusion

Dinuclear copper(II) cations bridged by bimpydz have similar Cu ··· Cu separations to that in the nitrite reductase isolated from *A. cycloclastes* (12.5 Å).[1] They differ, however, with the bimpydz conformation; the transoid and cisoid arrangements of the imidazole rings in complexes **5** and **7** lead to separations of 13.28 and 12.88 Å, respectively. The dications are not discrete; anions co-ordinate in axial positions to the copper(II) co-ordination sphere to form polymeric structures. In **5**, bridging nitrate anions give a chain structure with ladder motif; in **7**, bridging nitrite anions give a chain with a helical structure.

Table 3 Hydrogen-bonding interactions in complexes **5** and **7**

Interaction N–H ··· X	Symmetry of X	r(N–X)/Å	r(H ··· X)/Å	N–H ··· X/°
Complex **5**				
N(11)–H(111) ··· O(61)	$2-x, 1-y, 1-z$	2.88(2)	2.18	125.4
N(11)–H(112) ··· O(62)	$2-x, 1-y, 1-z$	3.06(2)	2.25	136.5
N(14)–H(141) ··· O(61)	$1-x, 1-y, 1-z$	2.91(2)	1.93	169.0
N(17)–H(171) ··· O(52)	$2-x, 1-y, 1-z$	3.04(1)	2.10	156.1
N(17)–H(172) ··· O(72)	$1-x, 1-y, 1-z$	3.17(1)	2.34	139.7
N(21)–H(211) ··· O(53)	x, y, z	2.96(1)	1.99	162.8
N(21)–H(212) ··· O(42)	$2-x, -y, 1-z$	2.91(1)	2.22	125.5
N(24)–H(241) ··· O(62)	$1+x, -1+y, z$	3.20(1)	2.26	156.1
N(24)–H(241) ··· O(63)	$1+x, -1+y, z$	3.08(1)	2.31	133.3
N(27)–H(271) ··· O(71)	$1+x, y, z$	3.17(1)	2.24	154.3
N(27)–H(271) ··· O(73)	$1+x, y, z$	3.23(1)	2.38	142.9
N(27)–H(272) ··· N(4)	$3-x, -y, 1-z$	3.23(1)	2.23	171.9
Complex **7**				
N(11)–H(111) ··· F(12)	$-0.5+x, y, 1-z$	3.035(12)	2.15	146.9
N(11)–H(112) ··· F(13)	x, y, z	3.124(11)	2.24	146.5
N(17)–H(171) ··· N(3)	$-0.5+x, y, 1-z$	3.213(12)	2.27	156.7
N(17)–H(172) ··· F(21)	$2-x, y, 1.5-z$	2.985(10)	2.00	169.3

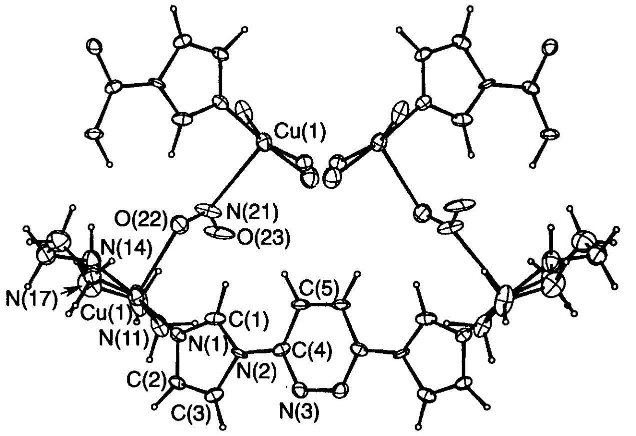


Fig. 2 Projection of the structure of **7** onto the xz plane showing the linking of the $[\{Cu(dien)\}_2(\mu\text{-bimpydz})]^{4+}$ dinuclear cations by the nitrite anions to build chains, parallel to the a axis (BF_4^- anions and the carbon backbones of some dien molecules are omitted for clarity)

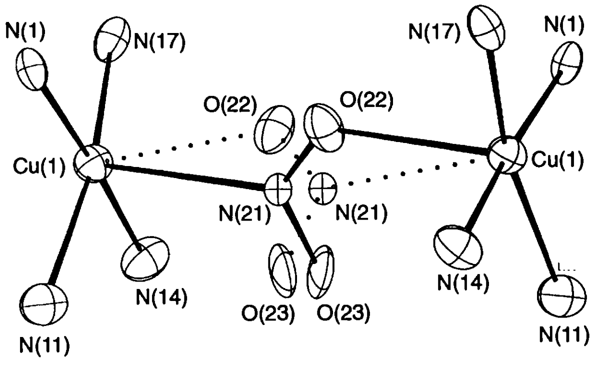


Fig. 3 Detail of the structure of **7** showing the geometry and disorder of the μ-nitrito-κO:κN bridge

Compound **7** is the first example of a dinuclear copper(II) complex with N-donor supporting ligands to contain co-ordinated nitrite. The bridging nitrite adopts a μ-nitrito-κO:κN mode with copper co-ordination to the *syn* oxygen lone pair. This arrangement is very unusual. Nitrite normally adopts a bidentate chelating mode[34] or less frequently a nitrito[35,36] or nitro[36,37] mode. Bridging nitrite is very rare, and previously has exclusively involved copper co-ordination to the *anti* oxygen lone pair.[27,28] The novel co-ordination mode in **7** may be due to the fact that the nitrite is located in a weakly binding copper(II) co-ordination site, the strongly binding equatorial positions being occupied by the dien and bimpydz nitrogens. In all other copper(II)–nitrites with supporting N-donor ligands,[34–37] the copper(II)–nitrite interaction involves a short Cu–O or Cu–N contact.

The failure to generate dicopper(II) complexes with bidentate terminal N-donor ligands (Type A) is attributed to the stability of the bis(chelate) structures of $[CuL_2(FBF_3)_2]$ (L = en[23] or 2,2′-bipy[24]). The weakly co-ordinating tetrafluoroborate anion seems to be an ideal ligand for the weakly binding axial site of the tetragonally elongated ($d_{z^2}{}^2\, d_{x^2-y^2}{}^1$) copper(II) octahedral co-ordination sphere.[38] Conversely, the formation of the corresponding complexes with tridentate terminal N-donor ligands (Type B) is attributed to the much lower stability of the $[CuL_2]^{2+}$ (L = dien) cation[39] in which the *mer* chelating ligands dictate the very rare tetragonally squashed ($d_{x^2-y^2}{}^2\, d_{z^2}{}^1$) copper(II) co-ordination sphere with four weakly binding equatorial sites and two strongly binding axial sites.

Experimental

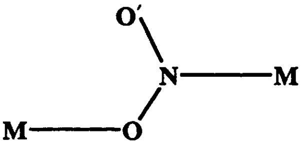
All 4,4′-bipy and bimpydz containing complexes were characterised using elemental analyses, infrared and UV/VIS spectroscopy, mass spectrometry and magnetic measurements; pertinent data are collated in Table 1. Carbon, nitrogen and hydrogen analyses (microanalysis) and copper analyses (atomic absorption spectroscopy) were carried out in the University of Nottingham Chemistry Department by Mr. T. J. Spencer and Mr. M. Guyler, respectively. Infrared spectra were obtained as KBr pressed pellets on either a Perkin-Elmer PE983G or PE 1600 series FTIR spectrophotometer, UV/VIS spectra on either a Perkin-Elmer Lambda 5 or Unicam UV2-100 spectrometer, mass spectra on a Vacuum Generators VG 70E micromass spectrometer and NMR spectra in $CDCl_3$ on a Bruker 250 MHz spectrometer (reference $CHCl_3$).

Acetonitrile, CH_2Cl_2 and toluene were distilled from CaH_2 prior to use.[40] Dimethylformamide was dried over freshly regenerated Linde type 4 Å molecular sieve before distillation under reduced pressure.[40]

Copper(II) salts [$CuCl_2{\cdot}2H_2O$, $Cu(BF_4)_2{\cdot}xH_2O$, $Cu(NO_3)_2{\cdot}3H_2O$] and $NaNO_2$ were obtained from Aldrich Chemical Company Ltd. and recrystallised from deionised water prior to use. The multidentate N-donors, en, 2,2′-bipy, dien and 4,4′-bipy, were obtained from Aldrich Chemical Company Ltd. and used without further purification.

The compound bimpydz was prepared as described previously.[2] The analogous compound biimpydz was prepared similarly from potassium (1.98 g, 50.6 mmol), 2-isopropylimid-

Table 4 Structural features of the μ-nitrito-κ*N*:κ*O* bridges in [{Cu(dien)}$_2$(μ-bimpydz)(NO$_2$)][BF$_4$]$_3$·0.5MeCN,[a] [{Cu(Pr$^i_3$[9]aneN$_3$)}$_2$(NO$_2$)]-[PF$_6$],[b] [{Co(NO)}$_2$(NO$_2$)],[c] [{Ni(en)}$_2$(NO$_2$)][ClO$_4$]$_3$[d] and [{Ni(en)}$_2$(NO$_2$)][BF$_4$]$_3$[e]



M	M–N/Å	M–O/Å	N–O/Å	N–O′/Å	O–N–O′/°	M–O–N/°	M–N–O/°	M–N–O′/°
Cu^{II}[a]	2.484(15)	2.328(16)	1.171(13)	1.266(12)	120.8(9)	122.8(11)	130.4(11)	108.8(11)
Cu^{I}[b]	1.899(2)	1.968(2)	1.279(3)	1.235(3)	116.0(2)	117.7(7)	119.8(2)	124.1(2)
Co^{I}[c]	1.98	2.15	1.08	1.23	110	—	—	—
Ni^{II}[d]	2.172(6)	2.184(6)	1.247(8)	1.268(8)	111.8(5)	—	120.7(5)	127.5(4)
Ni^{II}[e]	2.16(2)	2.22(2)	1.28(3)	1.22(3)	112(2)	—	—	—

[a] Present work. [b] Ref. 30. [c] Ref. 31. [d] Ref. 32. [e] Ref. 33.

azole (5.95 g, 54.0 mmol) and 3,6-dichloropyridazine (4.00 g, 26.8 mmol). Yield 2.56 g, 8.6 mmol, 34% [Found (Calc. for $C_{16}H_{20}N_6$): C, 64.85 (64.85); H, 6.80 (6.80); N, 28.25 (28.35%)]. M.p. 126–128 °C. Electron impact mass spectrum: *m*/*z* 296 [biimpydz]$^+$. IR: 3120m, 3027m, 1598s, 1498s, 1431m, 1313s, 1158w, 1035s and 837s cm^{-1}.

The tridentate chelate, bppy, was prepared by a variation of the method described by Jameson and Goldsby.[41] A solution of pyrazole (3.00 g, 44.1 mmol) in dry dmf (40 cm^3) was added to a stirred suspension of NaH (60% in oil, 1.76 g, 44.0 mmol) in dry dmf (30 cm^3) under nitrogen. The resultant yellow solution was stirred for 60 min before addition of a solution of 2,6-dichloropyridine (3.24 g, 21.9 mmol) in dmf (30 cm^3). After refluxing for 72 h, the mixture was added to iced water to yield a white precipitate, which was isolated by vacuum filtration and recrystallised from EtOH. Yield 3.0 g, 14.2 mmol, 65% [Found (Calc. for $C_{11}H_9N_5$): C, 61.95 (62.55); H, 4.55 (4.30); N, 33.85 (33.15%)]. M.p. 126–128 °C. Electron impact mass spectrum: *m*/*z* 211 [bppy]$^+$, 144 [bppy − ($C_3H_3N_2$)]$^+$, 77 [bppy − 2($C_3H_3N_2$)]$^+$ and 67 [$C_3H_3N_2$]$^+$. IR: 2919m, 1607s, 1482s, 1392m, 1036s and 760m cm^{-1}. ^{1}H NMR: δ 8.56 (dd, 2 H), 7.96–7.81 (m, 3 H), 7.44 (dd, 2 H) and 6.48 (dd, 2 H).

Preparation of complexes

[{Cu(dien)}$_2$(μ-4,4′-bipy)][NO$_3$]$_4$·2H$_2$O 1. A dmf solution (40 cm^3) of 4,4′-bipy (1.03 g, 6.6 mmol) was added to an aqueous solution (60 cm^3) of Cu(NO$_3$)$_2$·3H$_2$O (3.13 g, 13.0 mmol) followed by an aqueous solution (40 cm^3) of dien (1.36 g; 13.0 mmol). After heating for 30 min, solvent was removed under reduced pressure, yielding a royal blue powder, which was recrystallised from aqueous ethanol. Yield 3.52 g, 4.6 mmol, 69%.

[{Cu(dien)}$_2$(μ-4,4′-bipy)][BF$_4$]$_4$·4MeCN 2. This complex was prepared as for **1**, using Cu(BF$_4$)$_2$·*x*H$_2$O [1.91 g, 6.4 mmol (*x* ≈ 3.4 by copper analysis)] in place of Cu(NO$_3$)$_2$·3H$_2$O together with dien (0.66 g, 6.4 mmol) and 4,4′-bipy (0.50 g, 3.2 mmol). Reduction of solvent volume gave a blue oil which was treated with methanol–ethanol (40 cm^3) and sonicated. An extremely hygroscopic solid formed, which was recovered by filtration. Recrystallisation from MeCN by addition of toluene gave a bright blue solid, which was washed several times with Et$_2$O. Yield 1.76 g, 1.76 mmol, 55%.

Attempted preparation of [{Cu(dien)}$_2$(μ-4,4′-bipy)]Cl$_4$; formation of [CuCl$_2$(dien)]. This reaction was carried out as for the preparation of **1**, using CuCl$_2$·2H$_2$O (2.45 g, 13 mmol) in place of Cu(NO$_3$)$_2$·3H$_2$O. Yield 2.19 g, 9.22 mmol, 71% [Found (Calc. for $C_4H_{13}Cl_2CuN_3$): C, 20.60 (20.20); H, 5.85 (5.50); Cu, 25.50 (26.75); N, 18.05 (17.70%)]. FAB mass spectrum: *m*/*z* 201 [CuCl(dien)]$^+$ and 166 [Cu(dien)]$^+$. IR: 3237s, 2941m, 1587s, 1085s, 1033m and 816m cm^{-1}.

[{Cu(dien)}$_2$(μ-bimpydz)]Cl$_4$·4H$_2$O 4. A dmf solution (25 cm^3) of bimpydz (0.70 g, 3.3 mmol) was added to an aqueous solution (40 cm^3) of CuCl$_2$·2H$_2$O (1.24 g, 6.6 mmol) followed by an aqueous solution (25 cm^3) of dien (0.68 g, 6.6 mmol). After heating for 30 min, solvent was removed under reduced pressure, yielding a royal blue powder, which was recrystallised from aqueous ethanol. Yield 1.31 g, 1.72 mmol, 52%.

[{Cu(dien)}$_2$(μ-bimpydz)][NO$_3$]$_4$ 5. This complex was prepared as for **4**, using Cu(NO$_3$)$_2$·3H$_2$O (1.59 g, 6.6 mmol) in place of CuCl$_2$·2H$_2$O. Yield 1.61 g, 2.0 mmol, 61%. Vapour phase diffusion of Et$_2$O into a dmf–water (95 : 5) solution of the product gave crystals suitable for X-ray structural analysis. FAB mass spectrum: *m*/*z* 275 [Cu(bimpydz)]$^+$, 228 [Cu(dien)(NO$_3$)]$^+$ and 166 [Cu(dien)]$^+$.

[{Cu(dien)}$_2$(μ-bimpydz)][BF$_4$]$_4$·4MeCN 6. This complex was prepared as for **4**, using Cu(BF$_4$)$_2$·*x*H$_2$O [1.98 g, 6.6 mmol (*x* ≈ 3.4 by copper analysis)] in place of CuCl$_2$·2H$_2$O. Reduction of solvent volume gave a royal blue gum which was treated with methanol–ethanol (40 cm^3) and sonicated. An extremely hygroscopic solid formed, which was recovered by filtration. Recrystallisation from MeCN by addition of toluene gave a royal blue powder, which was washed several times with Et$_2$O. Yield 1.57 g, 1.49 mmol, 45% yield.

[{Cu(bppy)}$_2$(μ-bimpydz)][NO$_3$]$_4$·4H$_2$O 8. A dmf solution (25 cm^3) of bimpydz (1.00 g, 4.7 mmol) was added to an aqueous solution (40 cm^3) of Cu(NO$_3$)$_2$·3H$_2$O (2.25 g, 9.3 mmol) followed by an aqueous solution (25 cm^3) of bppy (2.0 g, 9.5 mmol). After heating for 60 min solvent was removed under reduced pressure and EtOH added yielding an emerald green powder, which was recrystallised from aqueous EtOH. Yield 2.76 g, 2.71 mmol, 58%. Vapour phase diffusion of Et$_2$O into a dmf–water (95 : 5) solution of the product gave crystals suitable for X-ray structural analysis. FAB mass spectrum: *m*/*z* 274 [Cu(bppy)]$^+$.

Reactions of NaNO$_2$

With complex 2; formation of [{Cu(dien)}$_2$(μ-4,4′-bipy)]-[NO$_2$][BF$_4$]$_3$ 3. Solid NaNO$_2$ (0.13 g, 1.88 mmol) was added to a stirring solution of complex **2** (1.0 g, 1.0 mmol) in MeOH–MeCN (5 : 1, 50 cm^3). After 16 h a royal blue precipitate was recovered by filtration and recrystallised by addition of Et$_2$O to a saturated MeCN solution. Yield 0.36 g, 0.45 mmol, 45%.

With complex 6; formation of [{Cu(dien)}$_2$(μ-bimpydz)]-[NO$_2$][BF$_4$]$_3$·0.5MeCN 7. This reaction was carried out as above using **6** (1.0 g, 0.95 mmol) in place of **2**. Yield 0.36 g, 0.45 mmol, 43%. Vapour phase diffusion of Et$_2$O into a MeCN

Table 5 Data collection parameters for complexes **5** and **7**

	5	**7**
Formula	$C_{18}H_{34}Cu_2N_{16}O_{12}$	$C_{18}H_{34}B_3Cu_2F_{12}N_{13}O_2{\cdot}0.5CH_3CN$
M	793.66	872.59
Crystal system	Triclinic	Orthorhombic
Space group	$P\bar{1}$ (no. 2)	*Ccca* (no. 68)
a/Å	7.594(3)	13.987(7)
b/Å	12.684(4)	29.324(20)
c/Å	16.801(4)	17.419(8)
α/°	83.45(5)	
β/°	84.28(5)	
γ/°	81.71(5)	
Z	2	8
U/Å^3	1585.2	7144.5
μ_{calc}/cm^{-1}	14.24	12.74
D_c/g cm^{-3}	1.663	1.623
D_m/g cm^{-3}	1.67	1.59
$F(000)$	816	3528
Crystal dimensions/mm	0.23 × 0.2 × 0.07	0.18 × 0.14 × 0.12
Radiation (λ/Å)	Mo-Kα (0.710 73)	Mo-Kα (0.710 73)
hkl Ranges	−8 to 8, −14 to 14, 0–18	0–15, 0–34, 0–18
Reflections collected	6566	13 179
Independent reflections	4330 (R_{int} 0.0554)	4667 (R_{int} 0.0785)
Refinement method (full-matrix least squares on)	F^2	F^2
Absorption correction factors; minimum, maximum	0.898, 1.079	—
ρ_{min}, ρ_{max}	−0.549, 1.471	−3.551, 2.534
$(\Delta/\sigma)_{max}$	0.119	0.076
Final R, $wR2$	0.092, 0.191	0.169, 0.257
Conventional final R, $wR2$*	0.055, 0.131	0.059, 0.131

* $I > 2\sigma(I)$ for both **5** (2405 reflections) and **7** (1081 reflections).

solution of the product gave crystals suitable for X-ray structure data collection. FAB mass spectrum: m/z 166 $[Cu(dien)]^+$.

With complexes 1, 4 and 5. These reactions were carried out as above using **1** (1.0 g, 1.29 mmol), **4** (1.0 g, 1.31 mmol) or **5** (1.0 g, 1.20 mmol) in place of **2**. In all three experiments, a 2 : 1 molar ratio of $NaNO_2$ to substrate was used; nonetheless, the recovered product comprised starting material only.

Crystallography

Oscillation and Weissenberg photographs revealed preliminary cell parameters for selected crystals of **5** (triclinic), **7** and **8** (both orthorhombic) mounted in Lindemann tubes under dry nitrogen. X-Ray diffraction data for the refinement of cell parameters and structure determination were collected at 150 K using a Delft Instruments FAST TV area detector situated at the window of a rotating molybdenum anode generator operating at 50 kV, 55 mA (for **5** and **7**)[42] or at 298 K using a Hilger and Watts Y290 four-circle diffractometer (for **7** and **8**). Details of the 150 K data collection and structure solution for **5** and **7** are collated in Table 5. For **8**, the diffraction data set confirmed orthorhombic cell parameters [a = 13.898(3), b = 13.917(3), c = 27.676(5) Å, U = 5353 Å^3], and indicated space group *Abam* but could not be solved, despite many attempts using both heavy atom and diverse direct method programs.

For **5**, somewhat more than one hemisphere of data was collected at 150 K; 6566 reflections were recorded giving 4330 unique reflections. The data were corrected for Lorentz and polarisation effects and also for absorption effects (DIFABS[43]). The structure was solved by direct methods (SIR 92[44]) and refined (CRYSTALS[45]) by full-matrix least squares against F^2 to final R and $wR2$ indices (unit weights) of 0.092 and 0.191 [R = 0.055, $wR2$ = 0.131 for 2405 reflections with $I > 2\sigma(I)$] in space group $P\bar{1}$. All atoms except hydrogen were anisotropic. The hydrogen atoms were placed and allowed to 'ride' on their parent atoms in the calculated position (X–H 1.00 Å; U_{iso} 0.05 Å^2).

For **7**, data were collected at both 298 and 150 K. The 150 K data set was collected to confirm the novel co-ordination geometry of the disordered nitrite bridging anion in view of the high R values of the 298 K data set solution {full least-squares matrix refinement (CRYSTALS[45]) against F values [912 data with $I > 3\sigma(I)$] with three-parameter Chebyshev weighting scheme converged to R = 0.098 and R' = 0.114 for 199 parameters (dien carbon and nitrogen, nitrite nitrogen and oxygen, copper and fluorine atoms anisotropic, bimpydz carbon and nitrogen and boron atoms isotropic, hydrogen atoms placed) in space group *Ccca*}. The 150 K solution was essentially the same as that at 298 K, but with much lower thermal displacement parameters, standard deviations and R indices. Somewhat more than one hemisphere of data was collected at 150 K; 13179 reflections were recorded giving 4667 unique reflections. The data, which were quite weak, were corrected for Lorentz and polarisation effects but not for absorption effects. The structure was solved by direct methods (SIR 92[44]) and refined (CRYSTALS[45]) by full-matrix least squares against F^2 to final R and $wR2$ indices (unit weights) of 0.169 and 0.257 [R = 0.059, $wR2$ = 0.131 for 1081 reflections with $I > 2\sigma(I)$] in space group *Ccca*. All atoms except hydrogen were anisotropic. The hydrogen atoms were placed and allowed to 'ride' on their parent atoms in the calculated position (X–H 1.00 Å; U_{iso} 0.05 Å^2).

The nitrite anion was disordered about a two-fold axis with equal occupancies of the two sites. The acetonitrile molecule was located on a two-fold axis with the methyl group carbon close to an intersection with a second two-fold axis. The resultant disorder gave 50% site occupancy of the special sites, chemical site occupancy 0.25. Its position was not refined.

Atomic coordinates, thermal parameters, and bond lengths and angles have been deposited at the Cambridge Crystallographic Data Centre (CCDC). See Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1996, Issue 1. Any request to the CCDC for this material should quote the full literature citation and the reference number 186/239.

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