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# Oxidation of the pyrazine(pyz)-bridged polymeric copper(I) cation $[Cu(cnge)(MeCN)(pyz)]^+$ by $NOBF_4$ and formation of the corresponding copper(II) cation $[Cu(MeCN)_4(pyz)]^{2+}$ (cnge = 2-cyanoguanidine)

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The complex $[Cu(cnge)(MeCN)(pyz)]BF_4{\cdot}0.5pyz$ **1** (pyz = pyrazine, cnge = 2-cyanoguanidine) resulted from treatment of $[Cu(MeCN)_4]BF_4$ with mixtures of pyz and cnge in MeCN. Oxidation of compound **1** with $NOBF_4$ in $CH_2Cl_2$ yielded $Cu(pyz)(cnge)(BF_4)_2$ **2**. Recrystallisation from MeCN resulted in loss of cnge and formation of $[Cu(MeCN)_4(pyz)][BF_4]_2$ **3**. Reaction of **1** with $NBu^t_4NO_2$ in MeCN led to $Cu(pyz)(cnge)(MeCN)(NO_2)_2$ **4**. Single-crystal X-ray structural analysis has shown compound **1** to contain a one-dimensional zigzag cationic chain based on four-co-ordinate tetrahedral copper(I); each metal atom is ligated by two bridging pyz molecules and terminal MeCN and cnge molecules. The unco-ordinated pyz molecule, which is located at an inversion centre, connects parallel copper(I) chains *via* N • • • H–N bonds involving the amino moieties of ligating cnge molecules. The crystal structure of compound **3** contains a one-dimensional linear cationic chain based on six-co-ordinate copper(II), the tetragonally distorted octahedral co-ordination geometry of which comprises two bridging pyz molecules (equatorial) and four terminal MeCN molecules (two equatorial, two axial).

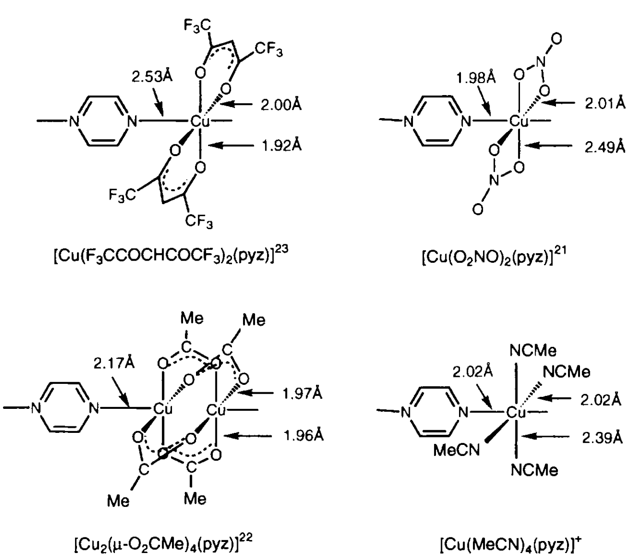
In a recent paper[1] we described the synthesis, characterisation and chemistry of a series of discrete dinuclear cationic complexes containing two co-ordinatively unsaturated copper(I) centres bridged by the diimines 4,4′-bipyridine (4,4′-bipy) or 1,2-bis(4′-pyridyl)ethene (bpe) and stabilised by 2-cyanoguanidine (cnge),[2–4] *viz.* $[\{Cu(cnge)_2\}_2(\mu\text{-diimine})]^{2+}$. In this paper we report the results of our studies of the corresponding pyrazine (pyz)-containing systems which led to structural characterisation of a polymeric four-co-ordinate copper(I) product $[Cu(cnge)(MeCN)(pyz)]BF_4{\cdot}0.5pyz$ and a polymeric six-co-ordinate copper(II) product $[Cu(MeCN)_4(pyz)][BF_4]_2$.

Although known for many years,[5] copper(I)–pyz and -substituted pyz complexes have been little studied[6] and structural investigations of them are all of recent origin.[7–13] A diversity of structural types has been observed, including one-dimensional chains,[7–10] two-dimensional sheets[10–12] and three-dimensional matrices.[13] Kitagawa *et al.*[12] have considered the role of the pyz derivatives in building polymeric structures; increasing substitution leads to higher co-ordination numbers and more condensed structures. Very recent work on copper(I)–phenazine complexes[14] has resulted in the formation of mono- and di-nuclear and one-dimensional infinite-chain complexes.

Simple one-dimensional polymers similar to that described here are extremely rare with unsubstituted pyz. They are typified by $[\{Cu(pyz)(OSO_2CF_3)(\mu\text{-pyz})\}_n]$[7] in which $Cu(pyz)(OSO_2CF_3)$ moieties are linked by bridging pyz molecules giving a zigzag chain based on four-co-ordinate tetrahedral copper(I); the terminal pyz and $OSO_2CF_3^-$ ligands are arranged syndiotactically along the polymer chain.

Many pyz-bridged copper(II) complexes have been structurally characterised owing to their interesting magnetic properties.[15–20] The majority have infinite-chain structures[18,19,21–23] but some have sheet structures.[20] There are several instances within the literature where substituted pyrazines promote the formation of mononuclear complexes.[24–26] Similarly, the use of multidentate terminal ligands (*e.g.* diethylenetriamine) to generate dinuclear complexes has been described.[23,27,28]

Previously characterised linear copper(II)–pyz polymers, similar to that described here, fall into three groups (Scheme 1).



$[Cu(F_3CCOCHCOCF_3)_2(pyz)]$[23] $[Cu(O_2NO)_2(pyz)]$[21]

$[Cu_2(\mu\text{-}O_2CMe)_4(pyz)]$[22] $[Cu(MeCN)_4(pyz)]^+$

**Scheme 1**

Two are exemplified by $[Cu(O_2NO)_2(\mu\text{-pyz})]$[21] and $[Cu(F_3CCOCHCOCF_3)_2(\mu\text{-pyz})]$,[23] which comprise $CuX_2$ moieties ($X = O_2NO^-$ or $F_3CCOCHCOCF_3^-$) bridged by pyz molecules. They differ in the location of the pyz ligands in the tetragonally elongated copper(II) $d^9$ co-ordination sphere; they are equatorially positioned in the nitrate and axially in the hexafluoroacetylacetonate (Scheme 1). The third is exemplified by $[Cu_2(\mu\text{-}O_2CMe)_4(\mu\text{-pyz})]$,[22] in which pyz molecules bridge dinuclear $Cu(\mu\text{-}O_2CMe)_4Cu$ moieties, co-ordinating axially (Scheme 1). Pertinent interatomic distances for all three structural types are collated in Scheme 1.

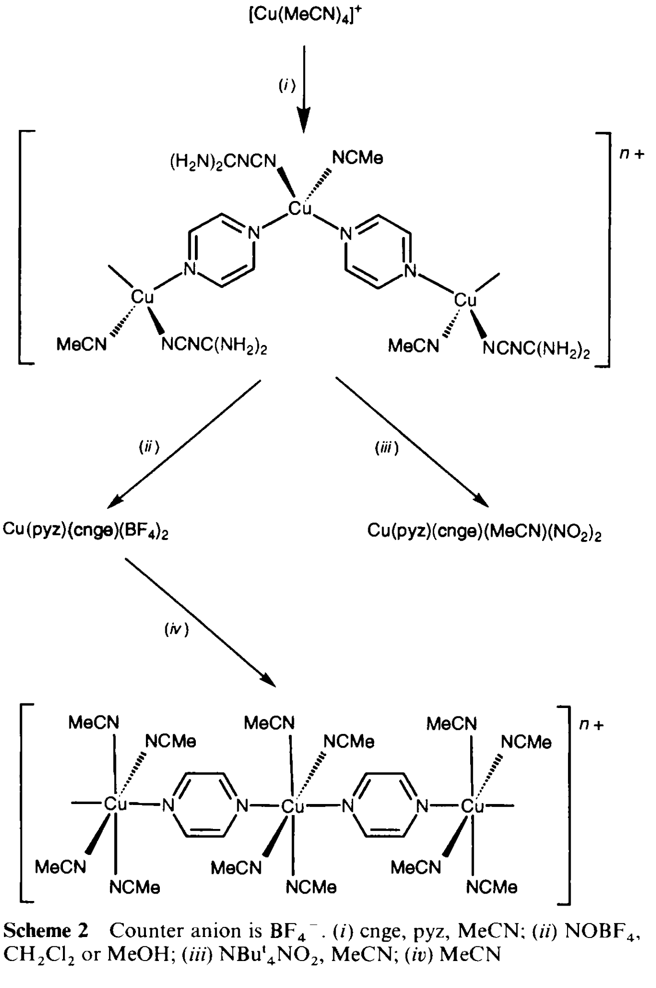
## Results and Discussion

The chemistry of the $[Cu(MeCN)_4]BF_4$–pyz–cnge system in MeCN is summarised in Scheme 2. Orange crystals of $[Cu(cnge)(MeCN)(pyz)]BF_4{\cdot}0.5pyz$ **1** were obtained regardless

**Table 1** Analytical and IR spectral data for $[Cu(cnge)(MeCN)(pyz)]BF_4{\cdot}0.5pyz$ **1**, $Cu(pyz)(cnge)(BF_4)_2$ **2**, $[Cu(MeCN)_4(pyz)][BF_4]_2$ **3** and $Cu(pyz)(cnge)(MeCN)(NO_2)_2$ **4**

| | Analysis (%)* | | | | IR spectra/cm$^{-1}$ | | | |
|---|---|---|---|---|---|---|---|---|
| Compound | C | H | N | Cu | cnge | pyz | $BF_4^-$ | $NO_2$ |
| Free ligand | — | — | — | — | 2209, 2165 | 1411.6, 790.4 | 1080–1035 | 1269 |
| **1** | 30.95 (30.35) | 3.20 (3.30) | 28.45 (28.30) | 16.55 (16.05) | 2216, 2166 | 1417, 803 | 1095–1020 | — |
| **2** | 17.45 (17.95) | 2.25 (2.00) | 21.05 (20.95) | — | 2213, 2168 | 1413, 800 | 1080–1035 | — |
| **3** | 29.85 (29.95) | 3.20 (3.35) | 17.25 (17.45) | 13.00 (13.20) | — | 1410, 804 | 1085–1035 | — |
| **4** | 26.55 (26.65) | 3.55 (3.05) | 35.30 (34.95) | 16.90 (17.60) | 2226, 2188 | 1418, 803 | — | 1262 |
| $NBu^t_4BF_4$ | 58.40 (58.35) | 10.90 (11.00) | 4.30 (4.25) | — | | — | 1080–1055 | — |

* Calculated values in parentheses.



**Scheme 2** Counter anion is $BF_4^-$. (*i*) cnge, pyz, MeCN; (*ii*) $NOBF_4$, $CH_2Cl_2$ or MeOH; (*iii*) $NBu^t_4NO_2$, MeCN; (*iv*) MeCN

of the reactant molar ratio. For 2:1:4 molar ratios, rather, than the anticipated pyz analogue of $[\{Cu(cnge)_2\}_2(\mu\text{-}4,4'\text{-}bipy)]^{2+}$,[1] the product comprised compound **1** contaminated with white crystals of the starting material $[Cu(MeCN)_4]BF_4$. Pure samples of **1** could only be obtained by starting with the appropriate molar ratio (2:2:3) as the separation of **1** from $[Cu(MeCN)_4]BF_4$ was very difficult owing to their similar solubilities in non-polar solvents (*e.g.* MeCN, $CH_2Cl_2$). Compound **1** was initially characterised from elemental analysis (Table 1), IR (Table 1) and FAB mass spectrometry. Subsequently, single crystals suitable for structural analysis were grown by diffusion of $Et_2O$ into MeCN solution. Cyclic voltammetry indicated that the complex undergoes irreversible oxidation.

The reaction of compound **1** with $NOBF_4$, carried out under diverse conditions, is summarised in Scheme 2. In $CH_2Cl_2$ at room temperature a pale blue solid was formed immediately on addition of $NOBF_4$. Recrystallisation from MeCN (the only organic solvent in which the blue product was moderately soluble) gave blue crystals of $[Cu(MeCN)_4(pyz)][BF_4]_2$ **3**. In MeOH at low temperature (−78 °C), no reaction occurred on addition of $NOBF_4$. It was only after warming to +5 °C that reaction commenced forming an insoluble blue solid which gave the same product on recrystallisation from MeCN. Compound **3** was initially characterised from elemental analysis, IR and FAB mass spectrometry. Subsequently, single crystals suitable for structural analysis were grown by diffusion of $Et_2O$ into MeCN solution.

Characterisation of the initially formed blue solid is speculative in the absence of structural data. Elemental analysis suggests the formulation $Cu(pyz)(cnge)(BF_4)_2$ **2**. This is supported by IR spectroscopy which indicates the presence of pyz, co-ordinated cnge and isolated $BF_4^-$ anions. Square-planar copper(II) co-ordination can be envisaged if cnge, as well as pyz, acts as a bridging ligand. Several complexes, including $[\{Cd(H_2O)_2\}_2(\mu\text{-}cnge)_2][SO_4]_2$,[29] $[Cu_2(\mu\text{-}X)X(cnge)]$ (X = Cl or Br),[2] $[CuBr(cnge)]$[2] and $[\{Cu(cnge)\}_2(\mu\text{-}cnge)_2][S_2O_6]$,[4] are precedents for bridging cnge but none involves copper(II).[30,31] The $\nu_{asym}(NCN)$ doublet for the co-ordinated cnge in compound **3** shows a small shift ($\approx 5$ cm$^{-1}$) to higher energy relative to that for free cnge. Unfortunately, this small shift is not diagnostic of bridging cnge. Although bridging cnge generally gives rise to smaller shifts than terminal cnge, small shifts have been noted for weakly bound terminal cnge.[4] The broad absorption band at 1085–1035 cm$^{-1}$, attributed to B–F stretching vibrations, has no fine structure consistent with $C_{3v}$ or $C_{2v}$ symmetry.[30] It may be concluded that the $BF_4^-$ anion has $T_d$ symmetry and is not co-ordinated to the copper(II), not even in the weakly binding axial positions of the Jahn–Teller distorted tetragonally elongated octahedral co-ordination geometry.[30]

The reaction of compound **1** with 2 equivalents of $NBu^t_4NO_2$ in MeCN (Scheme 2) gave three products; two solid and one gaseous. The solids were a white powder shown to be $NBu^t_4BF_4$ (Table 1) and a pale blue powder, which was preliminarily characterised on the basis of elemental analysis as $Cu(pyz)(cnge)(MeCN)(NO_2)_2$ **4**, IR spectroscopy confirming the presence of pyz, cnge and $NO_2^-$ and the absence of $BF_4^-$. A more complete analysis was not possible owing to its insolubility in organic solvents. Without structural information, the co-ordination sphere of the copper(II) atom and the mode of co-ordination of the nitrite anion in **4** are difficult to ascertain. However, the IR spectrum is particularly helpful, the large shift ($\approx 20$ cm$^{-1}$) to higher energy of $\nu_{asym}(NCN)$ (Table 1) being indicative of strongly bound terminal cnge[4] and the broad band at 1262 cm$^{-1}$ being attributable to bidentate chelating $NO_2^-$.[32]

## Crystal and molecular structures of complexes 1 and 3

Complex **1** comprises one-dimensional zigzag polymeric cationic chains, *catena*-$[Cu(cnge)(MeCN)(pyz)]^+$, unco-ordinated $BF_4^-$ anions, and separate pyz molecules. The copper

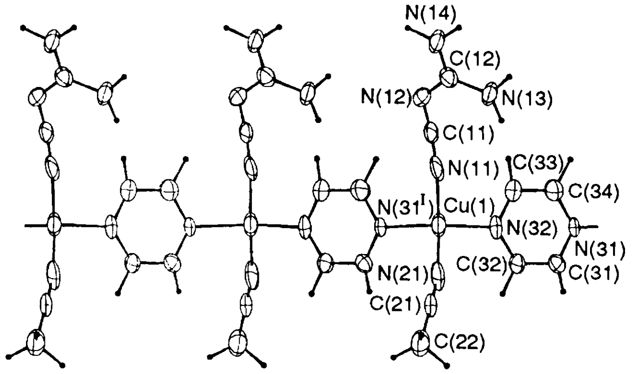


**Fig. 1** Molecular structure of the cationic chain [Cu(cnge)(MeCN)(pyz)]$^+$. Symmetry relation: I $x, \frac{1}{2} - y, -\frac{1}{2} + z$

**Table 2** Interatomic distances (Å) and angles (°) in the copper co-ordination spheres of [{Cu(cnge)(MeCN)}(pyz)]$BF_4$·0.5 pyz **1** and [{Cu(MeCN)$_4$}(pyz)][$BF_4$]$_2$ **3**

| Compound **1** | | Compound **3** | |
|---|---|---|---|
| Cu(1)–N(11) | 1.965(20) | Cu(1)–N(1) | 2.024(6) |
| Cu(1)–N(21) | 1.928(20) | Cu(1)–N(2) | 2.022(6) |
| Cu(1)–N(31$^{I}$) | 2.100(12) | Cu(1)–N(11) | 2.017(6) |
| Cu(1)–N(32) | 2.076(13) | Cu(1)–N(21) | 2.389(6) |
| N(11)–Cu(1)–N(21) | 116.7(7) | N(1)–Cu(1)–N(2) | 180 |
| N(11)–Cu(1)–N(31) | 105.5(6) | N(1)–Cu(1)–N(11) | 90.8(2) |
| N(11)–Cu(1)–N(32) | 109.1(7) | N(1)–Cu(1)–N(21) | 92.1(2) |
| N(21)–Cu(1)–N(31$^{I}$) | 105.7(6) | N(2)–Cu(1)–N(11) | 89.3(2) |
| N(21)–Cu(1)–N(32) | 107.7(7) | N(2)–Cu(1)–N(21) | 87.9(2) |
| N(31$^{I}$)–Cu(1)–N(32) | 112.3(5) | N(11)–Cu(1)–N(21) | 90.0(3) |
| | | N(11)–Cu(1)–N(11$^{II}$) | 178.5(3) |
| | | N(21)–Cu(1)–N(21$^{II}$) | 175.9(3) |

Symmetry relations: I $x, \frac{1}{2} - y, -\frac{1}{2} + z$; II $\frac{1}{2} - x, \frac{1}{2} - y, z$.

atoms in the chain (Fig. 1) are separated by 6.93(1) Å; their four-co-ordinate, tetrahedral, geometry is generated by two bridging pyz molecules, one terminal cnge and one terminal MeCN molecule. The copper–nitrogen interatomic distances (Table 2) vary with the hybridisation of the ligating nitrogen atom, those to the sp$^2$ pyz nitrogen atoms being considerably longer than those to the sp MeCN and cnge nitrogen atoms. Both the bridging pyz and terminal cnge molecules are planar, the maximum deviation from the best-fit least-squares planes being 0.011 [C(34)] and 0.048 Å [N(14)], respectively. The lattice pyz molecule is also planar, the maximum deviation from the best-fit least-squares plane being 0.020 Å [C(41)].

As predicted from the lack of structure associated with the $T_2$ $\nu_3(BF_4^-)$ stretching vibration band, the $BF_4^-$ anions have tetrahedral symmetry and are not co-ordinated to the copper atom. This is not unexpected as co-ordination of $BF_4^-$ to copper(I) is extremely rare.[33] Although non-co-ordinated $BF_4^-$ anions tend to be highly disordered, in this structure they have been precisely located owing to their being hydrogen bonded to the cnge molecules through N–H ··· F interactions. Full details are given in Table 3. This feature is shown in the packing diagram for compound **1** (Fig. 2). Also clear from this diagram is the hydrogen-bonding network which holds the unco-ordinated pyz molecule in the lattice. This molecule, which is located at an inversion centre, links two copper centres in adjacent parallel chains by strong N(13)–H(131) ··· N(41) hydrogen bonds involving the amino moieties of ligating cnge molecules (Table 3). The corresponding copper–copper separation [7.44(1) Å] is somewhat longer than the minimum copper–copper separation [5.21(1) Å] between chains. Interestingly, the interaction between the co-ordinated and non-co-ordinated pyz molecules is minimised by their being stacked in a parallel orientation with a dihedral angle of 0.87° (Fig. 2).

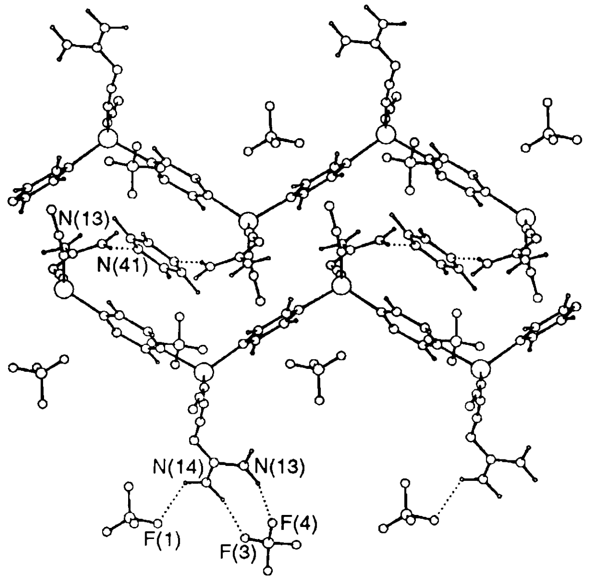


**Fig. 2** View of the crystal structure of [Cu(cnge)(MeCN)(pyz)]$BF_4$·0.5pyz showing the hydrogen-bonding network linking parallel chains through the unco-ordinated pyz molecule

The cationic copper(I)–pyz chain in compound **1** is novel. Similar chains do exist in [Cu(pyz)$_2$(OSO$_2$CF$_3$)][7] and [Cu(dmpyz)$_2$(OSO$_2$CF$_3$)] (dmpyz = 2,5-dimethylpyrazine)[8] but are neutral. Cationic copper(I) chains based on pyz or substituted pyz have been prepared but are more complex. Thus, [Cu$_2$(tmpyz)$_3$]$^{2+}$ (tmpyz = 2,3,5,6-tetramethylpyrazine)[10] comprises Cu(μ-tmpyz)Cu(tmpyz) dinuclear moieties linked by tmpyz; although the copper(I) atoms in the chain are three-co-ordinate giving a planar zigzag arrangement, those in the pendant groups are two-co-ordinate. In [Cu$_4$(pyz)$_3$(mpydz)$_4$]$^{4+}$ (mpydz = 3-methylpyridazine)[9] bridging pyz link [Cu$_4$(pyz)$_2$(mpydz)$_4$]$^{4+}$ tetranuclear units to give an infinite zigzag cationic chain. The tetranuclear cluster comprises pairs of Cu(μ-mpydz)$_2$Cu units bridged by pairs of pyz molecules. The copper atoms adopt either three- or four-co-ordinate geometries.

Complex **3** comprises one-dimensional linear polymeric cationic chains [Cu(MeCN)$_4$(pyz)]$^{2+}$, which lie on two-fold axes of symmetry parallel to the *c* direction, and unco-ordinated $BF_4^-$ anions. The copper atoms within the chain (Fig. 3) are separated by 6.812(5) Å. They are co-ordinated by four terminal MeCN molecules and two bridging pyz molecules in a tetragonally elongated octahedral geometry typical of the copper(II) d$^9$ electronic configuration. Two MeCN molecules and two pyz molecules occupy equatorial positions, and two MeCN molecules axial positions. Apart from the differences in metal to ligand interatomic distances (Table 2), the pseudo-octahedral co-ordination sphere is relatively regular, N–Cu–N angles varying within the limits 90 ± 2.1°. Unlike complex **1**, the Cu–N distances in the equatorial plane do not vary significantly with the hybridisation of the ligating nitrogen atom; although those to the sp$^2$ pyz nitrogens are longer than those to the sp MeCN nitrogens they are within the standard deviation.

The pyz ligand is essentially planar {maximum deviation from least-squares best-fit plane = 0.004 Å [C(1), C(2)]}. However, each repeating unit along the chain is rotated by ± 34.4° as depicted in Fig. 4. The corresponding rotation angle for the Cu(MeCN)$_4$ moieties is ± 43.4° giving a torsion angle of 6.3° between the pyz and MeCN molecules.

Although the $BF_4^-$ anions lie in holes in the crystal lattice and are involved in neither co-ordination nor hydrogen-bonded interactions, there is no evidence of any disorder in the structure.

**Table 3** Hydrogen-bonding interactions (distances/Å and angles/°) in complex **1**

| Contact (N–H ··· X) | Symmetry of X | N ··· X | N ··· H | H ··· X | N–H ··· X | H ··· N–C | H ··· F–B |
|---|---|---|---|---|---|---|---|
| N(13)–H(131) ··· N(41) | $1-x, -\frac{1}{2}+y, \frac{1}{2}-z$ | 2.91(2) | 0.99 | 1.96 | 161.9 | 125.4 | — |
| N(13)–H(132) ··· F(4) | $2-x, -y, 1-z$ | 2.88(2) | 1.02 | 1.90 | 161.0 | — | 141.6 |
| N(14)–H(141) ··· F(3) | $2-x, -y, 1-z$ | 3.14(2) | 1.03 | 2.15 | 160.0 | — | 99.4 |
| N(14)–H(142) ··· F(1) | $2-x, -\frac{1}{2}+y, \frac{1}{2}-z$ | 3.03(2) | 0.97 | 2.31 | 130.4 | — | 95.2 |

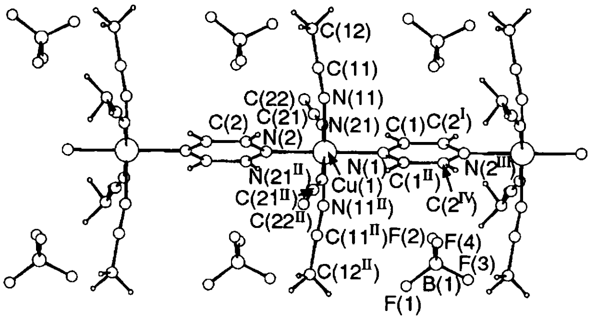


**Fig. 3** View of the crystal structure of $[Cu(MeCN)_4(pyz)][BF_4]_2$ showing the cationic chain parallel to the $c$ axis. Symmetry relations: I $x, \frac{1}{2}-y, -\frac{1}{2}+z$; II $\frac{1}{2}-x, \frac{1}{2}-y, z$; III $x, y, -\frac{1}{2}+z$; IV $\frac{1}{2}-x, y, -\frac{1}{2}+z$

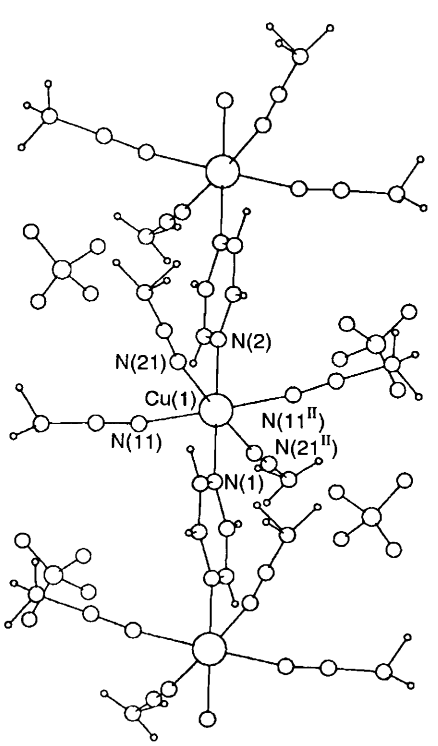
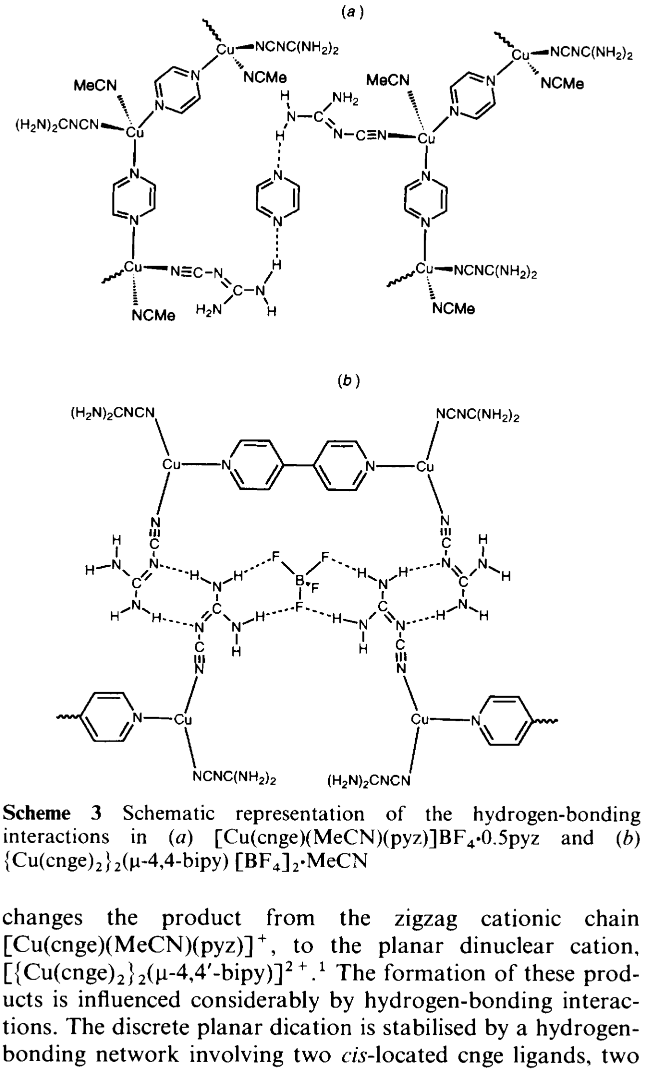


**Fig. 4** View of the crystal structure of $[Cu(MeCN)_4(pyz)][BF_4]_2$ along the cationic chain showing the twisting of the pyz (torsion angle 34.4°) and $Cu(MeCN)_4$ moieties (torsion angle 43.4°)

The geometry of the linear chain in compound **3** is comparable to that of $[Cu(O_2NO)_2(pyz)]$[21] (Scheme 1). The bridging pyz molecules are located in equatorial positions of the tetragonally elongated octahedral copper(II) co-ordination sphere; the MeCN molecules occupy the remaining equatorial and axial positions. A novel feature, however, is the fact that the chain is cationic; previously structurally characterised pyz-bridged linear copper(II) chains are neutral (Scheme 1).[21–23]

## Conclusion

The product identity in the copper(I)–cnge–diimine (diimine = pyz or 4,4′-bipy[1]) systems differs with the *N*-donor bidentate bridge. Increasing the bridge length from pyz to 4,4′-bipy changes the product from the zigzag cationic chain $[Cu(cnge)(MeCN)(pyz)]^+$, to the planar dinuclear cation, $[\{Cu(cnge)_2\}_2(\mu\text{-}4,4'\text{-bipy})]^{2+}$.[1] The formation of these products is influenced considerably by hydrogen-bonding interactions. The discrete planar dication is stabilised by a hydrogen-bonding network involving two *cis*-located cnge ligands, two cnge ligands from adjacent dications and a $BF_4^-$ anion (Scheme 3). The bridging 4,4′-bipy generates a Cu ··· Cu separation (11.23 Å) which is ideal for this network, the hydrogen bonds being quite regular (average angles N–H–N 173, N–H–F 169°; average distances N ··· N 3.06, N ··· F 2.94 Å).[1] With bridging pyz, the Cu ··· Cu separation (6.93 Å) is too short for such an arrangement. Instead, parallel cationic chains are linked by a hydrogen-bonding interaction involving cnge ligands and an unco-ordinated pyz molecule (Scheme 3). The linking pyz is oriented to be parallel to the bridging pyz molecules.



**Scheme 3** Schematic representation of the hydrogen-bonding interactions in (*a*) $[Cu(cnge)(MeCN)(pyz)]BF_4{\cdot}0.5pyz$ and (*b*) $\{Cu(cnge)_2\}_2(\mu\text{-}4,4\text{-bipy})\,[BF_4]_2{\cdot}MeCN$

Despite their differing structures, reaction of these compounds with $NOBF_4$ gives similar copper(II) products $[Cu(MeCN)_4(diimine)][BF_4]_2$ (diimine = pyz, 4,4′-bipy[1] or bpe[1]). Comparable copper(II) products, $Cu(pyz)(cnge)(MeCN)(NO_2)_2$ or $Cu(diimine)(cnge)_2(NO_2)_2$ (diimine = 4,4′-bipy or bpe),[1] are also obtained in their reactions with $NBu^t_4NO_2$.

Our failure to generate a copper–nitrosyl product by this route is consistent with earlier observations. Thus far, mononuclear copper nitrosyl complexes 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).[34,35] 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 $\mu$-$\eta^1:\eta^1$-bridging ligand, and then only with binucleating heptadentate ligands.[36]

## Experimental

All reactions were carried out under an argon or nitrogen atmosphere unless otherwise noted. Infrared, mass spectra (fast atom bombardment) 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.

Prior to use, MeCN, $CH_2Cl_2$, MeOH and toluene were distilled from $CaH_2$, and $Et_2O$ from Na–K alloy.[37] The complex $[Cu(MeCN)_4]BF_4$ was prepared using a literature procedure[38] involving the reduction of copper(II) tetrafluoroborate with an excess of copper metal suspended in dry MeCN. Pyrazine, cnge, $NOBF_4$ and $NBu^t_4NO_2$ were obtained from Aldrich Chemical Company Ltd. Pyrazine and cnge were purified by recrystallisation from MeCN–$Et_2O$ and water, respectively; $NOBF_4$ and $NBu^t_4NO_2$ were used without further purification.

### Preparation of $[Cu(cnge)(MeCN)(pyz)]BF_4 \cdot 0.5pyz$ 1

Freshly prepared $[Cu(MeCN)_4]BF_4$ (1.88 g, 6.0 mmol) was dissolved in MeCN (80 $cm^3$) and added with stirring to an MeCN solution (50 $cm^3$) of pyz (0.72 g, 9.0 mmol) over cnge (0.50 g, 6.0 mmol). As reaction proceeded the cnge dissolved and the solution turned bright yellow. After stirring for 16 h the solution was isolated from the excess of cnge by cannula filtration. Addition of toluene afforded an air- and moisture-sensitive orange solid, which analysed for $[Cu(cnge)(MeCN)(pyz)]BF_4 \cdot 0.5pyz$ (Table 1). Crystals of suitable quality for X-ray study were obtained by slow diffusion of toluene into an MeCN solution (2.04 g, 5.13 mmol, 85% yield).

### Oxidation of complex 1 by $NOBF_4$: formation of $[Cu(MeCN)_4(pyz)][BF_4]_2$ 3

**Method A.** Under nitrogen cover gas, solid $NOBF_4$ (0.12 g, 1.1 mmol) was added to a $CH_2Cl_2$ solution (60 $cm^3$) of compound **1** (0.42 g, 1.1 mmol). Initially yellow, the solution immediately turned green and a pale grey-blue precipitate formed. After stirring overnight, the solid was filtered off and dried. Yield 0.27 g; 0.67 mmol, 61%. Although insoluble in most non-polar solvents, the blue solid did dissolve to a limited extent in MeCN from which blue crystals of suitable quality for X-ray diffraction study were isolated by slow vapour diffusion of $Et_2O$. Elemental analysis and spectroscopic studies (Table 1) indicated that the initial product **2** was different from the recrystallised product **3**.

**Method B.** The reaction was repeated as for method A but under a static vacuum. Identical behaviour was observed. Both products analysed as before.

**Method C.** Under nitrogen cover gas, solid $NOBF_4$ (0.37 g, 3.2 mmol) was placed in the side arm of a vessel containing a solution of compound **1** (1.26 g, 3.2 mmol) in methanol (120 $cm^3$). The vessel was cooled to −78 °C and evacuated for 30 min. With the system under a static vacuum, the $NOBF_4$ was introduced to the MeOH solution which was then stirred for 2 h. No reaction occurred, even after warming to −40 °C (solid $CO_2$–MeCN) for 2 h and to 0 °C (ice–water) for 2 h. As the temperature approached 5 °C the yellow reaction mixture turned blue and a precipitate formed. This initial precipitate analysed as before as did the product recrystallised from MeCN.

### Reaction of complex 1 with $NBu^t_4NO_2$: formation of $Cu(pyz)(cnge)(MeCN)(NO_2)_2$ 4

Solid $NBu^t_4NO_2$ (0.69 g, 2.4 mmol) was placed in the side arm of a reaction vessel containing a solution of compound **1** (0.47 g, 1.2 mmol) in MeCN (60 $cm^3$). The solution was 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 over 30 min. Initially yellow, the solution became green before yielding a blue-green precipitate. The entire process was accompanied by effervescence. After stirring overnight the solid was filtered off and dried. Rotary evaporation of the filtrate gave a green oil. Repeated washing with diverse solvents had no effect on the oil. However, an off-white solid was obtained from it by column chromatography using MeCN as eluent. Analytical data (Table 1) for the blue-green and white solids were consistent with $Cu(pyz)(cnge)(MeCN)(NO_2)_2$ **4** (0.28 g, 0.78 mmol, 65% yield) and $NBu^t_4BF_4$ (0.30 g, 0.91 mmol, 76% yield), respectively. $NBu^t_4BF_4$: FAB mass spectrum *m*/*z* 242 ($[NBu^t_4]^+$), 185 ($[NBu^t_3]^+$), 128 ($[NBu^t_2]^+$), 71 ($[NBu^t]^+$) and 57 ($Bu^+$); IR 2693m, 2872m, 2132s, 1487s, 1385s, 1080–1055s (br) and 801m $cm^{-1}$.

### Crystallography

Several crystals of each product were mounted in Lindemann tubes under dry nitrogen for preliminary study. Oscillation and Weissenberg photographs revealed monoclinic cell parameters with space group either $P2/c$ (no. 13) or $P2_1/c$ (no. 14) for complex **1** and orthorhombic cell parameters with space group $Pccn$ (no. 56) for **3**. X-Ray diffraction data for the refinement of cell parameters and structure determination were collected for suitable crystals using a Hilger and Watts Y290 four-circle diffractometer. For each crystal, one unique set of data was collected in the ranges $1 < \theta < 20$ (for **1**) and $1 < \theta < 25°$ (for **3**) using graphite-monochromated Mo-Kα radiation (λ 0.710 73 Å). Standard reflections were constant throughout the course of the data collections indicating that the crystals were stable. Data were corrected for Lorentz-polarisation effects; absorption corrections were not applied.

For both complexes, the positions of the copper atoms were determined by Patterson methods and those of the carbon, nitrogen and pyz hydrogen atoms by Fourier-difference

**Table 4** Data collection parameters for complexes **1** and **3**

| | **1** | **3** |
|---|---|---|
| Formula | $C_{10}H_{13}BCuF_4N_8$ | $C_{12}H_{16}B_2CuF_8N_6$ |
| $M$ | 395.62 | 481.46 |
| Crystal system | Monoclinic | Orthorhombic |
| Space group | $P2_1/c$ (no. 14) | $Pccn$ (no. 56) |
| $a$/Å | 11.822(3) | 11.738(3) |
| $b$/Å | 14.135(3) | 12.390(4) |
| $c$/Å | 11.582(5) | 13.624(5) |
| $\beta$/° | 121.09(2) | 90 |
| $U$/Å$^3$ | 1657.4 | 1981.4 |
| $\mu_{calc}$/$cm^{-1}$ | 13.7 | 11.8 |
| $D_c$/g $cm^{-3}$ | 1.586 | 1.614 |
| $F(000)$ | 796 | 964 |
| Crystal dimensions/mm | 0.3 × 0.3 × 0.05 | 0.5 × 0.3 × 0.1 |
| $\theta_{max}$/° | 20 | 25 |
| *hkl* Ranges | −11 to 9, 0–13, 0–11 | 0–13, 0–14, 0–16 |
| Reflections collected (unique) | 1643 | 2019 |
| Reflections with $I > 3\sigma(I)$ | 1010 | 1192 |
| Number of parameters | 241 | 141 |
| Data/parameter ratio | 4.19 | 8.45 |
| $R$ | 0.080 | 0.060 |
| $R'$ | 0.081 | 0.061 |
| $\rho_{min}, \rho_{max}$ | −0.61, 0.739 | −0.625, 0.677 |
| $(\Delta/\rho)_{max}$ | 0.020 | 0.047 |

Details in common: Scan type ω–2θ; $Z = 4$.

syntheses using the CRYSTALS suite of programs.[39] The remaining hydrogen atoms were fixed at X–H 1.00 Å (X = C or N) with $U_{iso} = 0.05$ Å$^2$. The $BF_4^-$ anions did not exhibit any disorder in either compound. Although this could be attributed to their being hydrogen bonded to the cnge amino hydrogens in **1**, no such interaction exists in **3**. Full-matrix least-squares refinement (unit weights) on *F* with anisotropic thermal parameters for all atoms except hydrogen (those hydrogen atoms which had been found were refined isotropically) converged in space group $P2_1/c$ to $R = 0.080$ and $R' = 0.081$ for **1** and in space group *Pccn* to 0.060 and 0.061 for **3**. Details of the data collection and structure solution for both complexes are collated in Table 4.

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 186/32.

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