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The role of hydrogen-bonding interactions in stabilising trigonal planar copper(I) in Cu(BF_4)–pyridazine–nitrile systems†

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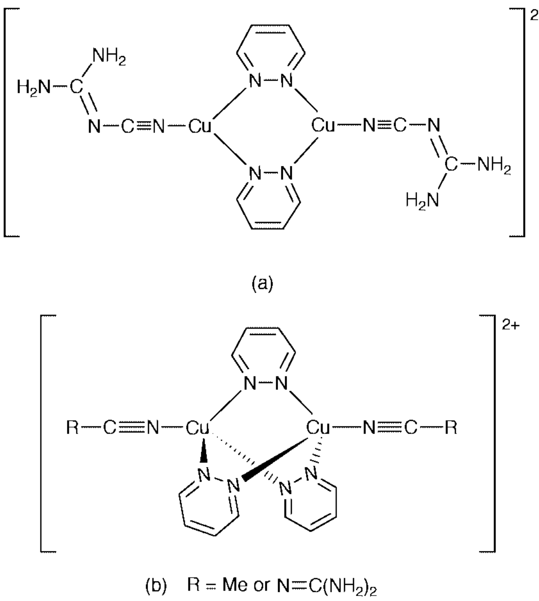
Regardless of conditions, reaction of $[Cu(NCMe)_4][BF_4]$ with pyridazine (pydz) or 3-methylpyridazine (Mepydz) in MeCN or with pydz in PhCN invariably gave tris-bridged dinuclear cations, $[\{Cu(NCR)\}_2(\mu\text{-diimine})_3]^{2+}$. Structural analysis, by single crystal X-ray diffraction, of complexes containing $[\{Cu(NCMe)\}_2(\mu\text{-pydz})_3]^{2+}$, $[\{Cu(NCMe)\}_2(\mu\text{-Mepydz})_3]^{2+}$ and $[\{Cu(NCPh)\}_2(\mu\text{-pydz})_3]^{2+}$ confirmed the presence of two tetrahedral copper(I) centres bridged by three pyridazine molecules and terminally co-ordinated by nitriles. This chemistry contrasts with that for 2-cyanoguanidine (cnge), a planar nitrile with considerable hydrogen-bonding potential, which leads to both bis- and tris-bridged dinuclear cations, $[\{Cu(cnge)\}_2(\mu\text{-pydz})_2]^{2+}$ and $[\{Cu(cnge)\}_2(\mu\text{-pydz})_3]^{2+}$. Whereas the tris-bridged cation is based on four-co-ordinate tetrahedral copper(I), the bis-bridged cation contains three-co-ordinate trigonal planar copper(I). The unique ability of cnge to stabilise co-ordinatively unsaturated copper(I) in the solid state with pydz bridged dications is attributed to the formation of an extended 2-D sheet architecture based on hydrogen-bonding intermolecular interactions. This type of molecular construction, which is common to all copper(I)–cnge three-co-ordinate structures, suggests that the three-co-ordinate geometry is not an intrinsic property of copper(I) systems but a result of the efficient packing of parallel two-dimensional sheets. Treatment of $[\{Cu(NCMe)\}_2(\mu\text{-diimine})_3]^{2+}$ with CO led to $[\{Cu(CO)\}_2(\mu\text{-diimine})_3]^{2+}$; reaction of $[\{Cu(cnge)\}_2(\mu\text{-diimine})_2]^{2+}$ with CO or PPh_3 gave $[\{Cu(cnge)(L)\}_2(\mu\text{-diimine})_2]^{2+}$ (L = CO or PPh_3). Recrystallisation of $[\{Cu(cnge)(PPh_3)\}_2(\mu\text{-diimine})_2]^{2+}$ yielded a variety of crystalline products including $[Cu(pydz)_2(PPh_3)_2][BF_4]$ and $[\{Cu(PPh_3)\}_2(\mu\text{-pydz})_3][PF_6]_2$. Structural studies confirmed the former to be a mononuclear cation with four monodentate (two pydz and two Ph_3P) ligands and the latter to be a tris(μ-pydz) dinuclear cation with terminal Ph_3P molecules. The copper(I) co-ordination geometries in both complexes are tetrahedral, the three-co-ordinate copper(I) geometry of $[\{Cu(cnge)\}_2(\mu\text{-diimine})_2]^{2+}$ being lost on treatment with Ph_3P. In the absence of structural data, $[\{Cu(CO)\}_2(\mu\text{-diimine})_3]^{2+}$ and $[\{Cu(cnge)(CO)\}_2(\mu\text{-diimine})_2]^{2+}$ are considered to comprise tris- and bis-(μ-diimine) dinuclear cations based on tetrahedral copper(I) with terminal CO.

Three-co-ordinate copper(I) is relatively rare, four-co-ordinate geometries being the norm.[1] It is commonly stabilised by use of either bulky monodentate,[2] structurally demanding bidentate[3] or sterically constraining multidentate[4] and macrocyclic[5] ligands. 2-Cyanoguanidine (cnge), a ligand we have used successfully to stabilise co-ordinatively unsaturated copper(I),[6–9] fits none of these categories. Extended Hückel calculations[6] undertaken to examine co-ordination of copper(I) by cnge, although inconclusive, did show that pyramidalisation of planar Cu^IL_3 makes the LUMO more accessible for nucleophilic attack if L is a σ or a π donor such as H^- or Cl^-, whereas no such benefit arises for a π acceptor such as NCR, a cnge analogue, thereby supporting the preferred formation of $[Cu^I(NCR)_3]^+$ as a trigonal planar cation and of $[Cu^IH_4]^{3-}$ and $[Cu^ICl_4]^{3-}$ as tetrahedral anions.

We have recently reported both bis- and tris-(pyridazine) bridged dinuclear copper(I) cations with cnge as terminal ligands, $[\{Cu(cnge)\}_2(\mu\text{-pydz})_2][BF_4]_2$ **1** and $[\{Cu(cnge)\}_2(\mu\text{-pydz})_3][BF_4]_2$ **2**,[7] and a tris(pyridazine) bridged dinuclear copper(I) cation with terminal acetonitrile molecules, $[\{Cu(NCMe)\}_2(\mu\text{-pydz})_3][PF_6]_2$ **3**.[10] The bis(μ-pydz) molecule is trigonal planar, the tris(μ-pydz) molecules tetrahedral (Scheme 1).



Scheme 1 Formation of (a) bis- and (b) tris-pyridazine bridged dicopper(I) species with terminal nitriles.

To assess further the ability of nitriles to stabilise three-co-ordinate copper(I) we have extensively investigated complex formation by copper(I) tetrafluoroborate in the presence of pydz and diverse nitriles. Thus, in this paper, we report further

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† *Supplementary data available*: rotatable 3-D crystal structure diagram in CHIME format. See http://www.rsc.org/suppdata/dt/1999/4251/

Table 1 Analytical data for $[\{Cu(NCMe)\}_2(\mu\text{-pydz})_3][BF_4]_2{\cdot}MeCN$ **5**, $[\{Cu(NCMe)\}_2(\mu\text{-Mepydz})_3][BF_4]_2$ **6**, $[\{Cu(NCPh)\}_2(\mu\text{-pydz})_3][BF_4]_2$ **7**, $Cu(pydz)(NCMe)(OH)(BF_4)$ **8**, $Cu(pydz)_{1.5}(NCMe)(OH)(BF_4)$ **9**, $[\{Cu(CO)\}_2(pydz)_3][BF_4]_2$ **10**, $[\{Cu(CO)\}_2(Mepydz)_3][BF_4]_2$ **11**, $[\{Cu(cnge)(PPh_3)\}_2(\mu\text{-pydz})_2][BF_4]_2$ **12**, $[Cu(PPh_3)_2(pydz)_2][BF_4]$ **13**, $[\{Cu(PPh_3)\}_2(\mu\text{-pydz})_3][PF_6]_2{\cdot}CH_2Cl_2$ **14** and **15**, the product of the reaction of **6** with cnge, $Cu_2(BF_4)_2(Mepydz)(cnge)_3$

	Analysis (Found/calc.) (%)				IR spectral data/cm^{-1}		
Complex	C	H	N	Cu	pydz or Mepydz	CO or cnge	BF_4^-
5[a]	31.15/32.55	2.85/3.20	18.10/19.00	20.05/19.15	3055m, 1441s, 1417m, 762s	—	1050s
6	34.45/34.30	3.60/3.65	17.00/16.85	19.10/19.10	2962w, 1586w, 1435m, 798m	—	1060s
7	41.50/41.80	2.85/2.95	15.25/15.00	16.95/17.00	2983m, 1440s, 1417m, 761s	—	1065s
8[b]	24.85/25.00	2.60/2.80	14.60/14.55	—/—	1452m, 1414s, 771s[c]	—	1075s
9[b]	29.55/29.25	2.65/3.05	17.10/17.05	—/—	1452s, 1424m, 763m[c]	—	1065s
10[d]	27.90/28.15	2.30/2.05	14.70/14.10	—/—	3052m, 1439s, 1417m, 760m	2112s	1055s
11	31.50/31.95	2.80/2.85	12.90/13.15	—/—	2963w, 1591m, 1442m, 804m	2111s	1055s
12	49.80/50.00	2.95/3.95	16.30/16.55	—/—	1437s, 1416s, 762m[e]	2214m, 2173m	1080s
13	44.20/44.45	3.70/3.45	5.95/6.20	—/—	[f]	—	1070s
14	46.75/46.45	4.00/3.50	6.65/6.65	—/—	[f]	—	—
15[g]	19.85/20.40	2.70/2.80	30.00/30.31	—/—	1593s, 1440m, 802m[e]	2217s, 2212s, 2167s	1035s

[a] Calc. for $[\{Cu(MeCN)\}_2(\mu\text{-pydz})_3][BF_4]_2{\cdot}0.25MeCN$: C, 31.30; H, 3.00; Cu, 20.05; N, 18.25%. [b] Decomposition (hydrolysis/oxidation) products of complex **5**. [c] The pydz (Mepydz) absorption at ≈3055 (2960) cm^{-1} is masked by hydrogen bonded ν(OH) absorptions. [d] The formation of $[\{Cu(MeCN)(CO)\}_2(pydz)_2][BF_4]_2$ (calc. C, 28.05; H, 2.35; N, 14.05) cannot be ruled out from the analytical data. [e] The pydz (Mepydz) absorption at ≈3055 (2960) cm^{-1} is masked by cnge ν(NH) absorptions. [f] All pydz (Mepydz) absorptions are masked by PPh_3 absorptions. [g] Product of the reaction of complex **6** with cnge: $Cu_2(BF_4)_2(Mepydz)(cnge)_3$.

details of the structural chemistry of pydz bridged dinuclear copper(I) systems with MeCN, PhCN and cnge as terminal ligands and describe their reaction chemistry with the Lewis bases CO and PPh_3. As we have not been able to produce any co-ordinatively unsaturated bis(pydz) bridged species other than **1**, and reaction of **1** with Lewis bases invariably yields tetrahedral copper(I), we propose that the formation of three co-ordinate copper(I) in **1** and other $CuBF_4$–cnge complexes[6–9] is a result of the efficient packing of parallel sheets generated by hydrogen-bonding interactions templated by the planar cnge ligand.

Results and discussion

Synthesis of pyridazine bridged dicopper(I) cations terminally co-ordinated by nitriles

Reaction of $[Cu(NCMe)_4][BF_4]$ **4** with pydz in MeCN yields, regardless of reagent molar ratio, the bright yellow tris(μ-pydz) dicopper(I) complex $[\{Cu(NCMe)\}_2(\mu\text{-pydz})_3][BF_4]_2{\cdot}x$MeCN **5**. The corresponding 3-methylpyridazine (Mepydz) system behaved entirely analogously forming the bright yellow tris(μ-Mepydz) dicopper(I) complex, $[\{Cu(NCMe)\}_2(\mu\text{-Mepydz})_3][BF_4]_2$ **6**. No evidence was found in either system for the formation of a bis(μ-pydz) species, despite the Cu : pydz (Mepydz) molar ratio being varied from 1 : 1 to 4 : 1; those systems containing an excess of copper gave crystalline **4** as well as **5** or **6**.

Attempts to prepare benzonitrile terminally ligated complexes by treatment of **4** with pydz and PhCN in MeCN were unsuccessful, the only materials isolated being **4** and **5**. The bright yellow tris(μ-pydz) dicopper(I) complex $[\{Cu(NCPh)\}_2(\mu\text{-pydz})_3][BF_4]_2$ **7** could only be obtained by reaction of **4** with pydz in PhCN. Again, despite the Cu : pydz molar ratio being varied from 1 : 1 to 4 : 1, no evidence for a bis(μ-pydz) species was found.

These products are analogous to the yellow complex $[\{Cu(NCMe)\}_2(\mu\text{-pydz})_3][PF_6]_2$ **3**, obtained on addition of $[Cu(MeCN)_4][PF_6]$ to an equimolar amount of pydz dissolved in acetone.[10] They contrast with the air sensitive, yellow, bis(μ-pydz) dicopper(I) complex $[\{Cu(cnge)\}_2(\mu\text{-pydz})_2][BF_4]_2$ **1**, obtained by treatment of **4** with equimolar amounts of pydz and cnge in MeCN.[7] This species does, however, react rapidly with an excess of pydz to give the corresponding orange tris(μ-pydz) dicopper(I) complex, $[\{Cu(cnge)\}_2(\mu\text{-pydz})_3][BF_4]_2$ **2**.[7]

All the products, especially the bis(μ-pydz) species, were air sensitive and had to be synthesized and handled under anhydrous inert gas conditions. Initial characterisation relied on analytical and spectroscopic methods (Table 1). Subsequently, the growth of single crystals of **5**–**7** permitted their structural characterisation.

Table 2 Solution (CH_2Cl_2) IR spectral data/cm^{-1}[a] for reaction of complexes **5** and **6** with carbon monoxide

	CO	pydz or Mepydz	BF_4^-
Substrate **5**			
Prior to CO addition		1446m, 1415m	1055s
Following CO addition	2101m	1446m, 1414m	1065s
After purging with nitrogen		1447m, 1415m	1060s
Substrate **6**			
Prior to CO addition		1593m, 1443m	1060s
Following CO addition	2102m	1593m, 1443m	1055s
After purging with nitrogen		1593m, 1443m	1060s

[a] The IR spectrum of CH_2Cl_2 after purging with CO showed no evidence of the ν(CO) band.

Complex **5** decomposed upon exposure to the atmosphere for 15 min to give blue (**8**) and green (**9**) products. Although these complexes could not be characterised unambiguously, elemental and spectroscopic analysis suggested the formulations $Cu(pydz)(NCMe)(OH)(BF_4)$ and $Cu(pydz)_{1.5}(NCMe)(OH)(BF_4)$, respectively (Table 1). Complexes **6** and **7** also decomposed upon exposure to the atmosphere to give similarly coloured products which could not be identified.

Reaction of tris(μ-pyridazine)dicopper(I) cations terminally co-ordinated by acetonitrile with carbon monoxide

Bubbling carbon monoxide through a yellow dichloromethane solution of complex **5** or **6** at 298 K gave pale yellow solids under yellow solutions. Purging these solutions with nitrogen gas resulted in redissolution of the solids. The cycle could be repeated indefinitely for both substrates with no observable decomposition of the solution. Solution FTIR studies before and after CO addition and after purging with nitrogen (Table 2) confirmed the reversibility of the co-ordination of carbon monoxide to copper(I) in that the appearance/disappearance of ν(CO) bands at 2101 (for **5**) and 2102 cm^{-1} (for **6**) was monitored for several CO addition/N_2 purge cycles with no apparent loss of ν(CO) band intensity.

The pale yellow solids were isolated by cannula filtration.

Elemental and spectroscopic analysis (Table 1) suggested the formulation $[\{Cu(CO)\}_2(diimine)_3][BF_4]_2$ (diimine = pydz **10** or Mepydz **11**). For **10**, the pydz derivative, the formulation $[\{Cu(NCMe)(CO)\}_2(pydz)_2][BF_4]_2$ cannot be ruled out; the empirical formulae for both possibilities are identical and, in our experience,[11] the ν(CN) band of MeCN co-ordinated to copper(I) is too weak to be observed. However, for **11**, the Mepydz derivative, the formulation $[\{Cu(NCMe)(CO)\}_2(Mepydz)_2][BF_4]_2$ can be eliminated from the elemental analysis data (Table 1).

Crystallisation of complexes **10** and **11** by solvent evaporation was unsuccessful; passage of carbon monoxide through the gas space over a dilute solution inevitably yielded powdered samples. In the absence of structural data, **10** and **11** are considered to comprise tris(pydz) or tris(Mepydz) bridged dinuclear cations based on tetrahedral copper(I) with terminal carbon monoxide. These proposed formulations should be contrasted to the assumed identities of the colourless carbon monoxide and ethylene adducts $\{[Cu_2(pydz)_3X_2]^{2+}$, X = CO or $C_2H_4\}$ produced by reduction of $Cu(ClO_4)_2$ with copper wire in acetone containing pydz under carbon monoxide or ethylene.[10] As all structurally characterised bis- and tris-(μ-pydz) dinuclear complexes are yellow or orange and mononuclear complexes with terminal pydz molecules (see later) are colourless, we now suggest it is more probable that the highly reactive, colourless, carbon monoxide and ethylene adducts are mononuclear, tetrahedral cations, $[Cu(pydz)_xX_{4-x}]^+$.

Reaction of bis- and tris-(μ-pyridazine)dicopper(I) cations terminally co-ordinated by 2-cyanoguanidine with carbon monoxide

The addition of carbon monoxide to complexes **1** and **2** has been studied at 298 K in dichloromethane using FTIR spectroscopy. The IR spectrum (2700–1800 cm^{-1}) of **1** in degassed dichloromethane revealed a peak at 2256 cm^{-1} which was assigned to ν_{asym}(NCN) of co-ordinated cnge.[12,13] Addition of CO gave rise to two ν(CO) bands at 2107 and 2132 cm^{-1} and no shift in the cnge band at 2256 cm^{-1}. Purging the carbonylated solution with an inert gas (Ar) or the application of vacuum resulted in the regeneration of the spectrum of **1**. We tentatively assign the two ν(CO) bands to overlap of the spectra due to the *cis*- and *trans*-geometric isomers of the bis(CO) adduct, $[\{Cu(cnge)(CO)\}_2(\mu\text{-pydz})_2][BF_4]_2$ (Scheme 2). The isolation of a crystalline product could not be achieved, either by diffusion, both vapour/solution and solvent/solution interface were tried, or by cooling the solution to −20 °C. The lack of success was attributed to the presence of a mixture of isomers in solution.

$$\begin{array}{c} [\{Cu(cnge)\}_2(\mu\text{-pydz})_2]^{2+} \\ \Big\Updownarrow\ \text{CO} \\ \textit{cis-}\text{ and }\textit{trans-}[\{Cu(cnge)(CO)\}_2(\mu\text{-pydz})_2]^{2+} \end{array}$$

Scheme 2 Proposed equilibrium on addition of carbon monoxide to $[\{Cu(cnge)\}_2(\mu\text{-pydz})_2]^{2+}$ in CH_2Cl_2 at room temperature.

Variable temperature FTIR studies (213–298 K; 2200–2000 cm^{-1}) of the reaction of complex **2** with CO in degassed dichloromethane showed one very weak band in the ν(CO) region at room temperature (2138 cm^{-1}) but three weak bands at −20 °C and below (2122, 2138, 2152 cm^{-1}). On cooling, the 2138 cm^{-1} band initially increased and subsequently diminished in intensity, while the 2122 and 2152 cm^{-1} bands simply increased in intensity.

Some conclusions can be drawn from an analysis of the solution FTIR data. The differing band positions rule out the formation of either $[\{Cu(CO)\}_2(\mu\text{-pydz})_3]^{2+}$ [ν(CO) 2101 cm^{-1}] or $[\{Cu(cnge)(CO)\}_2(\mu\text{-pydz})_2]^{2+}$ [ν(CO) 2107, 2132 cm^{-1}]. The similarity of the ν(CO) band positions with that of free CO (2143 cm^{-1}) and the need for low temperatures for product formation are consistent with a weak Cu···CO interaction in an unstable product. The changes in relative band intensity suggest the presence of an equilibrium. We propose that a mono(CO) adduct, responsible for the single band, is in equilibrium with both the starting material and a bis(CO) adduct, the *cis* and *trans* isomers of which are responsible for the other two bands. The mono(CO) adduct could be an unsymmetrical bis(μ-pydz) complex, $[\{Cu(cnge)(CO)\}\{Cu(cnge)(pydz)\}(\mu\text{-pydz})_2]^{2+}$ and the bis(CO) adduct could be *cis* and *trans* isomers of a μ-pydz complex, $[\{Cu(cnge)(CO)(pydz)\}_2(\mu\text{-pydz})]^{2+}$ (Scheme 3).

$$\begin{array}{c} [\{Cu(cnge)\}_2(\mu\text{-pydz})_3]^{2+} \\ \Big\Updownarrow\ \text{CO} \\ [\{Cu(cnge)(CO)\}\{Cu(cnge)(pydz)\}(\mu\text{-pydz})_2]^{2+} \\ \Big\Updownarrow\ \text{CO} \\ \textit{cis-}\text{ and }\textit{trans-}[\{Cu(cnge)(CO)(pydz)\}_2(\mu\text{-pydz})]^{2+} \end{array}$$

Scheme 3 Proposed equilibria on addition of carbon monoxide to $[\{Cu(cnge)\}_2(\mu\text{-pydz})_3]^{2+}$ in CH_2Cl_2 at low temperature.

Reaction of bis(μ-pyridazine)dicopper(I) cations terminally co-ordinated by 2-cyanoguanidine with triphenylphosphine

A solution of complex **1**, generated by addition of equimolar quantities of **4**, pydz and cnge to deoxygenated, dry acetonitrile, when treated with an equimolar quantity of triphenylphosphine, gave a bright yellow solid suspended in a yellow solution. Elemental and IR spectroscopic analysis of the product (Table 1) suggested the formulation $[\{Cu(cnge)(PPh_3)\}_2(\mu\text{-pydz})_2][BF_4]_2$ **12**. However, crystallisation by heptane–acetone or hexane–dichloromethane solvent–solvent interface diffusion yielded crystalline products with different colours and morphologies. Elemental analysis (Table 1) suggested the products isolated to be $[\{Cu(cnge)(PPh_3)\}_2(\mu\text{-pydz})_2][BF_4]_2$ **12** (as microcrystalline yellow blocks) and $[Cu(pydz)_2(PPh_3)_2][BF_4]$ **13** (as large, colourless, air-stable blocks). The crystals of **13** but not **12** were suitable for X-ray study. Consequently, the reaction was repeated using $[Cu(NCMe)_4][PF_6]$ instead of **4**. This time, bright yellow plates of $[\{Cu(PPh_3)\}_2(\mu\text{-pydz})_3][PF_6]_2\cdot CH_2Cl_2$ **14**, suitable for X-ray analysis, were obtained (Table 1). Complex **14** is a tris(μ-pydz) dinuclear cation with terminal Ph_3P molecules; **13** is a mononuclear cation in which two pydz and two Ph_3P molecules act as terminal ligands. The copper(I) co-ordination geometries in both complexes are basically tetrahedral, the three-co-ordinate copper(I) geometry of **1** being lost on treatment with Ph_3P.

Reaction of tris(μ-3-methylpyridazine)dicopper(I) cations terminally co-ordinated by acetonitrile with 2-cyanoguanidine

Addition of cnge to a dichloromethane solution of complex **6** gave a yellow precipitate. Elemental analysis of the product suggested the formulation $Cu_2(BF_4)_2(Mepydz)(cnge)_3$ **15** (Table 1). IR Spectroscopic studies confirmed the presence of cnge, Mepydz and BF_4^-. Three bands in the ν_{asym}(NCN) region suggested the presence of two independent cnge molecules. Since attempts at crystallisation were unsuccessful it was not possible to identify positively this product.

Molecular structures of tris(pyridazine) bridged dinuclear cations with terminal acetonitrile or benzonitrile

The crystal structures of complexes **5**, **6** and **7** comprise tris(pyridazine) bridged dinuclear copper(I) cations, $[\{Cu(NCR)\}_2(\mu\text{-diimine})_3]^{2+}$, and BF_4^- anions and, for **5**, halves of two solvate acetonitrile molecules, which occupy special positions on twofold axes. Although the asymmetric unit of **5** comprises one cation, its associated anion and solvate molecules, that of **7** comprises two crystallographically independent cations and

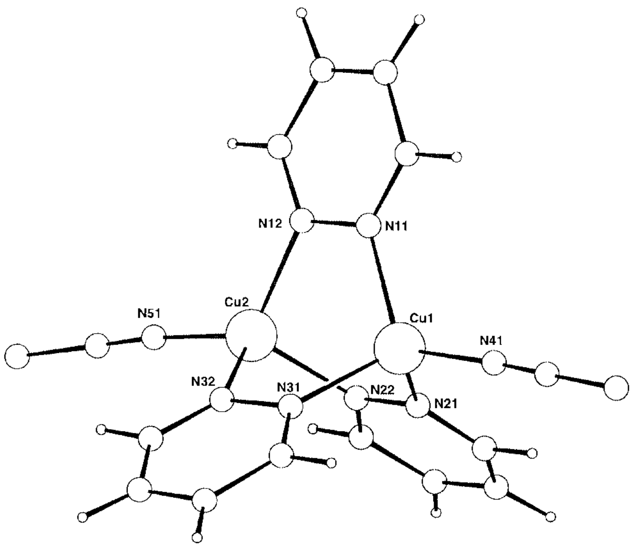


Fig. 1 Molecular structure of the $[\{Cu(NCMe)\}_2(\mu\text{-pydz})_3]^{2+}$ cation in the structure of complex **5** (methyl hydrogens omitted).

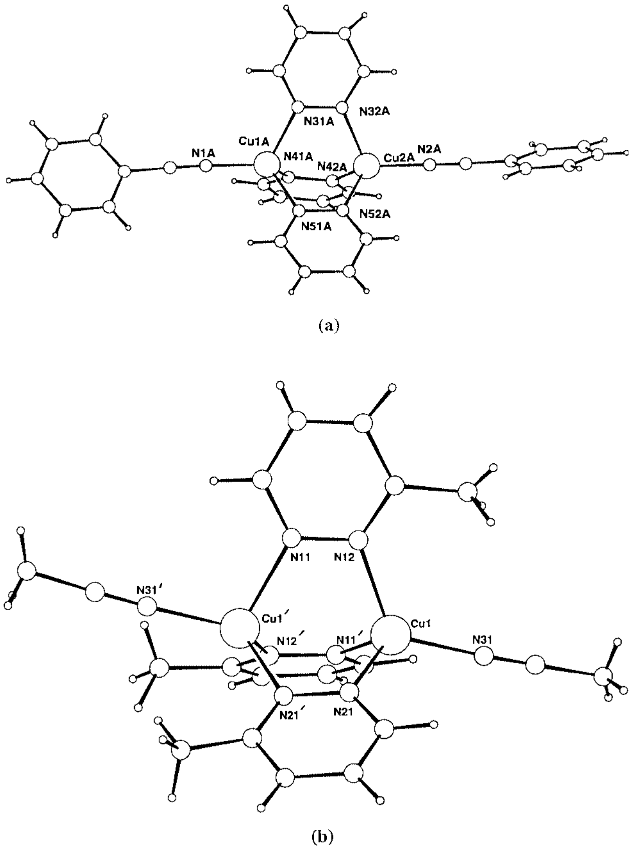


Fig. 2 Comparison of the molecular structures of the $[\{Cu(NCPh)\}_2(\mu\text{-pydz})_3]^{2+}$ (a) and $[\{Cu(NCMe)\}_2(\mu\text{-Mepydz})_3]^{2+}$ (b) cations in the structures of complexes **7** and **6**, respectively (atoms related by the twofold axis are primed).

anions. The cation in **6** lies on a twofold axis of symmetry giving half a molecule as the asymmetric unit. This necessarily results in 50% occupancy of the two disordered methyl positions of the Mepydz ligand bisected by the twofold symmetry axis. The structures of the pydz bridged cations of **5** (Fig. 1) and **7** are comparable and similar to those of **2** and **3**, the only differences lying in the terminal nitrile or anion. The Mepydz bridged cation of **6** is slightly different owing to the asymmetry of the bridge; it is compared with one of the cations of **7** in Fig. 2. Pertinent interatomic distances and angles for all six cations are compared with those of the Ph_3P terminally co-ordinated tris(μ-pydz) dinuclear cation in **14** and the cnge terminally co-ordinated bis(μ-pydz) dinuclear cation in **1** in Table 3. Dihedral angles between the normals to the bridging pydz molecules for all six cations are compared in Table 4.

The dinuclear cations in complexes **2**, **3**, **5**, **6** and **7** all comprise two tetrahedral copper(I) centres bridged by three pyridazine molecules and terminally co-ordinated by nitriles [Figs. 1 and 2]. For the tris(μ-pydz) cations in **2**, **3**, **5** and **7** [Figs. 1 and 2(a)] the nitrile groups lie on or near to the extensions of the Cu···Cu vectors with N (pydz)–Cu–N (nitrile) angles ranging from 109.5 to 124.6° and differing by up to 15.1° (Table 3). Minimum and maximum differences in N (pydz)–Cu–N (nitrile) angles are found for the cnge (4.0°) and PhCN (9.2, 10.7, 10.9, 15.1°) derivatives, respectively. Interestingly, the Ph_3P terminally ligated dication in **14** is even more symmetrical than the cnge complex with very small differences in N (pydz)–Cu–P (Ph_3P) angles (3.1 and 3.5°). For the tris(μ-Mepydz) cation in **6** [Fig. 2(b)] the steric requirements of the methyl substituents are so demanding that the nitrile is forced off the extensions of the Cu···Cu vector resulting in a minimum N (pydz)–Cu–N (nitrile) angle of 104.9° and a maximum difference in N (pydz)–Cu–N (nitrile) angle of 18.0° (Table 3).

The regularity of the tris(μ-pydz) bridges is given by the variation in the dihedral angles between the normals to the bridging ligands (Table 4). The maximum and minimum deviations from the ideal (threefold symmetry requires dihedral angles of 60°) are found in complexes **5** and **2**, respectively, with angles ranging from 44.4 to 70.1° and from 57.7 to 64.5°.

The fact that the average N (pydz)–Cu–N (nitrile) angle (115.2°) is greater than the tetrahedral angle is due to the steric requirements of the tris(μ-pydz) bridges which have an average N (pydz)–Cu–N (pydz) angle of 103.6°. The bis(μ-pydz) bridge generates a much more symmetrical copper(I) geometry with all three N–Cu–N angles in the narrow range 119.6 ± 0.5°. A corollary of these angle differences is the much shorter Cu···Cu interatomic distances for the tris(μ-pydz) dications (range 3.038–3.098 Å; Table 3) compared to the bis(μ-pydz) dication (3.325 Å; Table 3). The interatomic distances in the copper co-ordination spheres vary little with cation. They do, however, reflect both ligand type and co-ordination number. The sp^2 hybridised pyridazine nitrogen atoms are considerably further from the copper atom than the sp hybridised nitrile nitrogen atoms, and the distances to the trigonal planar copper atom are significantly shorter than those to the tetrahedral copper atoms (Cu–pyridazine N for trigonal planar copper atoms: range 1.97–1.98 Å Cu–pyridazine N for tetrahedral copper atoms: range 2.01–2.10 Å: Cu–nitrile N for trigonal planar copper atom: 1.88 Å: Cu–nitrile N for tetrahedral copper atoms: range 1.89–1.97 Å (Table 3)).

Molecular structure of the tris(μ-pyridazine)bis(triphenylphosphinecopper(I)) cation

The structure of complex **14** comprises $[\{Cu(PPh_3)\}_2(\mu\text{-pydz})_3]^{2+}$ cations, non-co-ordinated PF_6^- anions and CH_2Cl_2 solvate molecules. The molecular structure of the cation is shown in Fig. 3; selected interatomic distances and angles are compared with those of the nitrile complexes in Table 3; dihedral angles between the normals to the bridging pydz molecules in Table 4.

The tris(μ-pydz) dinuclear cation [(Fig. 3(a)] comprises two copper centres bridged by three pydz molecules and terminally ligated by PPh_3 molecules. It lies in the crystallographic mirror plane at $z = 0.25$ or 0.75. Fourteen non-hydrogen atoms including both copper atoms, both PPh_3 phosphorus atoms and an entire pydz bridge lie in this plane; two phenyl groups, one on each PPh_3 ligand, are bisected by the mirror plane such that the 1 and 4 carbons lie in the plane; the other two pyridazine bridges and the two pairs of phenyl groups on the PPh_3 ligand are symmetry related by the mirror plane. The PPh_3 ligand is

Table 3 Interatomic distances (Å) and angles (°) for $[\{Cu(NCMe)\}_2(\mu\text{-pydz})_3][BF_4]_2\cdot MeCN$ **5**, $[\{Cu(NCMe)\}_2(\mu\text{-Mepydz})_3][BF_4]_2$ **6**, $[\{Cu(NCPh)\}_2(\mu\text{-pydz})_3][BF_4]_2$ **7**, $[\{Cu(PPh_3)\}_2(\mu\text{-pydz})_3][PF_6]_2\cdot CH_2Cl_2$ **14**, $[\{Cu(cnge)\}_2(\mu\text{-pydz})_3][BF_4]_2$ **2**, $[\{Cu(NCMe)\}_2(\mu\text{-pydz})_3][PF_6]_2$ **3** and $[\{Cu(cnge)\}_2(\mu\text{-pydz})_2][BF_4]_2$ **1**

		Cu–N(pydz)^{a}			Cu–N(nitrile)^{a}
	Cu···Cu	Cu–N(1)	Cu–N(2)	Cu–N(3)	Cu–N(4)
Tris(pyridazine) bridged cations					
5 Cu(1)	3.038(3)	2.03(2)	2.02(2)	2.04(2)	1.94(2)
5 Cu(2)		2.02(2)	2.02(2)	2.05(2)	1.89(2)
6	3.049(2)	2.102(7)	2.048(8)	2.034(8)	1.97(1)
7A Cu(1)	3.078(1)	2.056(6)	2.065(7)	2.054(7)	1.931(8)
7A Cu(2)	—	2.059(7)	2.023(6)	2.046(8)	1.921(8)
7B Cu(1)	3.074(1)	2.087(7)	2.047(7)	2.065(7)	1.933(7)
7B Cu(2)	—	2.029(7)	2.059(7)	2.043(7)	1.917(8)
14 Cu(1)	3.209(1)	2.080(7)	2.080(5)	2.080(5)^{b}	2.217(2)^{c}
14 Cu(2)	—	2.055(7)	2.076(5)	2.076(5)^{b}	2.208(2)^{c}
2	3.098(3)	2.05(1)	2.04(1)	2.063(9)	1.91(1)
3	3.065(2)	2.067(5)	2.059(5)	2.037(5)	1.946(5)
Range	3.038–3.098^{d}		2.02–2.10^{e}		1.89–1.97^{d}
Average	3.067^{d} (3.087^{e})		2.058^{d} (2.052^{e})		1.93^{d}
Bis(pyridazine) bridged cations					
1	3.325(3)	1.972(9)	1.976(8)	—	1.885(9)

	Between pyridazine nitrogen atoms^{a}			Between pyridazine and nitrile nitrogen atoms^{a}		
	N(1)–N(2)	N(1)–N(3)	N(2)–N(3)	N(4)–N(1)	N(4)–N(2)	N(4)–N(3)
Tris(pyridazine) bridged cations						
5 Cu(1)	101.9(7)	107.1(7)	101.5(7)	117.6(7)	113.7(8)	113.2(7)
5 Cu(2)	101.2(7)	106.2(7)	104.8(7)	119.4(8)	114.5(8)	109.5(8)
6	100.2(3)	106.6(3)	104.6(3)	104.9(4)	115.6(4)	122.9(4)
7A Cu(1)	101.2(3)	105.9(3)	102.5(7)	115.5(3)	119.7(3)	110.5(3)
7A Cu(2)	105.3(3)	104.5(3)	101.5(3)	109.5(3)	124.6(3)	109.5(3)
7B Cu(1)	103.6(3)	99.9(3)	106.8(3)	119.6(3)	116.4(3)	108.7(3)
7B Cu(2)	104.4(3)	100.5(3)	106.9(3)	122.1(3)	110.4(3)	111.4(3)
14 Cu(1)	101.6(2)	101.6(2)^{b}	99.6(3)^{b}	115.0(2)^{f}	118.1(1)^{f}	118.1(1)^{f}
14 Cu(2)	101.5(2)	101.5(2)^{b}	101.4(3)^{b}	118.9(2)^{f}	115.4(2)^{f}	115.4(2)^{f}
2	103.0(4)	104.1(4)	102.6(4)	113.4(5)	114.6(5)	117.4(4)
3	97.7(2)	106.6(2)	106.3(2)	109.0(2)	117.2(2)	117.8(2)
Range		97.7–107.4^{e}			104.9–124.6^{e}	
Average		103.6^{d} (103.2^{e})			115.2^{d} (115.5^{e})	
Bis(pyridazine) bridged cations						
1	120.6(3)	—	—	119.1(4)	120.1(4)	—

^{a} N(1), N(2) and N(3) are generic labels for the pyridazine nitrogen atoms, N(4) for the nitrile nitrogen. ^{b} Symmetry relationship for N(3): x, y, $0.5 - z$. ^{c} Cu–P distance. ^{d} Excluding data for complex **14**. ^{e} Including data for complex **14**. ^{f} N–Cu–P angles.

Table 4 Dihedral angles (°) between the normals to the bridging ligands in complexes **5**, **6**, **7**, **14**, **2** and **3**

Complex	Angles			Range
5	44.4	65.5	70.1	25.7
6	52.7	52.7	74.6	21.9
7A	56.4	56.7	67.2	10.8
7B	52.7	55.2	72.5	19.8
14	57.2	57.2	65.7	8.5
2	57.7	57.7	64.5	6.8
3	48.9	48.9	85.3	36.4

oriented such that the phenyl rings are in the ‘staggered’ conformation with respect to the pydz rings but in the ‘eclipsed’ conformation with respect to the phenyl rings of the other PPh_3 ligand [Fig. 3(b)]. The torsion angles of both Ph_3P phenyl rings (≈0, ≈0, ≈90°) conform to a rare rotamer class. The rings subtending angles close to 0° are probably in their lowest energy orientation due to the minimum steric interactions of the *ortho* protons on adjacent pyridazine and phenyl moieties; the reason for the third ring subtending an angle close to 90° is not clear.[14]

Each copper atom has an approximately tetrahedral geometry. The complexes are, however, more symmetrical than the tris-bridged complexes with terminal nitriles. The N–Cu–N angles between pyridazines (99.6–101.6°) and the N–Cu–P angles between pyridazines and triphenylphosphines (115.0–118.9°) are not only very limited (Table 3) but also the range of dihedral angles between the normals to the bridging pydz ligands (57.2–65.7°; Table 4).

Molecular structure of the bis(pyridazine)bis(triphenylphosphine)copper(I) cation

The asymmetric unit of complex **13** comprises two $[Cu(pydz)_2(PPh_3)_2]^+$ cations, and two non-co-ordinated PF_6^- anions . The molecular structure of one of the cations is shown in Fig. 4; selected interatomic distances and angles are collated in Table 5. The cations only differ in detail. Each copper atom has a distorted tetrahedral geometry. The distortions are due to the steric bulk of the PPh_3 ligands which results in large P–Cu–P angles (Cu(1) 118.3°; Cu(2) 119.6°), intermediate P–Cu–N angles (average Cu(1) 109.0°; Cu(2) 108.0°) and small N–Cu–N angles (Cu(1) 101.1°; Cu(2) 102.7°). The only significant differences between the cations lie in the PPh_3 torsion angles (Table 6), which unlike those found in **14** fall into the expected classes for rotamers.[14]

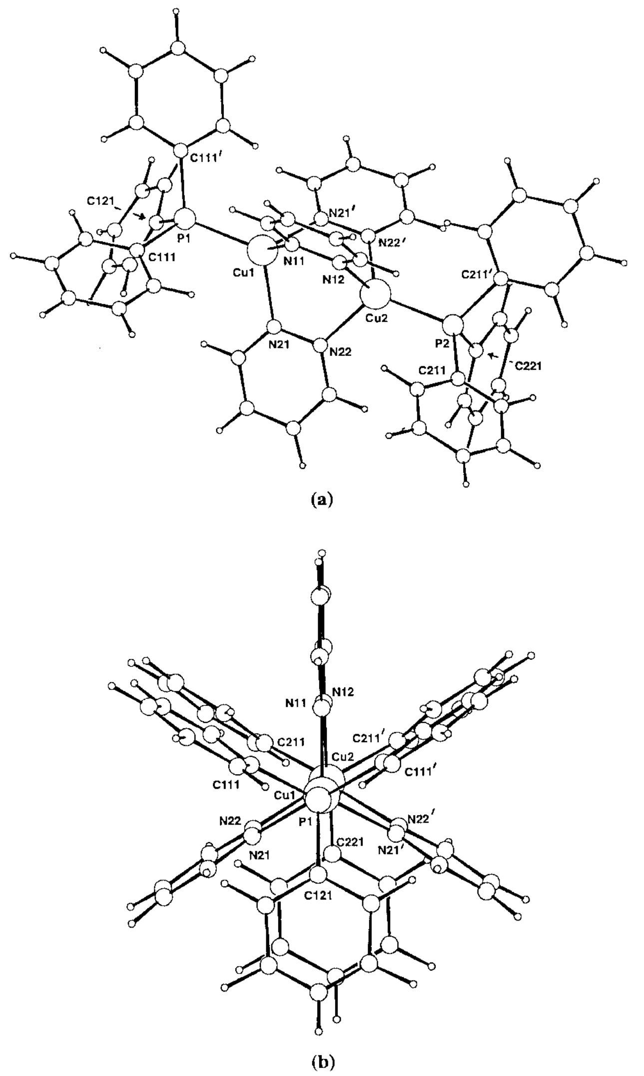


Fig. 3 Molecular structure of the $[\{Cu(PPh_3)\}_2(\mu\text{-pydz})_3]^{2+}$ cation in the structure of complex **14** viewed perpendicular to (a) and along (b) the Cu···Cu vector (atoms related by the mirror plane are primed).

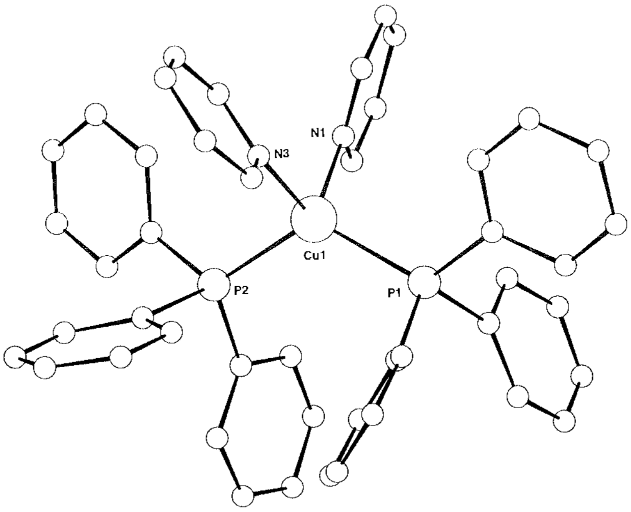


Fig. 4 Molecular structure of the $[Cu(PPh_3)_2(pydz)_2]^+$ cation in the structure of complex **13**.

Table 5 Interatomic distances (Å) and angles (°) for complex **13**

Cu(1)–N(1)	2.066(8)	Cu(2)–N(5)	2.059(8)
Cu(1)–N(3)	2.112(8)	Cu(2)–N(7)	2.094(9)
Cu(1)–P(1)	2.255(3)	Cu(2)–P(3)	2.271(3)
Cu(1)–P(2)	2.268(3)	Cu(2)–P(4)	2.248(3)
N(1)–Cu(1)–N(3)	101.1(3)	N(5)–Cu(2)–N(7)	102.8(3)
N(1)–Cu(1)–P(1)	110.7(2)	N(5)–Cu(2)–P(3)	107.7(3)
N(1)–Cu(1)–P(2)	108.4(2)	N(5)–Cu(2)–P(4)	113.8(2)
N(3)–Cu(1)–P(1)	112.6(2)	N(7)–Cu(2)–P(3)	97.6(3)
N(3)–Cu(1)–P(2)	104.2(3)	N(7)–Cu(2)–P(4)	113.0(3)
P(1)–Cu(1)–P(2)	118.3(1)	P(3)–Cu(2)–P(4)	119.6(1)

Table 6 Torsion angles (°) for the PPh_3 ligands in complexes **13** and **14**; comparison with those in free PPh_3[a] and those calculated for the most stable rotamer[b]

$[Cu(pydz)_2(PPh_3)_2][BF_4]$ **13**				
Cu(1)	P(1)	0	49	88
	P(2)	74	31	33
Cu(2)	P(3)	2	52	95
	P(4)	52	44	84
$[\{Cu(PPh_3)\}_2(\mu\text{-pydz})_3][PF_6]_2\cdot CH_2Cl_2$ **14**				
Cu(1)	P(1)	0	0	90
Cu(2)	P(2)	0	0	90
Free PPh_3[a]		24.8	61.8	28.0
Calculated data[b]		22.0	58.6	27.8

[a] Ref. 15. [b] Ref. 16.

Conclusion

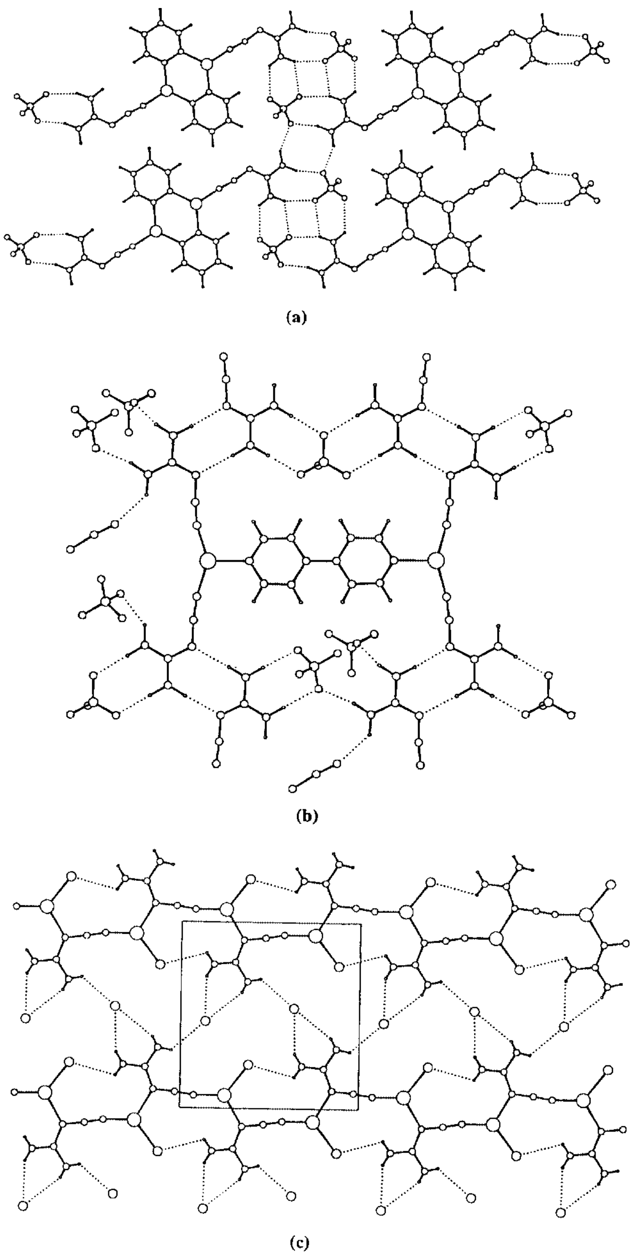
Of the three terminal nitriles, cnge, MeCN and PhCN, only cnge promotes trigonal planar copper(I) in bis(μ-pydz) dinuclear complexes; the others generate tetrahedral copper(I) in tris(μ-pydz) dinuclear complexes. It follows that the stabilisation of co-ordinatively unsaturated copper(I) in these systems cannot be attributed solely to the presence of π-acceptor ligands, reinforcing our earlier conclusions based on EHMO calculations.[6]

Detailed analysis of those copper(I)–cnge complexes which are three-co-ordinate, $[\{Cu(cnge)_2\}_2(\mu\text{-}4,4'\text{-bipy})][BF_4]_2\cdot MeCN$ **16** [Fig. 5(b)][9] and $[Cu_2Cl_2(cnge)]$ **17** [Fig. 5(c)][6] as well as **1** [(Fig. 5(a)] reveals that they all form 2-D sheet structures. Since similar packing arrangements to those in **1** can be envisaged for the analogous MeCN and PhCN complexes, the formation of the 2-D architecture involving cnge must be energetically more favourable.

Consideration of Fig. 5 shows that in each case the extended structure is generated by hydrogen-bonding interactions based on the planar cnge ligand. Donor N–H contacts with anions (N–H···FBF_3^- in **1** and **16**; N–H···Cl^- in **17**) and paired donor–acceptor interactions between cnge ligands (N–H···N in **16**) form the basis of these interactions (Scheme 4). Structural parameters for these contacts are collated with data for other complexes containing co-ordinated cnge in Table 7; they are very similar. They are also comparable to those of the N–H···FBF_3^- contacts (N–H 0.85 Å; H···F: range 2.03–2.22, average 2.13 Å; N···F: range 2.88–3.09, average 2.96 Å; N–H···F: range 146–174°, average 157°) in systems containing *N,N′*-substituted guanidine moieties and BF_4^- anions.[17] All of these N–H···FBF_3^- contacts lie in the middle of the range of N–H···F literature data. Shorter N–H···F hydrogen bonds involve the fluoride anion, a very strong proton acceptor;[18,19] longer ones involve organic fluorines, which have low proton affinities.[18–20]

The paired N–H···N donor–acceptor contacts between cnge molecules in complex **16** and the N–H···Cl^- interactions in **17**, both of which are similar to those in other cnge complexes (Table 7), are typical of N–H···N (N···N: range 2.8–3.2 Å) and N–H···Cl^- (N···Cl: range 3.2–3.4 Å) hydrogen bonds, respectively.[21]

To create sheet structures analogous to that of complex **1** [Fig. 5(a)] and hence stabilise three-co-ordinate copper(I),



(a)

(b)

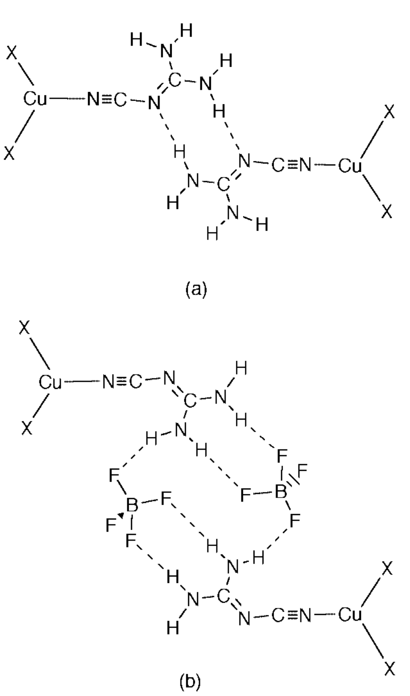
(c)

Fig. 5 Construction of 2-D sheet structures by hydrogen-bonding interactions involving co-ordinated cnge molecules and anions in [{Cu(cnge)}$_2$(pydz)$_2$][BF$_4$]$_2$ (a), [{Cu(cnge)$_2$}$_2$(4,4′-bipy)][BF$_4$]$_2$·MeCN (b) and [{Cu$_2$Cl$_2$(cnge)}$_\infty$] (c).

the terminal nitriles MeCN and PhCN would have to rely on C–H···F hydrogen-bonding interactions. Such contacts, indeed C–H···X (X = O, N, F, Cl or Br) contacts in general, are extremely weak[22] and hence exceedingly rare.[23] Consequently, with terminal ligands which do not possess the hydrogen-bonding capability of cnge, such as MeCN, PhCN, CO and PPh$_3$, the intermolecular interactions required to generate the sheet structure of **1** are absent and four-co-ordinate copper(I) is formed. Thus, we conclude that the three-co-ordinate copper(I) geometry of **1**, **16** and **17** is not an intrinsic property but is a consequence of the efficient packing of two-dimensional sheet architectures.

Experimental

All reactions were carried out under a nitrogen atmosphere using standard Schlenk techniques unless otherwise noted. Nitrogen gas (Air Products) was dried by passage over molecular sieve (Linde 4A). Carbon monoxide gas (Air Products) was used as received. All chemicals (Aldrich Chemical Company Ltd.) were reagent grade used as received unless otherwise noted. The solvents were dried before use by refluxing under dry nitrogen over the appropriate drying agent[24] and degassed using three freeze–thaw cycles.



Scheme 4 Direct (a) and anion mediated (b) intermolecular hydrogen-bonding contacts linking three-co-ordinate copper(I) through co-ordinated cnge.

The copper(I) starting material, [Cu(NCMe)$_4$][BF$_4$] **4**, was prepared either by addition of an excess of copper powder to the product of the reaction of copper gauze with NOBF$_4$ in MeCN[25] or by treatment of hydrated copper(II) tetrafluoroborate with copper powder in MeCN.[26]

Elemental analyses, mass spectra and infrared spectra (Table 1) were consistent with the proposed product structures. Microanalytical, copper analytical and mass spectral data were obtained by Mr T. J. Spencer (PE 240B mass elemental analyzer), Mr M. Guyler (PE Atomic Absorption Spectrophotometer) and Mr A. Hollingworth (VG70E Micromass Spectrometer), respectively, of the University of Nottingham Chemistry Department Analytical Services Group. The IR spectra were obtained on a Perkin-Elmer PE983G spectrometer as KBr pressed pellets, unless otherwise noted.

Preparation of complexes

Bis(acetonitrile)tris(μ-pyridazine)dicopper(I) tetrafluoroborate 5. Freshly prepared complex **4** (1.322 g, 4.2 mmol) was dissolved in MeCN (80 cm^3) and pydz (0.336 g; 4.2 mmol) added dropwise with stirring. After 12 h the solvent volume was reduced (≈30 cm^3) under vacuum and Et$_2$O (50 cm^3) added. The resulting air sensitive, yellow powder (2.18 g, 3.44 mmol, 82%), which analysed (Table 1) for [{Cu(NCMe)}$_2$(μ-pydz)$_3$][BF$_4$]$_2$·0.25MeCN, was recrystallised by slow interfacial diffusion of Et$_2$O into MeCN solution. Structural characterisation showed the air sensitive yellow crystals to be [{Cu(NCMe)}$_2$(μ-pydz)$_3$][BF$_4$]$_2$·MeCN.

Bis(acetonitrile)tris(μ-3-methylpyridazine)dicopper(I) tetrafluoroborate 6. Complex **6** was prepared as for **5** using 3-Mepydz (0.395 g; 4.20 mmol) in place of pydz. The air sensitive yellow product (2.15 g, 3.23 mmol, 77%) was recrystallised by slow interfacial diffusion of Et$_2$O into MeCN solution. The resulting pale orange crystals, which have the same composition as the yellow powder, were shown by elemental, spectroscopic (Table 1) and structural analysis to have the formulation [{Cu(NCMe)}$_2$(μ-Mepydz)$_3$][BF$_4$]$_2$.

Table 7 Structural parameters for hydrogen bonding interactions involving co-ordinated cnge[a]

Compound[b]	H···X/Å range; average	N···X/Å range; average	N–H···X/° range; average	Ref.
N–H···F (cnge···BF_4^-)				
$[\{Cu(cnge)\}_2(\mu\text{-}pydz)_2][BF_4]_2$ **1**	2.10–2.11; 2.11	3.00–3.09; 3.03	148–158; 151	7
$[\{Cu(cnge)_2\}_2(\mu\text{-}4,4'\text{-}bipy)][BF_4]_2\cdot MeCN$ **16**[c]	1.89–2.00; 1.95	2.89–2.99; 2.94	161–174; 169	9
$[Cu(bipy)(cnge)_2(BF_4)_2]$	1.90	2.87	162	13
$[Cu(bipy)_2(cnge)][BF_4]_2\cdot H_2O$	1.86–2.18; 2.04	2.86–3.13; 3.01	155–173; 162	13
$[\{Cu(cnge)\}_2(\mu\text{-}pydz)_3][BF_4]_2$	1.95–2.14; 2.04	2.90–3.02; 2.94	142–160; 149	7
$[Cu(cppd)(cnge)_2(H_2O)(BF_4)][BF_4]$[d]	1.99–2.29; 2.17	2.96–3.16; 3.08	143–163; 151	12
$[Cu(cmppd)_2(cnge)][BF_4]_2$	1.87–2.18; 1.97	2.86–3.06; 2.94	146–179; 168	12
N–H···N (cnge···cnge)				
$[\{Cu(cnge)_2\}_2(\mu\text{-}4,4'\text{-}bipy)][BF_4]_2\cdot MeCN$ **16**[c]	2.03–2.09; 2.06	3.03–3.08; 3.06	167–177; 173	9
$[Cu(bipy)(cnge)_2(BF_4)_2]$	2.08	3.07	170	13
$[Cu(bipy)(cnge)_2Cl_2]\cdot H_2O$	2.00	2.98	167	13
N–H···Cl (cnge···Cl^-)				
$[Cu_2Cl_2(cnge)]$ **17**	2.46–2.48; 2.47	3.39–3.41; 3.40	149–156; 153	6
$[Cu(bipy)(cnge)_2Cl_2]\cdot H_2O$	2.39–2.49; 2.44	3.24–3.46; 3.35	141–164; 153	13
$[Cu(cmppd)(cnge)Cl_2]\cdot H_2O$	2.41–2.49; 2.45	3.32–3.33; 3.33	142–151; 147	12

[a] Minimum N–H···X angle considered 140° and N–H 1.00 Å. [b] cppd = 3-chloro-6-(pyrazol-1-yl)pyridazine, cmpdd = 3-chloro-6-(3,5-dimethylpyrazol-1-yl)pyridazine. [c] Data for four independent cnge ligands. [d] Data for two independent cnge ligands.

Bis(benzonitrile)tris(μ-pyridazine)dicopper(I) tetrafluoroborate 7. Freshly prepared complex **4** (2.806 g, 8.92 mmol) was dissolved in PhCN (80 cm^3) and pydz (0.714 g; 8.92 mmol) added dropwise with stirring. After 12 h the solvent volume was reduced (≈30 cm^3) under vacuum and Et_2O (50 cm^3) added to give a fine, bright yellow, air sensitive, powder (4.60 g, 6.16 mmol, 70%) which was filtered off washed with Et_2O (5 × 50 cm^3) and dried under a flow of nitrogen. Bright yellow crystals were obtained by interfacial diffusion of Et_2O into MeCN solution. They had the same composition as the powder and were shown by elemental, spectroscopic (Table 1) and structural analysis to have the formulation $[\{Cu(NCPh)\}_2(\mu\text{-}pydz)_3][BF_4]_2$.

Bis(cyanoguanidine)bis(μ-pyridazine)bis(triphenylphosphine)-dicopper(I) tetrafluoroborate 12, bis(pyridazine)bis(triphenylphosphine)copper(I) tetrafluoroborate 13 and tris(μ-pyridazine)bis(triphenylphosphine)dicopper(I) hexafluorophosphate–dichloromethane (1/1) 14. To a solution of complex **4** (3.15 g; 10 mmol) in MeCN (25 cm^3) was added cnge (0.84 g; 10 mmol) and pydz (0.80 g; 10 mmol) to give a yellow solution of **1**. Triphenylphosphine (2.62 g; 10 mmol) was added and the solution stirred for 24 h. The resulting bright yellow, air sensitive powder (4.50 g, 3.90 mmol, 78%) analysed (Table 1) for $[\{Cu(cnge)(PPh_3)\}_2(\mu\text{-}pydz)_2][BF_4]_2$. Recrystallisation by diffusion of heptanes into an acetone solution gave both microcrystalline yellow blocks and large colourless blocks. The former, which slowly decomposed after removal from solvent, analysed for $[\{Cu(cnge)(PPh_3)\}_2(\mu\text{-}pydz)_2][BF_4]_2$. Although not sufficiently stable for diffraction data to be obtained, oscillation and Weissenberg photographs indicated an orthorhombic cell (space group *C*222, *Cmm*2 or *Cmmm*) with $a \approx 25.7$, $b \approx 11.0$, $c \approx 17.3$ Å and $U \approx 4891$ $Å^3$. Assuming $Z = 4$, the calculated density ($M = 1153.5$) is 1.566. The latter air-stable crystals were structurally characterised as $[Cu(pydz)_2(PPh_3)_2][BF_4]$.

In an attempt to obtain better quality crystals of the $[\{Cu(cnge)(PPh_3)\}_2(\mu\text{-}pydz)_2]^{2+}$ cation, the experiment was repeated using $[Cu(NCMe)_4][PF_6]$. Large yellow plates were obtained which were shown by elemental (Table 1) and structural analysis to have the formulation $[\{Cu(PPh_3)\}_2(\mu\text{-}pydz)_3][PF_6]_2\cdot CH_2Cl_2$.

Reaction of complex 5 with carbon monoxide

Bubbling carbon monoxide through a CH_2Cl_2 solution (20 cm^3) of complex **5** (0.05 g; 0.0753 mmol) gave a yellow precipitate under a yellow solution. Elemental and spectroscopic analysis (Table 1) of the yellow solid (0.035 g; 0.0586 mmol; 78%) suggested the formulation $[\{Cu(CO)\}_2(\mu\text{-}pydz)_3][BF_4]_2$ or $[\{Cu(CO)(NCMe)\}_2(\mu\text{-}pydz)_2][BF_4]_2$.

Reaction of complex 6 with carbon monoxide

This reaction was carried out as above, replacing complex **5** by **6** (0.05 g; 0.0752 mmol). Elemental and spectroscopic analysis (Table 1) of the yellow solid (0.03 g; 0.0469 mmol; 62%) suggested the formulation $[\{Cu(CO)\}_2(\mu\text{-}Mepydz)_3][BF_4]_2$.

Reaction of tris(μ-3-methylpyridazine)dicopper(I) cations terminally co-ordinated by acetonitrile with 2-cyanoguanidine

Addition of cnge to a dichloromethane solution of complex **6** gave a yellow precipitate. Elemental analysis of the product suggested the formulation $Cu_2(BF_4)_2(Mepydz)(cnge)_3$ **15** (Table 1). IR Spectroscopic studies confirmed the presence of cnge, Mepydz and BF_4^-. Three bands in the ν_{asym}(NCN) region suggested the presence of two independent cnge molecules.

Crystallography

X-Ray diffraction data for the refinement of cell parameters and structure determination were collected at room temperature using Hilger and Watts Y290 (**5**, **6**, **13** and **14**) or Siemens P4 (**7**) four-circle diffractometers. For each crystal one unique set of data was collected in the range $2\theta \leqslant 50$ (**5**, **6**, **13** and **14**) or $\leqslant 45°$ (**7**) using graphite monochromated Mo-Kα radiation ($\lambda = 0.71073$ Å). All five sets of data were corrected for Lorentz-polarisation effects. A semi-empirical absorption correction, based on 264 Ψ scans of 11 reflections, was also applied for complex **7** with minor effect ($T_{min} = 0.676$; $T_{max} = 0.726$).[27] Crystallographic data for all five complexes are in Table 8.

The positions of the copper atoms in complexes **5**, **6**, and **14** were determined by Patterson methods (CRYSTALS[28]); those in **13** were obtained by direct methods (MULTAN 80[29]). The positions of the remaining non-hydrogen atoms were obtained by Fourier-difference syntheses (CRYSTALS[28]). The hydrogen atoms were placed and allowed to ride on the parent atom in the calculated position. Full matrix least squares refinement (CRYSTALS[28]) against *F* was undertaken.

Owing to the weak data set for complex **5** only the copper, nitrogen and fluorine atoms were refined anisotropically; the carbon atoms were refined isotropically. Three crystallographically independent BF_4^- anions and two crystallographically

Table 8 Crystallographic data for complexes **5**, **6**, **7**, **13** and **14**

Complex	**5**	**6**	**7**	**13**	**14**
Formula	$C_{16}H_{18}B_2Cu_2F_8N_8\cdot$ MeCN	$C_{19}H_{24}B_2Cu_2F_8N_8$	$C_{26}H_{22}B_2Cu_2F_8N_8$	$C_{44}H_{38}BCuF_4N_4P_2$	$C_{48}H_{42}Cu_2F_{12}N_6P_4\cdot CH_2Cl_2$
M	664.13	665.16	747.22	835.12	1266.81
Crystal system	Monoclinic	Monoclinic	Triclinic	Triclinic	Orthorhombic
Space group	$C2/c$ (no. 15)	$C2/c$ (no. 15)	$P\bar{1}$ (no. 2)	$P\bar{1}$ (no. 2)	*Pnam* (no. 62)
a/Å	12.726(1)	25.289(4)	12.932(1)	10.814(4)	29.281(9)
b/Å	41.705(4)	8.514(2)	13.138(1)	15.523(4)	8.567(3)
c/Å	12.571(1)	14.211(3)	18.800(2)	26.746(7)	21.389(7)
α/°	—	—	92.45(2)	86.86(3)	—
β/°	113.57(2)	114.31(3)	91.86(2)	100.39(2)	—
γ/°	—	—	90.07(2)	100.91(2)	—
U/Å^3	6115(1)	2789(1)	3190(1)	4335(1)	5365(1)
Z	8	4	4	4	4
μ(Mo-Kα)/mm^{-1}	1.463	1.605	1.410	0.626	1.093
Observed reflections[a]	1463	1298	4875	7498	2929
$wR2$ (all data); R ($I \geq 2\sigma(I)$)	—	—	0.173; 0.062	—	—
R; R' ($I \geq 2\sigma(I)$)[a]	0.095; 0.101	0.083; 0.093	—	0.069; 0.088	0.063; 0.090

[a] [$I \geq 2\sigma(I)$] except for complexes **13** and **14** for which [$I \geq 3\sigma(I$].

independent MeCN solvate molecules occur in the structure. One anion, which lies on a 2-fold axis, is disordered; it was modelled by four 50% occupancy fluorine atoms with large thermal parameters. One of the solvate MeCN molecules is disordered over two positions related by a 2-fold axis on which the nitrogen is located.

A 2-fold axis of symmetry bisects the cation in complex **6**. Restraints had to be applied to model successfully the disordered Mepydz bridge. Although the atoms comprising this ligand could only be refined isotropically, the remaining non-hydrogen atoms were refined anisotropically. Disorder in the BF_4^- anion was modelled by six 67% occupancy fluorine atoms with large thermal parameters.

The structure of complex **13** exhibits no disorder. The only disorder in **14** involves the CH_2Cl_2 solvate molecule, which is located on an inversion centre with 50% overall occupancy of the two symmetry related positions but 100% chlorine occupancy.

The structure of complex **7** was solved by direct methods (SHELXS 86[30]). Full least squares matrix refinement (SHELXL 93[31]) of all non-hydrogen atoms with anisotropic displacement parameters was completed against F^2 with the hydrogens riding in calculated positions. All structure diagrams were generated using the CAMERON suite of programs.[32]

CCDC reference number 186/1694.

See http://www.rsc.org/suppdata/dt/1999/4251/ for crystallographic files in .cif format.

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