Bis(μ-pyridazine)-bis[(2-cyanoguanidine)copper(I)] Cation: A Molecule containing two Co-ordinatively Unsaturated Copper(I) Centres†

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2-Cyanoguanidine [$(NH_2)_2CNCN$ (cnge)] stabilises co-ordinatively unsaturated copper(I) in bis(μ-pyridazine)-bis[(2-cyanoguanidine)copper(I)] tetrafluoroborate **1**, which has been structurally characterised by single-crystal X-ray diffraction analysis [triclinic, space group $P\bar{1}$, a = 754.8(2), b = 971.3(2), c = 937.2(2) pm, α = 118.94(2), β = 94.72(2), γ = 107.44(2)°]. The cation in **1** contains two trigonal-planar copper(I) atoms bridged by two pyridazine (pydz) molecules and terminally co-ordinated by a cnge molecule. It acts as a receptor molecule binding a further pydz to form tris(μ-pyridazine)-bis[(2-cyanoguanidine)copper(I)] tetrafluoroborate **2**. The structure of **2** was also determined [monoclinic, space group $C2/c$, a = 2229.3(7), b = 850.0(3), c = 1568.5(3) pm, β = 99.13(2)°]. It contains two distorted-tetrahedral copper(I) atoms bridged by three pydz molecules and terminally co-ordinated by a cnge molecule. Thermogravimetric analysis of **2** showed that heating removes the third bridging pydz molecule to regenerate **1**; this behaviour is ascribed to the unusually high stability of the co-ordinatively unsaturated copper(I) moiety in **1**.

A large number of copper(I) complexes have been structurally characterised. They are dominated by four-co-ordinate tetrahedral copper(I) ions, with fewer examples of co-ordinatively unsaturated (*i.e.* two- or three-co-ordinate) copper(I).[1-5] Recently, the isolation of co-ordinatively unsaturated copper(I) has become increasingly more significant owing to its postulated importance in many catalytic[6] and biological[7] systems. We are thus engaged in the study of the successful stabilisation and isolation of three-co-ordinate copper(I) with a variety of different ligands. From a study of the properties and reactions of the new copper(I) complexes we hope to gain an insight into the mechanisms of action of many copper-containing catalysts and enzymes. Previously, we have published[8,9] accounts of the structural characterisation of three-co-ordinate copper(I) moieties crystallised from aqueous solution. The present paper reports the results from an extension to those studies, aimed at preparing and isolating a discrete cation containing *two* unsaturated copper(I) centres separated by *ca.* 350 pm, similar to the active centre in the dioxygen-carrying proteins, haemocyanins.[10,11]

The factors which control the stabilisation of three-co-ordinate copper(I) have been shown to be based on steric or electronic effects;[3,4,12-15] early examples of complexes with approximate local D_{3h} symmetry used either very bulky ligands[16] or ligands with π-acceptor capability (*e.g.* CN^-)[17] to prevent co-ordination by a fourth ligand. Recently, extended-Hückel calculations[9] have rationalised the ability of π-bonding ligands including 2-cyanoguanidine $(NH_2)_2CNCN$ (cnge) as well as CN^- to stabilise unsaturated copper(I) to such an extent that the copper(I) complex can be crystallised from an aqueous solution without decomposition.[8,9]

The complexes reported herein have cnge as a ligand, affording three-co-ordinate copper(I) centres. They also contain pyridazine (pydz) to generate binuclear complexes with Cu ··· Cu separations close to that in deoxy- (≈360 pm)[10] and oxy-haemocyanins (≈340 pm).[11] Although the use of tetradentate N-donor ligands based on pydz, typically 3,6-bis(2-pyridyl)pyridazine,[18] 3,6-bis(pyrazol-2-yl)pyridazine[19] and pyridazine-3,6-dicarbaldehyde dioximate,[20] to generate binuclear complexes has been described in detail, the potential of pydz and its alkyl and aryl derivatives as bridges has been little considered.[21] Initially used mainly to bridge transition-metal carbonyl fragments,[22-31] they are now being used in more diverse systems.[32-41] Structurally characterised pydz-bridged complexes are rare; they are limited to molybdenum(V),[32] iron-(0),[22] -(I),[23] ruthenium-(0),[24,25] -(II),[40] rhodium-(II),[40] -(III)[33] and tin(IV),[34] as well as copper-(I)[35-37] and -(II).[38] Although the majority of these are dinuclear,[22-25,32-35,40] several are polymeric.[36-38] In all the dinuclear complexes the pydz bridge is supported by either a metal–metal bond,[22-25,40] a second bridging unit (sulfide,[32] oxide,[32,40] chloride,[33] methylene,[34] maleic anhydride,[23] carbon monoxide[22] or metal carbonyl fragment[24,25]) or a binucleating macrocycle (L = 5,5,16,16-tetramethyl-23,24-dioxa-3,7,14,18-tetraazatricyclo-[18.2.1.1^{9,12}]tetracosa-2,7,9,11,13,18,20,22-octaene[35]). All the copper(I) complexes contain four-co-ordinate copper; [$\{Cu(pydz)(CN)\}_n$] contains two interlocking copper(I) chains bridged by either single pydz molecules or cyanide anions.[36] Tetra-(μ-3-methylpyridazine)-tri-μ-pyrazine-tetracopper(I) perchlorate comprises a chain of tetrameric copper(I) units linked by bridging pyrazine molecules; within each unit the four copper atoms are bridged alternatively by two 3-methylpyridazine molecules and one pyrazine molecule.[37] The complex $[Cu_2L(pydz)_2][ClO_4]_2$ comprises two copper(I) atoms located in the binucleating macrocycle and bridged by two pydz molecules.[35]

Results and Discussion

A novel, dimeric, unsaturated copper(I) cation has been prepared by treating tetrakis(acetonitrile)copper(I) tetrafluoroborate with equimolar amounts of pydz and cnge in acetonitrile (Scheme 1). The resulting air-sensitive yellow complex was structurally characterised as the bis(μ-pyridazine)-bis[2-cyanoguanidine)copper(I)] tetrafluoroborate **1**. This species reacts very readily with a further pydz molecule to form an orange complex which was structurally characterised as the novel tris(μ-pyridazine)-bis[(2-cyanoguanidine)copper(I)]

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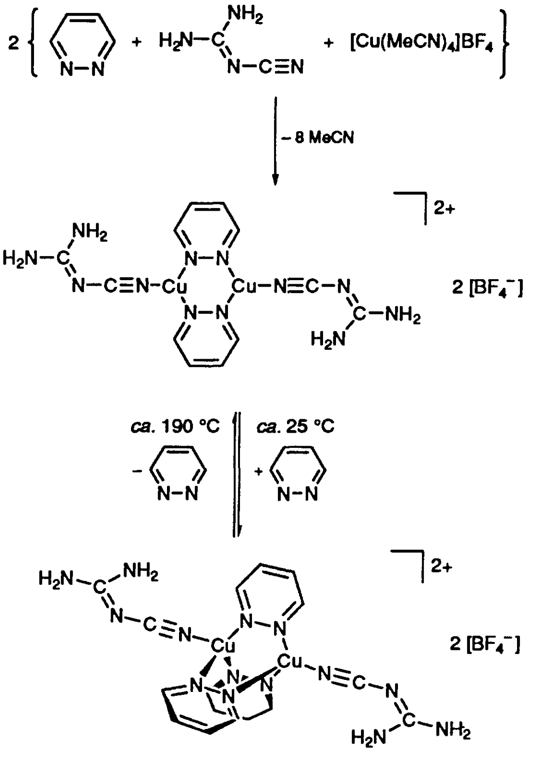
† *Supplementary data available:* see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1994, Issue 1, pp. xxiii–xxviii.

fluoroborate **2**. The tris(pydz)-bridged complex is interesting insofar as thermogravimetric analysis shows that heating removes one pydz molecule at *ca.* 190 °C to regenerate the bis(pydz)-bridged species. This behaviour is reminiscent of the reversible binding of substrates to the unsaturated dicopper(I) site in deoxyhaemocyanins.[7] It is rare that co-ordinatively saturated copper(I) will afford three-co-ordinate copper(I) by facile ligand loss. This behaviour can be ascribed to the unusual high stability of the unsaturated copper(I) configuration in the presence of cnge.



Scheme 1

Crystal and Molecular Structures of Complexes **1** *and* **2**.—The fractional coordinates of the atoms are given in Table 1, selected interatomic distances and angles in Table 2. The structure of complex **1** consists of a centrosymmetric dicopper(I) cation with bridging pydz molecules and terminal cnge molecules and independent BF_4^- anions. The cation is essentially planar (Fig. 1), with the maximum deviation from the best-fit least-squares plane being 17 pm (a pydz carbon atom, Table 3). The planar cations are stacked in a stepped fashion with the nitrile moiety of one cnge positioned directly above a copper atom in an adjacent cation. There is no significant interaction, other than van der Waals contacts, between adjacent cations. The BF_4^- anions lie between the cation stacks, and are held in place by weak hydrogen bonds to the cnge moiety *via* fluorine–amino hydrogen contacts (Table 4). These interactions, although long in comparison with the calculated $NH_n \cdots F^-$ distance (290 pm),[43] provide for a well ordered structure with no disordering of the anions.

The copper and its ligating atoms essentially lie in a plane with only a slight deviation of the copper atom (3.7 pm, Table 3) out of the plane towards the nitrile moiety of an adjacent planar cation. Best-fit least-squares planes were also calculated for the pydz (deviation from plane $\leqslant$0.9 pm) and cnge (deviation from plane $\leqslant$2.8 pm) molecules. The dihedral angles between the three planes (Table 3) are all small (maximum 11.8° between pydz and cnge best-fit planes), the cnge molecule being almost

Table 1 Fractional coordinates for all atoms in $[Cu_2(\mu\text{-pydz})_2(cnge)_2][BF_4]_2$ and $[Cu_2(\mu\text{-pydz})_3(cnge)_2][BF_4]_2$

Atom	*X/a*	*Y/b*	*Z/c*	Atom	*X/a*	*Y/b*	*Z/c*
(*a*) $[Cu_2(\mu\text{-pydz})_2(cnge)_2][BF_4]_2$							
Cu(1)	0.139 2(2)	0.391 5(2)	0.482 3(2)	B(1)	0.799(2)	0.729(2)	0.108(2)
C(1)	0.436(2)	0.233(1)	0.454(1)	F(1)	0.645(1)	0.691(1)	0.170(1)
C(2)	0.701(2)	0.211(1)	0.558(1)	F(2)	0.743(1)	0.714(1)	−0.038 4(9)
N(1)	0.318(1)	0.287(1)	0.457(1)	F(3)	0.894(1)	0.619 4(9)	0.090 0(9)
N(2)	0.556(1)	0.153(1)	0.428(1)	F(4)	0.926(1)	0.899(1)	0.227(1)
N(3)	0.730(2)	0.335(2)	0.712(1)	H(31)	0.64(1)	0.40(1)	0.74(1)
N(4)	0.825(2)	0.132(2)	0.525(2)	H(32)	0.84(2)	0.37(2)	0.80(2)
C(11)	0.314(2)	0.653(2)	0.836(2)	H(41)	0.94(2)	0.17(1)	0.62(1)
C(12)	0.352(2)	0.802(2)	0.990(2)	H(42)	0.81(2)	0.04(2)	0.41(2)
C(13)	−0.246(2)	0.104(2)	−0.001(2)	H(111)	0.40(2)	0.59(1)	0.83(1)
C(14)	−0.106(2)	0.167(2)	0.140(1)	H(121)	0.45(1)	0.84(1)	1.09(1)
N(11)	0.177(1)	0.596(1)	0.702(1)	H(131)	−0.27(2)	−0.01(2)	−0.11(2)
N(12)	−0.070(1)	0.308(1)	0.285(1)	H(141)	−0.02(2)	0.10(2)	0.13(2)
(*b*) $[Cu_2(\mu\text{-pydz})_3(cnge)_2][BF_4]_2$							
Cu(1)	0.470 23(8)	0.164 5(2)	0.332 8(1)	F(2)	0.173 5(5)	0.346(1)	0.157 0(6)
C(1)	0.411 8(6)	0.171(1)	0.495 8(8)	F(3)	0.136 9(6)	0.104(1)	0.123 5(7)
C(2)	0.343 7(7)	0.085(2)	0.576 6(8)	F(4)	0.226 6(6)	0.144(1)	0.221 6(7)
N(1)	0.435 1(5)	0.171(1)	0.435 9(7)	F(5)	0.180(3)	0.178(9)	0.214(4)
N(2)	0.389 6(5)	0.178(1)	0.568 1(7)	F(6)	0.198(3)	0.036(8)	0.131(5)
N(3)	0.319 7(6)	−0.016(2)	0.519 0(8)	F(7)	0.141(4)	0.23(1)	0.096(6)
N(4)	0.322(1)	0.090(3)	0.650(1)	F(8)	0.238(6)	0.20(1)	0.115(9)
C(11)	0.579 7(9)	0.354(2)	0.412(1)	H(31)	0.336(8)	−0.03(2)	0.46(1)
C(12)	0.635(1)	0.426(2)	0.414(1)	H(32)	0.284(4)	−0.09(1)	0.526(7)
C(13)	0.337 7(9)	0.418(2)	0.158(1)	H(41)	0.341(8)	0.16(2)	0.70(1)
C(14)	0.367 7(7)	0.340(2)	0.226(1)	H(42)	0.29(1)	0.02(3)	0.66(2)
N(11)	0.552 6(5)	0.277(1)	0.343 6(6)	H(111)	0.560(6)	0.36(2)	0.468(9)
N(12)	0.420 1(5)	0.273(1)	0.228 8(8)	H(121)	0.658(7)	0.49(2)	0.47(1)
C(21)	0.471 5(7)	−0.187(1)	0.320(1)	H(131)	0.295(6)	0.47(2)	0.160(9)
C(22)	0.485 6(7)	−0.329(2)	0.284(1)	H(141)	0.346(5)	0.33(1)	0.281(7)
N(21)	0.486 6(4)	−0.054(1)	0.284 3(6)	H(211)	0.450(7)	−0.19(2)	0.37(1)
B(1)	0.190(1)	0.192(2)	0.078(1)	H(221)	0.474(9)	−0.44(2)	0.31(1)
F(1)	0.222 5(6)	0.187(2)	0.080 4(9)				

Table 2 Interatomic distances (pm) and bond angles (°) in complexes **1** and **2**

	1	**2**	Free cnge[42]
Cu(1) · · · Cu(1′)	332.5(3)	309.8(3)	
Cu(1)–N(1)	188.5(9)	191(1)	
Cu(1)–N(11)	197.2(9)	205(1)	
Cu(1)–N(12)	197.6(8)	204(1)	
Cu(1)–N(21)		206.3(9)	
N(1)–C(1)	115(1)	114(1)	117.4(3)
C(1)–N(2)	133(1)	131(1)	130.7(4)
N(2)–C(2)	133(1)	132(1)	134.3(3)
C(2)–N(3)	130(1)	130(1)	134.4(3)
C(2)–N(4)	134(1)	132(1)	133.5(3)
Root-mean-square difference	0.11	0.12	0

	1	**2**	Free cnge[42]
Difference from free cnge	Significant	Significant	None
N(11)–N(12′)	137(1)	137(1)	
N(11)–C(11)	132(1)	131(2)	
C(11)–C(12)	138(2)	137(2)	
C(12)–C(13′)	135(1)	137(2)	
C(13)–C(14)	137(1)	135(2)	
C(14)–N(12)	132(1)	130(1)	
N(21)–N(21′)		131(2)	
N(21)–C(21)		133(1)	
C(21)–C(22)		138(2)	
C(22)–C(22′)		133(3)	

	1	**2**
Cu(1)–N(1)–C(1)	174.7(9)	177(1)
N(1)–C(1)–N(2)	172(1)	174(2)
C(1)–N(2)–C(2)	117.6(9)	118(1)
N(2)–C(2)–N(3)	126(1)	125(1)
N(2)–C(2)–N(4)	115.8(9)	118(1)
N(3)–C(2)–N(4)	119(1)	117(1)
N(1)–Cu(1)–N(11)	119.1(4)	113.4(5)
N(1)–Cu(1)–N(12)	120.1(4)	114.6(5)
N(1)–Cu(1)–N(21)	—	117.4(4)
N(11)–Cu(1)–N(12)	120.6(3)	103.0(4)
N(11)–Cu(1)–N(21)	—	104.1(4)
N(12)–Cu(1)–N(21)	—	102.6(4)
Cu(1)–N(11)–N(12′)	119.6(6)	15.2(9)
Cu(1)–N(11)–C(11)	121.8(7)	126(1)

	1	**2**
Cu(1)–N(12)–N(11)	119.4(6)	114.5(9)
Cu(1)–N(12)–C(14)	122.0(7)	127(1)
Cu(1)–N(21)–N(21′)	—	115.6(2)
Cu(1)–N(21)–C(21)	—	122.9(8)
N(12′)–N(11)–C(11)	118.3(9)	119(1)
N(11)–C(11)–C(12)	123(1)	123(1)
C(11)–C(12)–C(13′)	118(1)	118(2)
C(12′)–C(13)–C(14)	117(1)	117(2)
C(13)–C(14)–N(12)	125(1)	125(1)
C(14)–N(12)–N(11′)	118.6(8)	119(1)
N(21′)–N(21)–C(21)		121.4(7)
N(21)–C(21)–C(22)		119(1)
C(21)–C(22)–C(22′)		119.5(7)

Symmetry operations for X′: $-x, 1-y, 1-z$ (for **1**) and $1-x, y, \frac{1}{2}-z$ (for **2**).

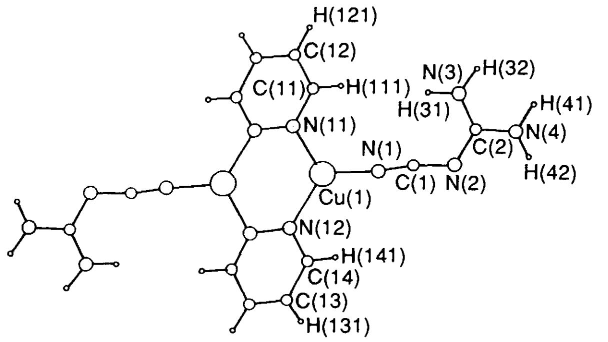


Fig. 1 Molecular structure of the bis(pyridazine)-bridged dicopper(I) cation $[Cu_2(\mu\text{-pydz})_2(cnge)_2]^{2+}$

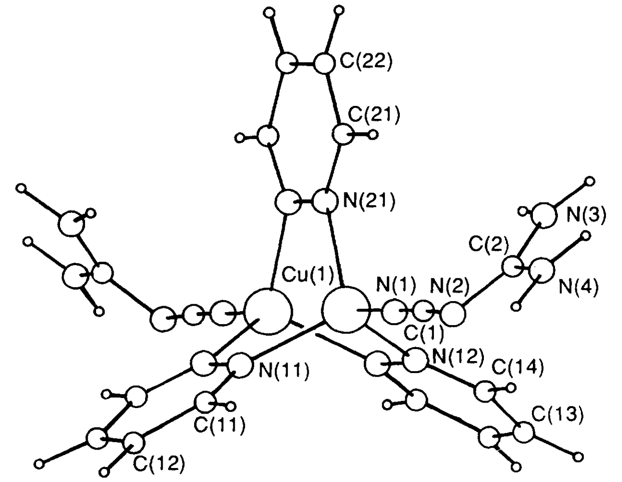


Fig. 2 Molecular structure of the tris(pyridazine)-bridged dicopper(I) cation $[Cu_2(\mu\text{-pydz})_3(cnge)_2]^{2+}$. The numbering scheme for the hydrogen atoms is similar to that in Fig. 1

coplanar with the plane described by the copper co-ordination sphere (dihedral angle 3.8°, Table 3).

The cation in complex **1** contains two symmetry-related co-ordinatively unsaturated copper(I) atoms, bridged in a typical μ-1,2 fashion by two pydz molecules and separated by 332.5 pm. The ligand cnge, co-ordinating *via* its nitrile nitrogen, completes the copper's co-ordination sphere, which can be described as slightly distorted trigonal planar. At the copper centre, deviations from the ideal 120° angle are small, with an average of 119.6(4)° between the cnge nitrogen atom and pydz nitrogen atoms and 120.6(4)° between the two pydz nitrogen atoms (Table 2). Distances between the pydz nitrogen atoms and the copper atom (197.2 and 197.6 pm, Table 2) are typical for a Cu · · · N interaction. That between the cnge nitrogen atom and the copper atom, although somewhat shorter (188.5 pm, Table 2), is typical of cnge terminally co-ordinated to copper(I).[8] Munakata *et al.*[44] have published an empirical correlation between the angles and distances around three-co-ordinate copper(I) for a variety of complexes. Riehl *et al.*[45] have studied the distortion from ideal trigonal geometry to Y- and T-shaped structures by means of extended-Hückel and *ab initio* calculations. The empirical correlation predicts that a copper(I) centre with angles of 120° will have equal copper-to-ligating atom distances. Clearly, in this cation this is not the case, with the rather short copper-to-cnge nitrogen distance differing from the other two Cu · · · N distances by *ca.* 9 pm. This again highlights the unusual co-ordination properties of cnge when interacting with copper(I).

The crystal structure of complex **2** (Fig. 2) shows a dicopper(I) cation with bridging pydz molecules and terminal cnge molecules and BF_4^- anions. The cation lies on a diad axis, which passes through the plane described by one bridging pydz molecule. As in the structure of **1**, the cations lie in a stack, but with the BF_4^- anions between the cations. Weak hydrogen bonds (Table 4) between the cnge amino hydrogen atoms and

Table 3 Best-fit least-squares planes for complexes **1** and **2**

Cation in **1**

Equation of best plane: $3.3427x + 6.6423y - 6.6776z = -0.018$ (plane 1)

Atom	Cu(1)	N(1)	C(1)	N(2)	C(2)	N(3)	N(4)	N(11)	N(12)	C(11)	C(12)	C(13)	C(14)
Deviation from plane/pm	−13.7	−6.8	−0.8	3.8	3.1	−6.6	14.7	12.2	−7.4	17.4	8.8	−10.5	−16.2

Copper co-ordination sphere in **1**

Equation of best plane: $-3.298x - 6.728y + 6.595z = 0.050$ (plane 2)

Atom	Cu(1)	N(1)	N(11)	N(12)
Deviation from plane/pm	3.7	−1.3	−1.2	−1.2

Dihedral angles/° between planes in **1**

Plane	cnge	pydz
Copper co-ordination sphere	3.8	8.4
cnge	—	11.8

Dihedral angles/° between planes in **2**

Plane	cnge*	pydz(1)	pydz(1)*	pydz(2)
cnge	89.0	13.6	−102.3	135.5
pydz(1)	—	—	−115.4	122.3

* Symmetry related by the operations: $1 - x, y, \frac{1}{2} - z$.

Table 4 Possible hydrogen-bond contacts in complexes **1** and **2**

Interaction X–H···X′	X′ Symmetry properties*	r(X···X′)/pm	r(X···H)/pm	r(H···X′)/pm	X–H···X′/°
(*a*) $[Cu_2(\mu\text{-pydz})_2(cnge)_2][BF_4]_2$					
N(3)–H(31)···F(1)	I	310(1)	100	244	123
N(3)–H(31)···F(2)	II	322(1)	100	256	124
N(3)–H(32)···F(3)	III	309(1)	100	211	158
N(3)–H(32)···F(3)	IV	306(1)	100	250	117
N(4)–H(41)···F(4)	V	301(1)	100	211	148
N(4)–H(42)···F(4)	VI	300(1)	100	210	148
(*b*) $[Cu_2(\mu\text{-pydz})_3(cnge)_2][BF_4]_2$					
N(3)–H(31)···F(2)	VII	302(2)	103	211	146
N(3)–H(31)···F(7)	VII	302(2)	103	230	125
N(3)–H(32)···F(1)	VIII	290(2)	103	192	160
N(3)–H(32)···F(1)	VII	299(2)	103	247	110
N(3)–H(32)···F(8)	VIII	300(2)	103	209	145
N(4)–H(41)···F(2)	IX	307(1)	102	236	126
N(4)–H(41)···F(5)	IX	291(7)	102	204	142
N(4)–H(42)···F(4)	VIII	323(2)	102	224	166
N(4)–H(42)···F(6)	VIII	292(7)	102	202	147
N(4)–H(42)···F(8)	VIII	311(14)	102	227	138

* I $1 - x, 1 - y, 1 - z$; II $x, y, 1 + z$; III $2 - x, 1 - y, 1 + z$; IV $x, y, 1 - z$; V $2 - x, 1 - y, 1 - z$; VI $x, -1 + y, z$; VII $\frac{1}{2} - x, -\frac{1}{2} + y, \frac{1}{2} - z$; VIII $x, -y, \frac{1}{2} + z$; IX $\frac{1}{2} - x, \frac{1}{2} - y, 1 - z$.

anion fluorine atoms again afford a fairly well ordered structure with only slight rotational disorder of the anions.

The Cu···Cu separation in complex **2** is maintained by three bridging pydz molecules which co-ordinate in an expected μ-1,2 fashion. Triply bridged dicopper(I) complexes are extremely rare.[46] The reduced Cu···Cu interatomic distance (309.8 pm, Table 2) compared to that in **1** (332.5 pm) is part of the trend towards decreasing interatomic distance with increasing number of bridging ligands, the separation in the polymeric mono(pydz)-bridged species $[\{Cu(pydz)(CN)\}_n]$ being 368 pm.[36] The ligand cnge, co-ordinating *via* its nitrile nitrogen, completes the distorted-tetrahedral co-ordination geometry around the copper in **2**. The angles subtended at the copper between the cnge nitrogen atom and the nitrogen atoms of the pydz rings range from 113.4 to 117.4°, all slightly larger than the ideal angle for tetrahedral co-ordination. This is probably due to the strain imposed on the co-ordination geometry by the tris(pydz) bridge which gives bond angles between the bridging pydz molecules at the copper ranging from 102.6 to 104.1° (Table 2); the limited range in these angles is reflected in the dihedral angles between the pydz planes (deviation from best-fit least-squares planes ⩽1.1 pm) which range from 115.4 to 122.3° (Table 3). There is also a difference in the interatomic distance between the copper and cnge nitrogen (191 pm, Table 2) and the copper and pydz nitrogens (average 205 pm).

The cnge molecules in complex **2** are essentially planar (deviation from best-fit least squares plane ⩽1.3 pm). The dihedral angle between the cnge planes for any given cation is 89.0° (Table 3). Therefore, the planes described by the cnge molecules are almost perpendicular and not coplanar as in **1**.

Multivariate comparison[47,48] of the bond lengths in the cnge molecules in complexes **1** and **2** and free cnge (Table 2) gives a semiquantitative assessment of the overall perturbation to the ligand caused by co-ordination to the copper centre. The comparison indicates that the cnge molecules in the two cations are 'significantly' perturbed (Table 2). In the case of the unsaturated complex the structural changes are probably partly due to the inductive effect of three-co-ordinate copper(I). They may also be related to fact that, as proposed from extended-Hückel molecular orbital calculations,[9] the interaction of cnge with three-co-ordinate copper(I) involves both π-donor cnge (π)–copper ($4p_z$) and π-acceptor cnge (π*)–copper ($3d_{xz,yz}$) interactions. In the absence of strong steric effects these electronic effects are expected to ensure that the cnge molecule is coplanar with the copper co-ordination plane. Notably, the orientation of the cnge molecule in **1** is coplanar with the copper co-ordination plane such that a cnge π-molecular orbital could overlap with the unoccupied copper 4p orbital in the putative interaction.

Infrared Spectra of Complexes **1** *and* **2**.—The IR spectra of pressed KBr pellets of **1** and **2** were obtained; for **1** the spectrum was found to change slowly with time and had to be recorded immediately after sample preparation. The IR spectrum of free cnge[49] contains a diagnostic doublet at *ca.* 2200 cm^{-1}. Upon co-ordination to a metal this changes in shape and moves to higher wavenumber.[8,9,50–52]

For complex **1**, ν_{asym}[N(1)–C(1)–N(2)] was shifted to 2228/2185 from 2209/2165 cm^{-1} for free cnge. This large shift (+19/20 cm^{-1}) corresponds to a significant perturbation to the force constants in cnge when co-ordinated to copper in **1**. For **2**, ν_{asym}[N(1)–C(1)–N(2)] occurred at 2210/2165 cm^{-1}, which, within experimental error, is the same position as for free cnge. Furthermore, the fingerprint region of the spectrum for **2** did not exhibit any significant shifts for the cnge bands. Overall, the perturbation to the cnge structure is far greater in **1** than in **2**. This evidence further supports the possibility of a cnge–copper π-donor/π-acceptor interaction in **1**.

Thermogravimetric Analysis of Complexes **1** *and* **2**.—The stability of complex **1** with respect to **2** was investigated by examining the thermal decomposition of the latter. The thermogravimetric analysis showed the loss of 1 equivalent of pydz per dimer at *ca.* 190 °C. At temperatures greater than 200 °C further weight loss was observed until complete decomposition. A similar analysis of **1** showed no weight loss until 200 °C, whereupon weight loss was observed until complete decomposition. The weight-loss pattern at greater than 200 °C for **1** matched that for **2** at similar temperatures. The loss of one pydz molecule from **2** at 190 °C to generate **1** describes these data adequately. Since **2** can be prepared from **1** it is proposed that the addition of one pydz molecule to **1** is reversible.

Conclusion

The structures and properties of two novel copper(I)–pydz–cnge complexes have been presented. To our knowledge, their constituent cations, $Cu^I_2(\mu\text{-pydz})_2(cnge)_2$ and $Cu^I_2(\mu\text{-pydz})_3(cnge)_2$, are the first examples of discrete dinuclear cations bridged solely by pydz molecules to be characterised by single-crystal X-ray diffraction techniques. Although similar cations containing pydz-bridged transition-metal fragments have been studied by IR methods,[28,29] in all previously structurally characterised species the pydz bridge is supported by either a metal–metal bond,[22–25,40] a second bridging moiety[22–25,32–34] or a binucleating macrocycle.[35] The bis(pydz)-bridged cation, which is the first structurally characterised planar three-co-ordinate copper(I) complex containing pydz, will bind a further pydz molecule to generate the tris(pydz)-bridged cation which contains two four-co-ordinate copper(I) centres; the latter is a rare example of a triply bridged dicopper(I) complex.[46] Remarkably, on heating, the latter complex loses a single pydz molecule, presumably to regenerate the former complex. The reversible addition of a pydz molecule to the unsaturated copper(I) centres is probably due to the unusual stability of the latter when ligated by cnge. The stability is thought to arise from proposed π interactions between cnge and the copper(I) centre, the existence of which is supported by the orientation of the cnge molecule with respect to the copper centre in the structure of the unsaturated complex and also by the IR spectra of the two complexes. These interactions could be important in understanding the properties of three-co-ordinate copper(I) moieties in other systems, such as the copper atoms at the dioxygen binding site of the dioxygen-carrying protein haemocyanin.

Experimental

All reactions were carried out under an argon or nitrogen atmosphere unless otherwise noted. Infrared spectra, mass spectra and elemental analyses were consistent with the proposed structures. Infrared spectra were obtained on a Perkin-Elmer PE983G spectrometer as KBr pressed pellets. Thermogravimetric analyses were carried out with a Stanton Redcroft TG-750 balance controlled by a TG-750/770 linear temperature programmer. Microanalyses were carried out by Mr. T. J. Spencer at the microanalysis facility at the University of Nottingham Chemistry Department.

Prior to use, acetonitrile and tetrahydrofuran were distilled from CaH_2 and sodium–benzophenone, respectively. The complex $[Cu(MeCN)_4]BF_4$ was prepared using a literature procedure[53] involving the addition of [NO][BF_4] to copper metal suspended in dry acetonitrile. The compounds cnge and pydz were obtained from Aldrich Chemical Company Ltd. Whereas cnge was purified by recrystallisation from water and dried at room temperature *in vacuo* prior to use, pydz was used without further purification.

Bis(μ-pyridazine)-bis[(2-cyanoguanidine)copper(I)] Tetrafluoroborate **1**.—Freshly prepared $[Cu(MeCN)_4]BF_4$ (3.14 g, 10 mmol) was added with stirring to a solution of pydz (0.80 g, 10 mmol) and powdered cnge (0.84 g, 10 mmol) in acetonitrile. The solution was stirred for 3 h. Removal of the solvent *in vacuo* at room temperature afforded a viscous, orange oil. Subsequent washing of the oil with CH_2Cl_2 afforded a yellow solid under a yellow solution. The air-sensitive solid was isolated by cannula filtration and washed with cold CH_2Cl_2 to give complex **1** (2.04 g, 65% yield) [Found (Calc. for $C_6H_8BCuF_4N_6$): C, 22.70 (22.90); H, 2.50 (2.55); N, 26.85 (26.75%)]. Complex **1** could be recrystallised by diffusion of hexanes into an acetone solution of the product.

Tris(μ-pyridazine)-bis[(2-cyanoguanidine)copper(I)] Tetrafluoroborate **2**.—*Method* (*a*). Freshly prepared $[Cu(MeCN)_4]BF_4$ (3.14 g, 10 mmol) was added with stirring to a solution of pydz (0.40 g, 5 mmol) in dry deoxygenated tetrahydrofuran containing powdered cnge (0.84 g, 10 mmol). The mixture was stirred for 100 h. The product was obtained as an insoluble orange powder. It was isolated by cannula filtration and washed with cold CH_2Cl_2. Drying *in vacuo* afforded complex **2** as an orange-brown powder (2.66 g, 75% yield) [Found (Calc. for $C_8H_{10}BCuF_4N_7$): C, 27.45 (27.10); H, 2.95 (2.85); N, 26.60 (27.65%)].

Method (*b*). Complex **1** (3.14 g, 5 mmol) was added to pydz (0.40 g, 5 mmol) in acetone. Crystals of **2** were obtained by diffusion of hexanes into the acetone solution of the product.

X-Ray Crystallographic Analyses.—Suitable crystals of each complex were selected and mounted in Lindemann tubes under dry nitrogen. Preliminary oscillation and Weissenberg photographs indicated that the unit cell of **1** was triclinic and that of **2** was monoclinic, space group *C*2/*c* (no. 15). After transfer to a Hilger and Watts Y290 four-circle diffractometer and prior to data collection, the cell constants were accurately determined by least-squares refinement of 24 reflections well positioned throughout reciprocal space. Throughout the data collection, intensity-control reflections were monitored periodically; no significant decrease in intensity was observed. Lorentz and polarisation corrections were applied to the data. Crystal data, together with details of the diffraction experiments are listed in Table 5.

The structures of complexes **1** and **2** were solved by identifying, in the respective Patterson maps, the copper–copper $2x,2y,2z$ vector (for **1**) and the copper–copper Harker peaks (for **2**). Subsequent refinement with the copper atoms in position revealed the rest of the complexes in Fourier difference syntheses, including hydrogen atoms and the BF_4^- anions. The BF_4^- anion in **2** was found to be disordered about two orientations. The relative occupancy (82% : 18%) of the disorder

Table 5 Data collection parameters for complexes $[Cu_2(\mu\text{-pydz})_2(cnge)_2][BF_4]_2$ **1** and $[Cu_2(\mu\text{-pydz})_3(cnge)_2][BF_4]_2$ **2***

	1	**2**
Formula	$C_{12}H_{16}B_2Cu_2F_8N_{12}$	$C_{16}H_{20}B_2Cu_2F_8N_{14}$
M	629.04	709.13
Crystal system	Triclinic	Monoclinic
Space group	$P\bar{1}$ (no. 2)	$C2/c$ (no. 15)
a/pm	754.8(2)	2229.3(7)
b/pm	971.3(2)	850.3(3)
c/pm	937.2(2)	1568.5(3)
$\alpha/^\circ$	118.94(2)	90
$\beta/^\circ$	94.72(2)	99.13(2)
$\gamma/^\circ$	107.44(2)	90
Z	1	4
10^{-6} U/pm^3	553(1)	2934(3)
μ_{calc}/cm^{-1}	20.2	15.4
D_c/g cm^{-3}	1.89	1.6
D_m/g cm^{-3} (bromoform–hexane)	1.84	1.7
F(000)	312	1416
Crystal dimensions/ mm	0.15 × 0.1 × 0.1	0.45 × 0.2 × 0.1
Reflections collected	1399	1997
Unique reflections	1399	1997
Reflections with $F_o^2 > 2\sigma(F_o^2)$	1023	1030
Number of parameters	195	246
$R = [\Sigma\lvert\Delta F\rvert/\Sigma\lvert\Delta F_o\rvert]$	0.065	0.062
$R' = [\Sigma w(\Delta F)^2/\Sigma w(\Delta F_o)^2]$	0.070	0.061

* Details in common: Mo-Kα radiation (λ 71.07 pm); $2\theta_{max}$ 44°; ω–2θ scan.

was included as a parameter in the least-squares refinement of the model. Full least-squares calculations, using the CRYSTALS suite of programs,[54] were carried out to refine the positions and anisotropic thermal parameters of all the atoms except the 18% occupancy fluorine atoms in **2** and the hydrogens, which were refined isotropically. For **1** the final cycle of refinement, with unit weighting scheme, gave residuals of $R = 0.065$ and $R' = 0.070$ for 1023 data with $F_o^2 > 2\sigma(F_o^2)$ and data to parameter ratio of 5.25:1. For **2** the final cycle of refinement, with unit weighting scheme, gave $R = 0.062$ and $R' = 0.061$ for 1030 data with $F_o^2 > 3\sigma(F_o^2)$ and data to parameter ratio of 4.19:1.

Additional material available from the Cambridge Crystallographic Data Centre comprises thermal parameters and remaining bond lengths and angles.

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