Bis(μ-2-cyanoguanidine)-bis[(2-cyanoguanidine)copper(I)], a Planar Dimeric Cation containing Co-ordinatively Unsaturated Copper(I)†

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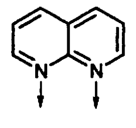
The air- and moisture-stable copper(I) salts $[Cu_2(\mu\text{-cnge})_2(cnge)_2]X\cdot 2H_2O$ (cnge = 2-cyanoguanidine; $X = S_2O_6^{2-}$ or SO_4^{2-}) have been prepared by sodium sulfite reduction of aqueous solutions of copper(II) chloride containing cnge. The two salts have been structurally characterised by single-crystal X-ray diffraction methods. The dithionate structure (triclinic, space group $P\bar{1}$, $a = 7.320$, $b = 7.315$, $c = 12.765$ Å, $\alpha = 97.10$, $\beta = 118.91$, $\gamma = 92.93°$) is more symmetrical than that of the sulfate (monoclinic, space group $P2_1/c$, $a = 6.920$, $b = 14.951$, $c = 21.042$ Å, $\beta = 95.17°$). Nonetheless, the two $[Cu_2(\mu\text{-cnge})_2(cnge)_2]^{2+}$ cations are very similar. They contain two trigonal-planar copper(I) atoms bridged by two cnge molecules and terminally co-ordinated by a single cnge molecule. To minimise interaction between the in-plane π systems of the bridging cnge molecules, the latter are separated by *ca.* 3.1 Å and angled such that they lie on two essentially parallel planes separated by *ca.* 0.75 Å. The perturbation of the IR spectrum of cnge on co-ordination is dependent not on the co-ordination type (bridging, terminal) but on the strength of its co-ordination to the metal.

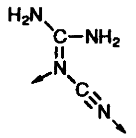
Multiply bridged cationic dicopper(I) species are rare;[1] those with co-ordinatively unsaturated copper(I) centres are even less common.[2] Geometrically suitable neutral bridging ligands with 'soft' donor atoms include the bis(N-donor) ligands, pyridazine (pydz), 1,8-naphthyridine (napy) and 2-cyanoguanidine (cnge), the bis(P-donor) ligand bis(diphenylphosphino)methane (dppm), and the mixed N,P-donor ligand, 2-(diphenylphosphino)pyridine (dppy). These ligands form both di- and tri-bridged species. The co-ordination geometries of the copper(I) centres are determined by the number of terminally located ligands. Dibridged species with four terminal ligands (Scheme 1, **I**) contain distorted-tetrahedral copper(I), *e.g.* $[Cu_2(\mu\text{-dppm})_2(MeCN)_4]^{2+}$,[3] those with two terminal ligands (**II**) distorted-trigonal copper(I), *e.g.* $[Cu_2(\mu\text{-pydz})_2(cnge)_2]^{2+}$,[2,4] $[Cu_2(\mu\text{-dppy})_2(MeCN)_2]^{2+}$ (ref. 5) and $[Cu_2(\mu\text{-dppm})_2L'_2]^{2+}$ [L′ = *trans*-1-(4-chlorobenzyl)-2-(4-pyridyl)ethene],[6] and those without terminal ligands (**III**) approximately linear copper(I), *e.g.* $[Cu_2(\mu\text{-napy})_2]^{2+}$.[7] Similarly, tribridged species with two terminal ligands (**IV**) contain distorted-tetrahedral copper(I), *e.g.* $[Cu_2(\mu\text{-dppy})_3(MeCN)_2]^{2+}$,[8] $[Cu_2(\mu\text{-pydz})_3(MeCN)_2]^{2+}$,[1] $[Cu_2(\mu\text{-pydz})_3(cnge)_2]^{2+}$ [2,4] and $[Cu_2(\mu\text{-pydz})_3(PPh_3)_2]^{2+}$,[4] and those without terminal ligands (**V**) distorted-trigonal copper(I), *e.g.* $[Cu_2(\mu\text{-dppm})_2(\mu\text{-mpyo})_2]^{2+}$ (mpyo = 6-methylpyridin-2-olate).[9]

The synthesis and characterisation of discrete dinuclear cations containing three-co-ordinate N-ligated copper(I) centres is of current interest[10,11] owing to their similarity to the active sites in the dioxygen-transporting proteins, haemocyanins.[12,13] We have recently described the use of 2-cyanoguanidine to stabilise trigonal-planar copper(I)[14] and reported the structure of the planar, binuclear cation $[Cu_2(\mu\text{-pydz})_2(cnge)_2]^{2+}$.[2] We now describe the synthesis and structural characterisation of the analogous $[Cu_2(\mu\text{-cnge})_2(cnge)_2]^{2+}$ cation as its dithionate and sulfate salts.

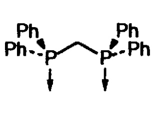
pydz



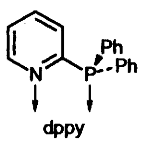
napy



cnge



dppm



dppy

Results and Discussion

(*i*) *Synthesis and Characterisation of* $[Cu_2(\mu\text{-cnge})_2(cnge)_2]X\cdot 2H_2O$ ($X = S_2O_6$ *or* SO_4).—Treatment of $CuCl_2\cdot 2H_2O$ with Na_2SO_3 in deoxygenated aqueous solution leads, depending on the amount of reductant, to the novel complexes $[Cu_2(\mu\text{-cnge})_2(cnge)_2][S_2O_6]\cdot 2H_2O$ (three-fold excess of Na_2SO_3) or $[Cu_2(\mu\text{-cnge})_2(cnge)_2][SO_4]\cdot 2H_2O$ (stoichiometric Na_2SO_3). The bulk of the product forms immediately as a white precipitate; following filtration, however, the mother-liquors yield small colourless crystals. In both experiments the crystals had the same properties as those of the original precipitate and the two were assumed to be identical.

The differing conditions were tried in an unsuccessful attempt to exclude the sulfur oxo anion from the product and hence extend the sequence of halides formed by the reduction of 2:1 and 1:1 CuX_2:cnge molar mixtures (X = Cl or Br), *viz.* $[\{Cu_2(\mu\text{-X})_2(\mu\text{-cnge})\}_n]$ and $[\{Cu(\mu\text{-X})(\mu\text{-cnge})\cdot H_2O\}_n]$.[14] Consideration of the reduction potentials [equations (1) and (2)][15]

$$S_2O_6^{2-} + 4H_3O^+ + 2e^- \longrightarrow 2H_2SO_3 + 4H_2O \quad E° = 0.57\ \text{V} \qquad (1)$$

$$SO_4^{2-} + 4H_3O^+ + 2e^- \longrightarrow H_2SO_3 + 5H_2O \quad E° = 0.17\ \text{V} \qquad (2)$$

indicates that the oxidation of an excess of sulfite to dithionate and of stoichiometric sulfite to sulfate must be under kinetic rather than thermodynamic control. This correlates with the

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† *Supplementary data available:* see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1995, Issue 1, pp. xxv–xxx.

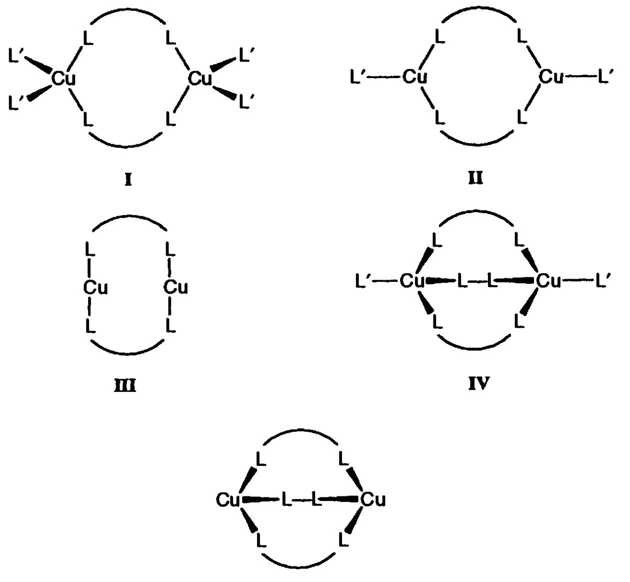
earlier observation[16] that the proportion of sulfate to dithionate resulting from sulfite oxidation at reducible metal centres is dependent on the conditions (pH, concentration, temperature, *etc.*).

The products were characterised initially by analytical and spectroscopic methods and subsequently by single-crystal X-ray diffraction. The presence of co-ordinated cnge in two different environments was shown by the shifting (to higher frequency) and splitting of the asymmetric and symmetric N(1)–C(1)–N(2) stretching vibrations of the cnge molecule.[17,18] The principal IR data for cnge in the products are compared with those for free cnge and for other copper(I)–cnge complexes in Table 1. Their interpretation is discussed later. The chemistry of these complexes is quite limited owing to their insolubility in water and most organic solvents; they do dissolve in aqueous alkaline solutions but with oxidation to a copper(II) product.

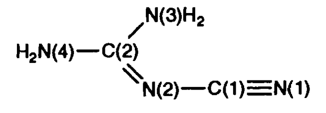
The formation of a dinuclear co-ordinatively saturated copper(I) complex in aqueous solutions containing halide anion is indicative of the remarkable ability of cnge to stabilise three-co-ordinate copper(I) and of the latter's preference for 'soft' ligands.

(*ii*) *Structural Analysis of* $[Cu_2(\mu\text{-cnge})_2(cnge)_2]X\cdot 2H_2O$ ($X = S_2O_6$ *or* SO_4).—Fractional atomic coordinates for all non-hydrogen atoms are given in Table 2, interatomic distances and angles in the copper co-ordination spheres and the cnge molecules in Tables 3 and 4, respectively. Also included in Table 4 are the interatomic distances and bond angles in free cnge.[21] The complexes are characterised by $[Cu_2(\mu\text{-cnge})_2(cnge)_2]^{2+}$ cations, either $S_2O_6^{2-}$ or SO_4^{2-} anions and unco-ordinated water molecules. The cations in the two salts are very similar despite the fact that that in the dithionate salt is crystallographically constrained to be centrosymmetric, whereas that in the sulfate salt contains two crystallographically independent copper atoms. The structure of the centrosymmetric cation is shown in Fig. 1. The three-co-ordinate copper(I) centres are bridged by two cnge molecules forming an eight-membered (–Cu–N–C–N–)$_2$ ring. Each cnge molecule uses its nitrile and imino nitrogen atoms to co-ordinate the copper(I) atoms, giving a copper–copper separation of 5.052 (dithionate salt) or 5.048 Å (sulfate salt). A similar ring system exists in $[\{Cd_2(\mu\text{-cnge})_2(\mu\text{-}O_2SO_2)(H_2O)_4\}_n]$, in which the cadmium–cadmium separation is 5.55 Å.[20] The distorted trigonal-planar co-ordination geometry of the copper(I) centres is completed by a monodentate planar cnge molecule, co-ordinating through its nitrile nitrogen atom. The two cations may be considered to be essentially planar, in which case the centrosymmetric cation is the flatter, the maximum deviations from the best-fit least-squares planes being 0.153 [N(11)] and 0.384 Å [N(41)], respectively. It is interesting, however, that in both structures the bridging cnge molecules really lie on two parallel planes, the maximum deviations from which are 0.013 [N(12)], 0.050 [N(32)] and 0.005 Å [N(42)]. This feature is shown clearly in a projection of the structure of the centrosymmetric cation along the Cu···Cu vector [Fig. 2(*a*)]. In the dithionate salt the planes are separated by 0.768 Å, in the sulfate salt by 0.719 Å. This behaviour contrasts with that in the bis(pyridazine)-bridged copper(I) cation $[Cu_2(\mu\text{-pydz})_2(cnge)_2]^{2+}$,[2] where the two pyridazine rings are essentially coplanar [Fig. 2(*b*)].

In both structures the cations are stacked in a parallel fashion (Fig. 3). The anions and water molecules lie between the cations and are hydrogen bonded to the cnge molecules by oxygen–amino hydrogen contacts. Whereas the average N–H···O (2.94 Å) contact is very similar to the calculated NH_n···O (2.95 Å) value,[22] the average O–H···O (3.01 Å) contact is greater than the calculated OH_n···O (2.94 Å) value.[22] The interatomic distances and angles associated with



Scheme 1



cnge numbering scheme

Table 1 IR spectral data / cm^{-1} for $[Cu_2(\mu\text{-cnge})_2(cnge)_2]X\cdot 2H_2O$ ($X = S_2O_6$ or SO_4), and various copper(I)–, copper(II)– and cadmium(II)–cnge complexes[a]

	ν_{asym}[N(1)C(1)N(2)]	ν_{sym}[N(1)C(1)N(2)]	ν_{sym}[N(2)C(2)N(3)]
cnge[b]	2209, 2165	1252	928
$[Cu_2(\mu\text{-cnge})_2(cnge)_2][S_2O_6]\cdot 2H_2O$[b]	2224, 2176	1215	930
	2212, 2164	1254	916
$[Cu_2(\mu\text{-cnge})_2(cnge)_2][SO_4]\cdot 2H_2O$[b]	2226, 2176	1220	*c*
	2206, 2164	1254	*c*
$[\{Cu_2(\mu\text{-Cl})_2(\mu\text{-cnge})\}_n]$[d]	2227, 2182	1248	930
$[\{Cu_2(\mu\text{-Br})_2(\mu\text{-cnge})\}_n]$[d]	2228, 2185	1248	951
$[\{Cu(\mu\text{-Br})(\mu\text{-cnge})\cdot H_2O\}_n]$[d]	2223, 2175	1234	958
$[Cu_2(\mu\text{-pydz})_2(cnge)_2][BF_4]_2$[e]	2228, 2185	1261	922
$[Cu_2(\mu\text{-pydz})_3(cnge)_2][BF_4]_2$[e]	2210, 2165	1259	929
$[Cu_2(\mu\text{-}O_2CMe)_4(cnge)_2]$[f]	2209, 2165	1265	926
$[\{Cd_2(\mu\text{-cnge})_2(\mu\text{-}O_2SO_2)_2(H_2O)_4\}_n]$[g]	2212, 2164	1269	923
$[Cd_2(\mu\text{-cnge})_2Cl_4]$[g]	2208, 2164	1235	942

[a] The assignment is based on that proposed by Jones and Orville-Thomas[17] for free cnge. [b] Present results. [c] Masked by anion vibrations. [d] Ref. 14. [e] Ref. 2. [f] Ref. 19. [g] Ref. 20.

Table 2 Fractional atomic coordinates for the non-hydrogen atoms in $[Cu_2(\mu\text{-cnge})_2(cnge)_2]X\cdot 2H_2O$ ($X = S_2O_6$ or SO_4)

Atom	*X*/*a*	*Y*/*b*	*Z*/*c*	Atom	*X*/*a*	*Y*/*b*	*Z*/*c*
$X = S_2O_6$							
Cu(1)	0.423 8(2)	0.318 6(2)	0.057 1(1)	N(22)	0.173(1)	0.834(1)	0.071 3(7)
N(11)	0.621(1)	1.154(1)	0.125 0(7)	C(22)	0.254(1)	0.954(1)	0.179 1(9)
C(11)	0.685(2)	1.014(1)	0.134 2(9)	N(23)	0.394(2)	0.919(2)	0.282 7(9)
N(12)	0.748(1)	0.846(1)	0.131 9(7)	N(24)	0.177(1)	1.117(1)	0.170 6(8)
C(12)	0.872(2)	0.791(1)	0.236(1)	S(1)	0.596 3(4)	0.618 8(3)	0.506 0(2)
N(13)	0.940(2)	0.890(2)	0.342 3(9)	O(11)	0.513(1)	0.226 3(8)	0.481 7(7)
N(14)	0.934(2)	0.624(1)	0.228(1)	O(12)	0.206(1)	0.382 4(9)	0.386 0(6)
N(21)	0.303(1)	0.533(1)	0.063 4(8)	O(13)	0.605(1)	0.588 8(9)	0.394 6(6)
C(21)	0.249(2)	0.675(1)	0.074 0(9)	O(1)	0.872(2)	0.259(1)	0.433 0(8)
$X = SO_4$							
Cu(2)	0.377 5(2)	0.401 17(8)	0.543 37(8)	C(52)	0.131(2)	0.715 8(6)	0.590 4(5)
Cu(3)	0.614 6(2)	0.103 22(8)	0.468 55(9)	N(53)	0.197(2)	0.693 7(7)	0.646 7(5)
N(31)	0.535(1)	0.306 7(5)	0.574 8(4)	N(54)	0.066(1)	0.800 6(5)	0.579 8(4)
C(31)	0.592(2)	0.234 6(6)	0.575 7(5)	N(61)	0.738(2)	−0.005 4(5)	0.458 9(5)
N(32)	0.655(1)	0.151 3(5)	0.570 2(4)	C(61)	0.801(2)	−0.074 7(6)	0.450 1(5)
C(32)	0.712(2)	0.109 0(6)	0.624 1(5)	N(62)	0.884(1)	−0.153 6(5)	0.450 2(4)
N(33)	0.725(2)	0.142 6(8)	0.681 4(6)	C(62)	0.868(2)	−0.200 4(6)	0.394 8(5)
N(34)	0.762(2)	0.021 9(6)	0.617 2(6)	N(63)	0.791(2)	−0.174 3(8)	0.341 2(6)
N(41)	0.448(1)	0.195 2(5)	0.436 1(4)	N(64)	0.942(1)	−0.284 2(5)	0.400 9(5)
C(41)	0.395(2)	0.268 2(7)	0.435 2(5)	S(2)	0.859 1(5)	0.403 6(2)	0.754 5(1)
N(42)	0.336(1)	0.351 8(5)	0.442 1(5)	O(21)	1.006(2)	0.397 0(5)	0.807 9(4)
C(42)	0.287(2)	0.400 0(6)	0.389 0(5)	O(22)	0.957(1)	0.409 3(5)	0.695 4(3)
N(43)	0.290(2)	0.373 1(7)	0.331 7(6)	O(23)	0.737(2)	0.484 2(5)	0.760 8(5)
N(44)	0.230(2)	0.484 0(6)	0.399 0(6)	O(24)	0.732(1)	0.323 0(5)	0.751 7(4)
N(51)	0.251(2)	0.509 8(5)	0.546 2(5)	O(2)	0.703(2)	0.481 0(5)	0.285 6(5)
C(51)	0.195(2)	0.582 2(6)	0.545 8(5)	O(3)	0.334(2)	0.206 2(5)	0.265 2(5)
N(52)	0.125(1)	0.662 7(5)	0.537 8(4)				

Table 3 Copper co-ordination geometries (distances in Å, angles in °) in $[Cu_2(cnge)_4]X\cdot 2H_2O$ ($X = S_2O_6$ or SO_4)

	Cu(1)	Cu(2)	Cu(3)
Cu–bridging nitrile nitrogen [N(1)]	1.874(4)	1.868(9)	1.883(9)
Cu–bridging imine nitrogen [N(2)]	2.246(4)	2.25(1)	2.250(9)
Cu–terminal nitrile nitrogen [N(1′)]	1.851(4)	1.849(8)	1.854(8)
N(1)–Cu–N(2)	96.3(6)	96.2(4)	97.5(4)
N(1)–Cu–N(1′)	153.6(6)	156.3(4)	150.8(4)
N(2)–Cu–N(1′)	110.1(6)	107.4(4)	111.4(4)

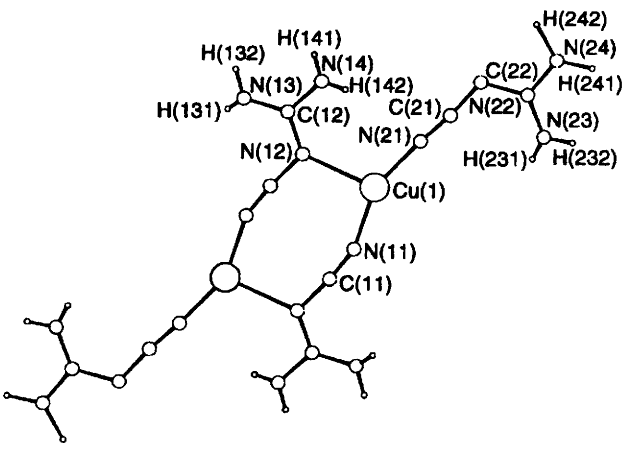


Fig. 1 Molecular structure of the $[Cu_2(\mu\text{-cnge})_2(cnge)_2]^{2+}$ cation in the dithionate salt

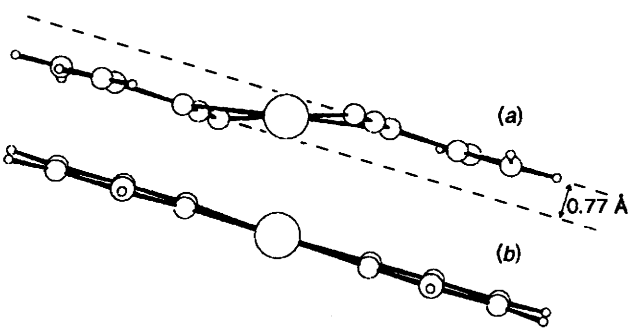


Fig. 2 Views of the $[Cu_2(\mu\text{-cnge})_2(cnge)_2]^{2+}$ (*a*) and $[Cu_2(\mu\text{-pydz})_2(cnge)_2]^{2+}$ (*b*) cations along the Cu ··· Cu vectors

the dithionate [*r*(S ··· S) = 2.123, *r*(S ··· O) = 1.439–1.456 Å, S–S–O 104.0–104.6, O–S–O 112.6–105.0°] and sulfate anions [*r*(S ··· O) = 1.449–1.490 Å, O–S–O 108.4–110.6°] are typical for these species [dithionate,[23] *r*(S ··· S) = 2.15–2.16, *r*(S ··· O) = 1.45 Å, S–S–O 103°; sulfate,[24] *r*(S ··· O) = 1.49 Å].

In the dithionate salt [Fig. 3(*a*)] the cations form a zigzag array with the copper atom located between a nitrile moiety of a terminal cnge (Cu ··· N 3.27, Cu ··· C 3.53 Å) and an amino nitrogen of a bridging cnge molecule (Cu ··· N 3.21 Å), giving a copper–copper interdimer distance of 3.58 Å. These copper–nitrile distances differ from those given in a preliminary communication,[25] which were erroneously quoted (Cu ··· N 2.99, Cu ··· C 3.10 Å). In the sulfate salt [Fig. 3(*b*)] the cations are stepped with the copper atoms located between a nitrile moiety of a terminal cnge (Cu ··· N 3.30, 3.58; Cu ··· C 3.50, 3.65 Å) and an amino nitrogen of a bridging cnge molecule

Table 4 Cyanoguanidine geometries (distances in Å, angles in °) in $[Cu_2(\mu\text{-cnge})_2(cnge)_2]X{\cdot}2H_2O$ (X = S_2O_6 or SO_4)

	Cyanoguanidine molecule[a]						
		Bridging			Terminal		
	Free[b]	1	3	4	2	5	6
N(1)–C(1)	1.169	1.14(2)	1.15(1)	1.15(1)	1.15(2)	1.15(1)	1.15(1)
C(1)–N(2)	1.305	1.34(2)	1.33(1)	1.33(1)	1.31(2)	1.30(1)	1.31(1)
N(2)–C(2)	1.341	1.33(2)	1.33(1)	1.35(1)	1.37(2)	1.36(1)	1.36(1)
C(2)–N(3)	1.339	1.30(2)	1.30(1)	1.27(1)	1.29(2)	1.27(1)	1.27(1)
C(2)–N(4)	1.333	1.33(2)	1.36(1)	1.34(1)	1.34(2)	1.36(1)	1.36(1)
N(1)–C(1)–N(2)	175.1	174(1)	174(1)	173(1)	173(1)	173(1)	170(1)
C(1)–N(2)–C(2)	118.4	119(1)	116.6(9)	118.0(9)	117(1)	116.8(9)	117.5(9)
N(2)–C(2)–N(3)	123.8	125(1)	127(1)	126.3(9)	125(1)	126.0(9)	127.1(9)
N(2)–C(2)–N(4)	117.5	116(1)	115(1)	115.3(9)	115(1)	115.2(9)	113.3(9)
N(3)–C(2)–N(4)	118.7	119(1)	118(1)	118(1)	121(1)	119(1)	120(1)

[a] The cnge molecules are identified by the numbering in Table 2; thus, molecule 1 is that comprising N(11), C(11), N(12), C(12), N(13), N(14), 2 that comprising N(21), C(21), N(22), C(22), N(23), N(24), *etc.* [b] Ref. 21.

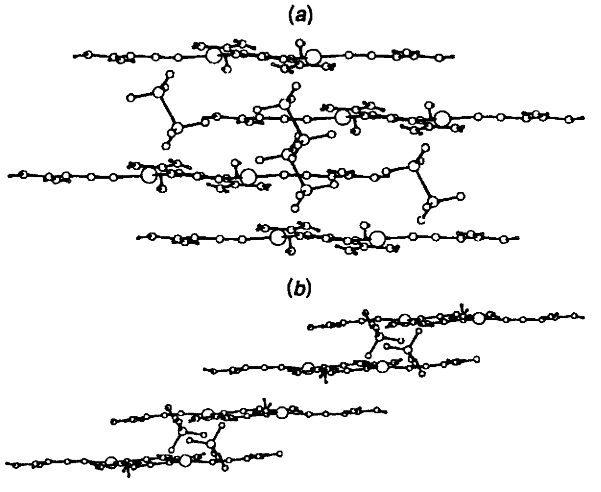


Fig. 3 Crystal-packing diagrams showing the zigzag and stepped parallel stacking of the $[Cu_2(\mu\text{-cnge})_2(cnge)_2]^{2+}$ cations in the dithionate (*a*) and sulfate (*b*) salts, respectively

(Cu···N 2.90, 3.13 Å), giving a copper–copper interdimer distance of 3.77 Å. The similar location of the copper atoms in the two complexes must be indicative of a weak interaction between the filled delocalised π orbitals of the cnge molecule (specifically of the nitrile and amino moieties) and the empty $4p_z$ orbital of the copper atom. Supporting evidence for this interaction is the fact that some of these copper–cnge contacts are shorter than the minimum interatomic distance (3.45 Å) between the parallel planes of cnge molecules in the structure of cnge.[21]

(*iii*) *Co-ordination of cnge to Copper*(I).—The six co-ordinated cnge molecules have very similar geometries. It is difficult to differentiate bridging and terminal species; their geometries are collated and compared with that of free cnge in Table 4.

The co-ordination modes of the bridging and terminal cnge molecules to copper(I) in the centrosymmetric $[Cu_2(\mu\text{-cnge})_2(cnge)_2]^{2+}$ cation are compared with those of bridging cnge in the monobridged species $[\{Cu_2(\mu\text{-Cl})_2(\mu\text{-cnge})\}_n]$[14] and of terminal cnge in $[Cu_2(\mu\text{-pydz})_2(cnge)_2]^{2+}$ (ref. 2) in Fig. 4. To facilitate the comparison the molecules are shown with the copper–nitrile nitrogen bond horizontal. The co-ordination of the terminal cnge molecules in $[Cu_2(\mu\text{-cnge})_2(cnge)_2]^{2+}$ [Fig. 4(*c*)] and $[Cu_2(\mu\text{-pydz})_2(cnge)_2]^{2+}$ [Fig. 4(*d*)] is very similar, the Cu(1)–N(1)–C(1) angles being 173 and 175°, respectively. Similar co-ordination is seen for the nitrile nitrogen of the monobridging cnge in $[\{Cu_2(\mu\text{-Cl})_2(\mu\text{-cnge})\}_n]$ [Fig 4(*b*), Cu(1)–N(1)–C(1) 172°], suggesting that bridging *per se* does not modify the co-ordination mode. That for the nitrile nitrogens of the bridging cnge molecules in the dibridged $[Cu_2(\mu\text{-cnge})_2(cnge)_2]^{2+}$ species [Fig. 4(*a*)] is quite different, however, the Cu(1)-N(1)-C(1) angle being 156°. We attribute this difference to steric and electronic repulsion between the two bridging cnge molecules. If the normal co-ordination mode were to be adopted by the dibridged species, the separation between the two parallel molecules (based on the co-ordination geometry of $[\{Cu_2(\mu\text{-Cl})_2(\mu\text{-cnge})\}_n]$) would be *ca.* 2.10 Å. To avoid this clash, which includes a repulsion between the in-plane π systems of the two nitrile moieties, the two bridging cnge molecules are displaced away from each other in $[Cu_2(\mu\text{-cnge})_2(cnge)_2]^{2+}$ to give a separation of 3.10 Å. As noted earlier, to reduce further the interaction, the two bridging cnge molecules are angled such that the separation between the two planes containing the two localised π systems is *ca.* 0.75 Å [Fig. 2(*a*)]. The displacement of the cnge molecules results in decreased Cu(1)–N(1)–C(1) and C(1)–N(2)–Cu(1′) angles thus giving rise to weaker bonding interactions and hence longer Cu···N distances (Fig. 4). A further manifestation is a reduction in the Cu(1)···Cu(1′) interatomic distance from the monobridged (5.42 Å in $[\{Cu_2(\mu\text{-Cl})_2(\mu\text{-cnge})\}_n]$) to the dibridged species (5.05 Å).

The 'CuN_3' co-ordination spheres in the $[Cu_2(\mu\text{-cnge})_2(cnge)_2]^{2+}$ cations, although planar [maximum deviation of the copper atoms from the least-squares best-fit planes: Cu(1) 0.001, Cu(2) 0.025 and Cu(3) 0.147 Å] are significantly distorted from classical trigonal planar {as in $[Cu_2(\mu\text{-pydz})_2(cnge)_2]^{2+}$ Fig. 4 (*d*)} towards a T-shaped arrangement [Fig. 4(*a*) and 4(*c*)]. Munakata *et al.*[26] have noted an empirical relationship between the angular distortion of a 'CuN_3' co-ordination sphere and its Cu···N interatomic distances; distortion to T-shaped results in the lengthening of a single Cu···N bond whereas distortion to Y-shaped results in the lengthening of two Cu···N bonds. Extended-Hückel and *ab initio* calculations undertaken by Riehl *et al.*[27] confirm the empirical analysis, indicating that the changes in bond strengths are related to the reorganisation of bonding interactions between (s,p) orbitals on the metal and ligand. The three 'CuN_3' co-ordination spheres in the two $[Cu_2(\mu\text{-cnge})_2(cnge)_2]^{2+}$ cations are located at the T-shaped extreme of Munakata's relationship.[26]

(*iv*) *IR Spectroscopy of Co-ordinated cnge.*—Pertinent features of the IR spectra of the salts containing the $[Cu_2(\mu\text{-cnge})_2(cnge)_2]^{2+}$ cations are collated in Table 1 together with

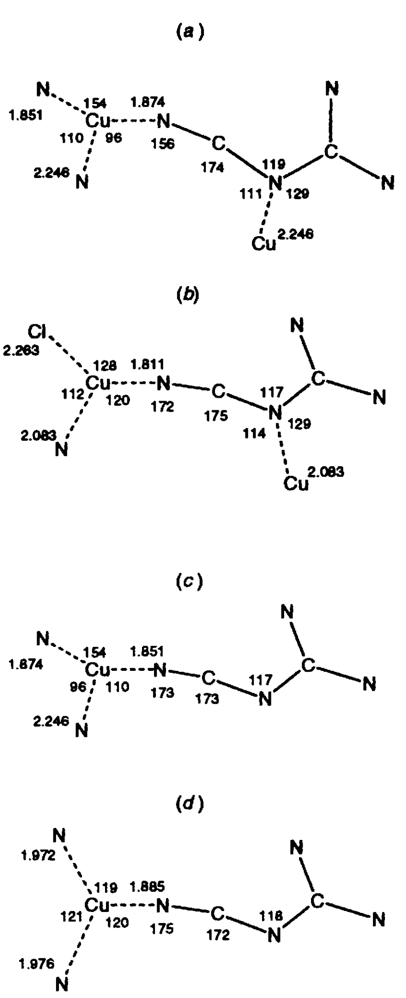


Fig. 4 Co-ordination of 2-cyanoguanidine to copper(I): (*a*) dibridging in $[Cu_2(\mu\text{-cnge})_2(cnge)_2]^{2+}$; (*b*) monobridging in $[\{Cu_2(\mu\text{-Cl})_2(\mu\text{-cnge})\}_n]$; (*c*) terminal in $[Cu_2(\mu\text{-cnge})_2(cnge)_2]^{2+}$; (*d*) terminal in $[Cu_2(\mu\text{-pydz})_2(cnge)_2]^{2+}$. Interatomic distances in Å, interatomic bond angles in °

those of free cnge and of other relevant copper(I)–, copper(II)– and cadmium(II)–cnge complexes. They are similar and consistent with the presence of two independent cnge molecules. Thus the region of the ν_{asym}[N(1)C(1)N(2)] doublet (2250–2150 cm^{-1}) contains four bands, that of the ν_{sym}[N(1)C(1)N(2)] singlet (1275–1225 cm^{-1}) two bands and that of the ν_{sym}[N(2)C(2)N(3)] singlet (950–900 cm^{-1}) two bands. Previous experience[18] has shown that the ν_{asym}[N(1)C(1)N(2)] doublet can be used to assess cnge co-ordination. This region of the spectra of the $[Cu_2(\mu\text{-cnge})_2(cnge)_2]^{2+}$ cations can be split into two pairs of bands (Table 1); when compared with free cnge (2209, 2165 cm^{-1}), one pair exhibits minimal change (+3, −1 cm^{-1}) and the other shows a significant shift to higher energy (+16, 11 cm^{-1}). We have assigned these bands by comparison with the spectra of other complexes containing either bridging or terminal cnge but not both (Table 1). Monobridging cnge occurs in $[\{Cu_2(\mu\text{-X})_2(\mu\text{-cnge})\}_n]$ (X = Cl or Br) and $[\{Cu(\mu\text{-Br})(\mu\text{-cnge})\cdot H_2O\}_n]$; all three exhibit shifts to higher energy (+17, 16 cm^{-1}).[14] Dibridging cnge occurs in $[\{Cd_2(\mu\text{-cnge})_2(\mu\text{-}O_2SO_2)_2(H_2O)_4\}_n]$ which exhibits virtually no change.[20] The terminal cnge molecule in $[Cu_2(\mu\text{-pydz})_2(cnge)_2][BF_4]_2$ exhibits a shift to higher energy (+19, 20 cm^{-1}) whereas that in $[Cu_2(\mu\text{-pydz})_3(cnge)_2][BF_4]_2$ is essentially unaltered.[2] Clearly, the ν_{asym}[N(1)C(1)N(2)] doublet cannot be used to differentiate between bridging and terminal cnge.

Consideration of Fig. 4, however, shows that the co-ordination mode of cnge in $[\{Cu_2(\mu\text{-X})_2(\mu\text{-cnge})\}_n]$ (X = Cl or Br), $[Cu_2(\mu\text{-pydz})_2(cnge)_2][BF_4]_2$ and the terminal cnge in the $[Cu_2(\mu\text{-cnge})_2(cnge)_2]^{2+}$ cation is very similar. All these complexes exhibit bands shifted to higher energy (+19, 20 cm^{-1}). Similarly, the co-ordination mode of bridging cnge in the $[Cu_2(\mu\text{-cnge})_2(cnge)_2]^{2+}$ cation, which is much more weakly bonded and subtends a smaller Cu(1)-N(1)-C(1) angle [Fig. 4(*a*), 156°], is similar to that in $[\{Cd_2(\mu\text{-cnge})_2(\mu\text{-}O_2SO_2)_2(H_2O)_4\}_n]$, where the Cd(1)-N(1)-C(1) angle is 165°.[20] 2-Cyanoguanidine is similarly weakly co-ordinated in $[Cu_2(\mu\text{-}O_2CMe)_4(cnge)_2]$, where it is located along the tetragonally elongated *z* axis of the copper(II) co-ordination sphere and subtends a Cu(1)–N(1)–C(1) angle of 135°.[19] All of these complexes exhibit minimal or zero shift in the position of the ν_{asym}[N(1)C(1)N(2)] doublet. We conclude that the perturbation of the IR spectra of cnge on co-ordination is dependent not on the co-ordination type (mono-, di-bridging or terminal) but on the strength of its co-ordination to the metal. 2-Cyanoguanidine strongly bonded to copper(I) with a Cu–N–C angle close to 180° exhibits a significant shift of the ν_{asym}[N(1)C(1)N(2)] doublet to higher energy; cnge weakly bonded to copper(I) with a Cu–N–C angle of 165° or less exhibits virtually no change. The behaviour of $[Cu_2(\mu\text{-pydz})_3(cnge)_2][BF_4]_2$ appears somewhat anomalous. It does differ, however, from the other copper(I)–cnge complexes considered here; its copper(I) centres are four-rather than three-co-ordinate and hence there is no possibility of a π interaction between the copper $4p_z$ orbital and the delocalised π system in the cnge molecule.

Experimental

All reactions were carried out under nitrogen using deoxygenated aqueous solutions. Infrared spectra were obtained on a Perkin-Elmer PE983G spectrometer as KBr pressed pellets. Microanalyses were carried out by Mr. T. J. Spencer of the microanalysis facility at the University of Nottingham Chemistry Department. Copper(II) chloride dihydrate and cnge were obtained from Aldrich Chemical Co. and purified by recrystallisation from water prior to use.

$[Cu_2(\mu\text{-cnge})_2(cnge)_2][S_2O_6]\cdot 2H_2O$.—A stirred deoxygenated aqueous solution containing $CuCl_2\cdot 2H_2O$ (1.70 g, 0.01 mol) and cnge (1.68 g, 0.02 mol) was treated with a three-fold excess of sodium sulfite (1.89 g, 0.015 mol). A precipitate formed immediately (yield 96%) which was removed by cannula filtration after ≈ 120 s. After standing for 7 d under nitrogen the clear filtrate afforded a crop of colourless crystalline blocks. After recovery using standard Schlenk procedures (yield < 1%), the crystals were washed with deionised water and dried in vacuum [Found (Calc. for $C_8H_{20}Cu_2N_{16}O_8S_2$): C, 14.65 (14.55); H, 3.50 (3.05); N, 34.35 (34.00)%].

$[Cu_2(\mu\text{-cnge})_2(cnge)_2][SO_4]\cdot 2H_2O$.—This was prepared as for $[Cu_2(\mu\text{-cnge})_2(cnge)_2][S_2O_6]\cdot 2H_2O$ but using a stoichiometric amount of sodium sulfite (0.63 g, 0.005 mol). Yield: precipitate 97%; colourless crystalline blocks < 1% [Found (Calc. for $C_8H_{20}Cu_2N_{16}O_6S$): C, 15.85 (16.15); H, 3.25 (3.40); N, 37.25 (37.65)%].

Crystallography.—Several crystals of each product were mounted in 0.2 mm Lindemann tubes under dry nitrogen for preliminary study. Oscillation and Weissenberg photographs revealed triclinic cell parameters for $[Cu_2(\mu\text{-cnge})_2(cnge)_2][S_2O_6]\cdot 2H_2O$ and monoclinic cell parameters with space group either *P*2/*c* (no. 13) or *P*2$_1$/*c* (no. 14) for $[Cu_2(\mu\text{-cnge})_2(cnge)_2][SO_4]\cdot 2H_2O$. 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 range 1 < θ < 25° using graphite-monochromated Mo-Kα radiation. Standard reflections were constant

Table 5 Data collection parameters for $[Cu_2(\mu\text{-cnge})_2(\text{cnge})_2]X\cdot 2H_2O$ ($X = S_2O_6$ or SO_4)

	Dithionate	Sulfate
Formula	$C_8H_{20}Cu_2N_{16}O_8S_2$	$C_8H_{20}Cu_2N_{16}O_6S$
M	659.56	595.50
Crystal system	Triclinic	Monoclinic
Space group	$P\bar{1}$ (no. 2)	$P2_1/c$ (no. 14)
a/Å	7.320(3)	6.920(3)
b/Å	7.315(3)	14.951(4)
c/Å	12.765(5)	21.042(5)
α/°	97.10(2)	90
β/°	118.91(2)	95.17(3)
γ/°	92.93(3)	90
Z	1	4
$10^{-6}U$/Å^3	589.1	2168.2
μ_{calc}/cm^{-1}	20.5	21.2
D_c/g cm^{-3}	1.86	1.82
D_m/g cm^{-3} (bromoform–hexane)	1.90	1.84
$F(000)$	334	1208
Crystal dimensions/mm	0.3 × 0.1 × 0.05	0.2 × 0.2 × 0.2
$2\theta_{max}$/°	23	25
Scan type	ω–2θ	ω–2θ
Reflections collected (unique)	1547	3990
Reflections with $F_o^2 > 3\sigma(F_o^2)$	1274	2500
Number of parameters	203	378
Data/parameter ratio	6.28	6.61
$R = [\Sigma\|\Delta F\|/\Sigma\|\Delta F_o\|]$	0.050	0.071
$R' = [\Sigma w(\Delta F)^2/\Sigma w(\Delta F_o)^2]$	0.068	0.076

throughout the course of the data collections indicating that the crystals were stable. Data were corrected for Lorentz and polarisation effects; absorption corrections were also applied.

For the dithionate salt, the positions of the copper atom and of the carbon and nitrogen atoms of the terminal cnge molecule were determined by direct methods using the MULTAN 80 suite of programs.[28] For the sulfate, the positions of the copper atom and the bridging cnge atoms were similarly determined.[28] The positions of the remaining atoms were obtained by Fourier-difference syntheses using the CRYSTALS suite of programs.[29] Full least-squares matrix refinement in space group $P\bar{1}$ converged to $R = 0.050$ and $R' = 0.068$ for the dithionate salt, and in space group $P2_1/c$ to 0.071 and 0.076 for the sulfate salt. Details of the data collection and structure solution for both complexes are collated in Table 5.

Additional material available from the Cambridge Crystallographic Data Centre comprises H-atom coordinates, thermal parameters and remaining bond lengths and angles.

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