# Three- and Four-co-ordinate Copper(I) Complexes: 1:1 and 1:2 1-Cyanoguanidine–Copper(I) Halide Adducts†

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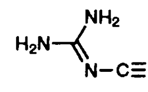
The air- and moisture-stable copper(I) complexes $Cu_2X_2$·cnge and CuX·cnge·$H_2O$ (X = Cl, Br or I) have been prepared by direct reaction of CuX and 1-cyanoguanidine (cnge) in organic solvents and by reduction of aqueous solutions of $CuX_2$ (X = Cl or Br) containing cnge with sodium sulfite. Single crystals of $Cu_2Cl_2$·cnge **1**, $Cu_2Br_2$·cnge **2** and CuBr·cnge·$H_2O$ **3** were obtained from the latter route. Complexes **1** and **2** are isostructural and comprise mutually perpendicular chains of $[XCu(cnge)]_n$ and $(CuX_2^-)_n$ joined at a common halogen. The $[XCu(cnge)]_n$ chain, which lies in the mirror plane of the *Pbcm* space group, is novel. The cyanoguanidine molecule uses both its nitrile and imino nitrogen atoms to bridge the copper atoms which complete their co-ordinatively unsaturated, trigonal-planar, geometry with the common halogen. The $(CuX_2^-)_n$ chain is unremarkable. Complex **3** is characterised by a zigzag $(CuBr)_n$ chain and a buckled $[BrCu(cnge)]_n$ chain joined at a common copper atom; an unco-ordinated water molecule completes its structure. The $[BrCu(cnge)]_n$ chain is similar to that in **1** and **2**. The main difference is the buckling which results in a dihedral angle between adjacent cnge molecules of 8.9°. The $(CuBr)_n$ chain consists of bridging bromine atoms strongly bonded to one copper and weakly bonded to the other, giving a trigonal-pyramidal copper(I) co-ordination sphere. Extended-Hückel calculations have been used to examine the factors controlling the choice of a trigonal-planar over a tetrahedral structure.

Copper(I) usually forms four-co-ordinate tetrahedral complexes;[1,2] compounds with lower co-ordination numbers are known but are much less common.[3,4] Monomeric trigonal-planar copper(I) complexes with local $D_{3h}$ symmetry are quite rare; structural evidence has been reported for both cations and anions including $[Cu\{SC(NMe_2)_2\}_3]^+$,[5] $[Cu(SPMe_3)_3]^+$,[6] $[Cu(C_6H_7N)_3]^+$,[7] $[Cu\{P(C_6H_4OMe\text{-}p)_3\}_3]^+$,[8] $[Cu(SPh)_3]^{2-}$[9] and $[Cu(CN)_3]^{2-}$.[10] It might be argued that steric effects enforce three-co-ordination in the first five complexes; however, these arguments are untenable for the stability of $[Cu(CN)_3]^{2-}$. Although spectroscopic studies of the facile equilibrium between tetrahedral $[Cu(CN)_4]^{3-}$ and trigonal-planar $[Cu(CN)_3]^{2-}$ in aqueous solution containing halide ions have provided evidence for the importance of π bonding in the three-co-ordinate complex,[11] the factors controlling the formation of such low-co-ordinate copper(I) complexes are not fully understood,[12] despite preliminary theoretical studies.[13,14]

The parameters governing structure choice must be extremely subtle as several species are known in which copper(I) adopts both three- and four-co-ordinate geometries with the same ligands, sometimes in the same complex. Many of these complexes are adducts formed between either copper(I) halides[15–17] or thiolates[18] and either nitrogen or phosphorus bases. For example, 2:3 copper(I) halide:base adducts of structure $[L_2Cu(\mu\text{-}X)_2CuL]$ (L = $PPh_3$, X = Cl[19] or I[20]) are based on a $Cu_2X_2$ four-membered ring and contain one three-co-ordinate copper(I) atom surrounded by two halogen atoms and one phosphine molecule and one four-co-ordinate copper(I) atom surrounded by two halogen atoms and two phosphine molecules. These molecules form part of a well defined hierarchy for various $[L_m(CuX)_n]$ classes which exhibit decreasing co-ordination number with increasing ligand bulk.[17]



cnge

The stability of $[Cu(CN)_3]^{2-}$ prompted us to investigate the binding of 1-cyanoguanidine (cnge) to copper(I) in an attempt to extend our understanding of the ligand-bonding characteristics required to stabilise three-co-ordinate copper(I) in the absence of sterically bulky ligands. The products of our experimental programme to prepare copper(I) halide adducts of cnge with differing stoichiometries are reported here. We also describe the results of extended-Hückel calculations undertaken to examine the factors controlling the choice of a trigonal-planar over a tetrahedral copper(I) structure.

1-Cyanoguanidine is a planar molecule which co-ordinates either as a monodentate ligand (nitrile *N*-donor) or as a bidentate bridging ligand (nitrile and imino *N*-donor):[21–24] it has a completely delocalised π system with which it can behave as either π-acceptor or -donor. Although theoretical calculations rationalise the observed ligating properties of cnge, predicting preferential co-ordination through the nitrile nitrogen and secondary co-ordination through the imino nitrogen,[25–30] we believe this choice is dominated by steric factors, co-ordination by the imino function presenting a structure with close contacts between adjacent ligands. This co-ordination mode is only observed when the nitrile function is already being used and when the metal is sterically unhindered.

The only reported copper(I) complex of cnge is the novel planar dinuclear copper(I) cation $[Cu_2(cnge)_4]^{2+}$, in which each copper atom is co-ordinated by three nitrogen atoms provided by cnge molecules.[21] Copper(I) complexes containing comparable ligands are also scarce. Several copper(I) halide adducts of nitrogen bases have been prepared.[15,16,31–37] They

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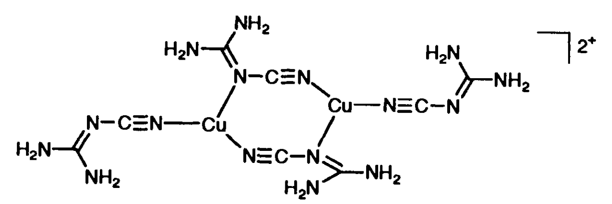
† *Supplementary data available:* see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1994, Issue 1, pp. xxiii–xxviii.

*Non-SI units employed:* cal = 4.184 J, eV ≈ 1.60 × $10^{-19}$ J.



$[Cu_2(cnge)_4]^{2+}$

form a structural hierarchy very similar to that of the phosphine adducts of copper(I) halides; control of the structure is thought to be determined by the relative stereochemical parameters of metal, halide and ligand.[15] The structures of the 1:1 CuX:monodentate N base adducts change from 'stair' polymer,[15,31] through tetrameric cubane,[32] 'split-stair' polymer[33] and planar dimeric[34] to linear monomeric[34] as the bases become more hindered and/or the halogen atoms become larger.[16]

The co-ordination of the potentially bidentate N-donor base pyridine-4-carbonitrile (L) to copper(I) halides has been studied;[35] $[\{CuL(X)\}_n]$ (X = Cl or Br) form 'split-stair' polymer strands woven into a two-dimensional sheet by cross-linking ligands; each copper(I) atom has a four-co-ordinate pseudo-tetrahedral geometry comprising two halogen atoms and two nitrogen atoms (one from the ring and one from the nitrile). A similar copper(I) co-ordination sphere is found in the more complex structure of $[\{Cu_4L_5I_4\}_n]$. In the mixed base (pyridine-4-carbonitrile–triphenylphosphine) adducts of the copper(I) halides there are no nitrile nitrogen–copper(I) interactions, dihalogeno-bridged dimers $[(PPh_3)LCu(\mu\text{-}X)_2CuL(PPh_3)]$ being formed.[36]

## Results and Discussion

(*i*) *Synthesis and Characterisation of* 2:1 *and* 1:1 CuX:cnge (X = Cl, Br *or* I) *Complexes*.—The complexes were synthesised by two routes. Route 1 involved the direct combination of copper(I) halides CuX (X = Cl, Br or I) with cnge in a suitable organic solvent [acetone, tetrahydrofuran (thf), chloroform, acetonitrile, 2,2-dimethoxypropane, ethanol, diethyl ether) under a dry nitrogen atmosphere using standard Schlenk procedures and reflux or ultrasound to solubilise the reactants. There was no visible evidence of reaction. A white (yellow in the case of CuI) solid was retained throughout the reaction, the reaction filtrate contained no product on evaporation and all product powders had the same weight as that of the reactants. Infrared spectroscopy gave evidence for reaction; the diagnostic $\nu_{asym}$(NCN) doublet, which occurs at 2209/2165 $cm^{-1}$ for free cnge, was shifted to higher wavenumber in the product, indicating that co-ordination to copper(I) had occurred.[21–24] In most cases, however, both free and complexed cnge were present indicating partial reaction and impure products.

Route 2 involved the addition of a three-fold molar excess of aqueous sodium sulfite solution to deoxygenated aqueous solutions of copper(II) halide–cnge mixtures; this route was limited to $CuX_2$ (X = Cl or Br). Reduction of the copper(II) solution led to immediate precipitation of a white powder. Cannula-wire filtration after *ca.* 2 min removed the residue, which was washed with deionised water and dried in vacuum, and gave a clear filtrate which afforded a colourless crystalline precipitate on standing. In all cases the crystals had the same properties as those of the original precipitate and the two were taken to be identical. The identity of the crystalline products depended on the initial $CuX_2$:cnge ratio. Analytical data are collected in Table 1, together with pertinent infrared spectral data. They indicate the formation of $Cu_2X_2$·cnge and CuX·cnge·$H_2O$ (X = Cl or Br) which was confirmed by single-crystal X-ray diffraction analysis of $Cu_2Cl_2$·cnge **1**, $Cu_2Br_2$·cnge **2** and CuBr·cnge·$H_2O$ **3**. The chemistry of these materials is very limited owing to their insolubility in water and most organic solvents. Dissolution does occur in aqueous alkaline solution but with concomitant oxidation to a copper(II) derivative.

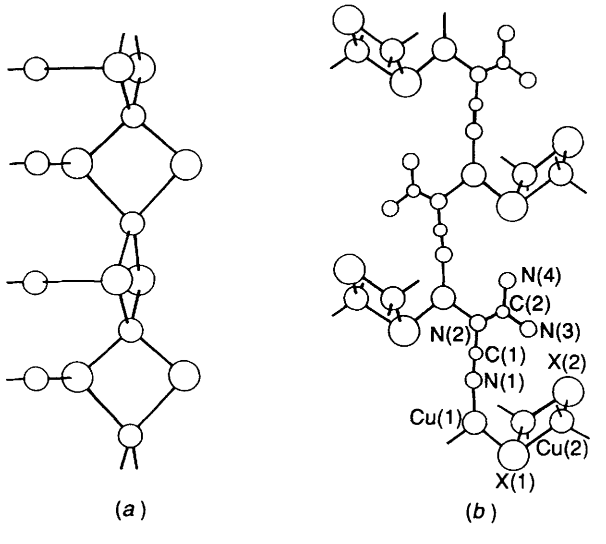


**Fig. 1** Molecular structure of $Cu_2X_2$·cnge showing the $(CuX_2^-)_n$ (*a*) and $[XCu(cnge)]_n$ (*b*) chains

(*ii*) *Structural Analysis of* $Cu_2X_2$·cnge (X = Cl *or* Br) *and* CuBr·cnge·$H_2O$.—Fractional atomic coordinates for all atoms are given in Table 2 and pertinent interatomic distances and bond angles in Table 3. Complexes **1** and **2** are isostructural; they are characterised by mutually perpendicular chains of $(CuX_2^-)_n$ and $[XCu(cnge)]_n$ joined at a common halogen; although the former has been observed in several copper(I) halide complexes,[1] the latter is novel.

The $(CuX_2^-)_n$ chain lies along the *z* axis and comprises edge-sharing '$CuX_4$' tetrahedra. The geometry of the chain is shown in Fig. 1(*a*). The copper atom exhibits a distorted-tetrahedral geometry; the halogen atoms exhibit two- and three-fold co-ordination, the common halogen, X(1), also being co-ordinated to the copper atom of the $[XCu(cnge)]_n$ chain. The Cu···Cl and Cu···Br distances within the chain [Cu(2)···Cl 231.8, 243.5; Cu(2)···Br 242.9, 256.8 pm] are typical of this moiety. Those to the pendant copper are relatively short [Cu(1)···Cl(1) 226.3, Cu(1)···Br(1) 236.4 pm].

The $[XCu(cnge)]_n$ chain lies in the mirror plane of the *Pbcm* space group (*z* = 0.25, 0.75) and is directed along the *y* axis; the chains are held in place by coplanar hydrogen-bonding interactions between the cnge amino-nitrogen atoms and the halogen atoms (Table 4). An interesting feature of the structure is the remarkably high number (13 out of a total of 14) of atoms of the asymmetric unit which are located on this plane. The geometry of the chain is shown in Fig. 1(*b*). Cyanoguanidine acts as a bridging ligand using both its nitrile and imino nitrogen atoms to co-ordinate the copper atoms which adopt a distorted trigonal-planar geometry. No co-ordination of the copper atom occurs in the axial positions, the nearest atoms being symmetry-related copper atoms in the adjacent mirror planes (Cu···Cu ≈ 313 pm). The copper–ligand distances are comparatively short (Table 3), especially the copper–nitrile nitrogen distance. Co-ordinated cnge shows significant differences in bond lengths and angles from those of free cnge (Table 5). The largest differences are in the N(1)–C(1) and C(1)–N(2) bond distances; whereas the former decreases from free cnge (117.4 pm) through the bromide (113 pm) to the chloride (110 pm), the latter increases from 130.7 through 133 to 137 pm. These changes accompany a corresponding increase in the Cu(1)–N(1) distance from the chloride (181.1 pm) to the bromide (190.1 pm). Quantification of the differences in the bond lengths for free and co-ordinated cnge by multivariate

**Table 1** Analytical and IR spectral data for crystalline products

| Reagents and molar ratio | Product | Analysis (%)* C | H | N | IR data/cm$^{-1}$ $\nu_{asym}$[N(1)C(1)N(2)] | $\nu_{sym}$[N(1)C(1)N(2)] | $\nu_{sym}$[N(2)C(2)N(3)] |
|---|---|---|---|---|---|---|---|
| cnge | | — | — | — | 2209, 2165 | 1252 | 928 |
| $2CuCl_2$ : cnge | $Cu_2Cl_2$·cnge | 8.30<br>(8.50) | 1.05<br>(1.40) | 20.00<br>(19.85) | 2227, 2182 | 1248 | 930 |
| $CuCl_2$ : cnge | CuCl·cnge·$H_2O$ | 13.25<br>(13.15) | 2.35<br>(2.20) | 30.45<br>(30.70) | 2223, 2180 | 1240 | 952 |
| $2CuBr_2$ : cnge | $Cu_2Br_2$·cnge | 6.35<br>(6.50) | 1.05<br>(1.10) | 14.95<br>(15.10) | 2228, 2185 | 1244 | 951 |
| $CuBr_2$ : cnge | CuBr·cnge·$H_2O$ | 9.95<br>(9.80) | 2.60<br>(2.45) | 22.50<br>(22.80) | 2223, 2175 | 1234 | 956 |

* Calculated values in parentheses.

**Table 2** Fractional atomic coordinates for all atoms

| Atom | X/a | Y/b | Z/c | Atom | X/a | Y/b | Z/c |
|---|---|---|---|---|---|---|---|
| $Cu_2Cl_2$·cnge | | | | | | | |
| Cu(1) | 0.068 59(8) | 1.249 31(7) | 0.25 | N(2) | 0.097 2(5) | 0.850 3(4) | 0.25 |
| Cu(2) | 0.350 2(2) | 1.25 | 0 | N(3) | 0.320 8(6) | 0.872 8(6) | 0.25 |
| Cl(1) | 0.233 9(1) | 1.381 8(1) | 0.25 | N(4) | 0.227 7(6) | 0.682 2(5) | 0.25 |
| Cl(2) | 0.462 9(1) | 1.135 4(2) | 0.25 | H(31) | 0.306(8) | 0.947(9) | 0.25 |
| C(1) | 0.084 9(6) | 0.971 4(5) | 0.25 | H(32) | 0.378(8) | 0.842(8) | 0.25 |
| C(2) | 0.215 7(6) | 0.803 0(5) | 0.25 | H(41) | 0.292(9) | 0.641(8) | 0.25 |
| N(1) | 0.068 0(5) | 1.075 7(5) | 0.25 | H(42) | 0.168(6) | 0.639(6) | 0.25 |
| $Cu_2Br_2$·cnge | | | | | | | |
| Cu(1) | 0.063 61(9) | 0.251 3(1) | 0.25 | N(2) | 0.088 6(6) | 0.853 7(6) | 0.25 |
| Cu(2) | 0.369 3(1) | 1.25 | 0 | N(3) | 0.302 4(7) | 0.879 2(9) | 0.25 |
| Br(1) | 0.236 38(7) | 1.379 76(7) | 0.25 | N(4) | 0.214 9(8) | 0.688 6(7) | 0.25 |
| Br(2) | 0.483 40(8) | 1.124 46(8) | 0.25 | H(31) | 0.311(8) | 0.946(8) | 0.25 |
| C(1) | 0.076 1(7) | 0.975 0(7) | 0.25 | H(32) | 0.37(1) | 0.846(9) | 0.25 |
| C(2) | 0.202 2(9) | 0.809 1(7) | 0.25 | H(41) | 0.27(1) | 0.659(9) | 0.25 |
| N(1) | 0.061 9(7) | 1.077 4(6) | 0.25 | H(42) | 0.15(1) | 0.643(8) | 0.25 |
| CuBr·cnge·$H_2O$ | | | | | | | |
| Cu(1) | 0.408 6(6) | 0.315 0(3) | 0.178 2(5) | N(4) | 0.245(3) | 0.871(2) | 0.259(3) |
| Br(1) | 0.243 2(5) | 0.180 4(3) | 0.260 0(5) | O(1) | 0.087(3) | 0.431(2) | 0.294(3) |
| C(1) | 0.401(3) | 0.589(2) | 0.252(3) | H(31) | 0.134(9) | 0.593(9) | 0.205(9) |
| C(2) | 0.250(3) | 0.754(2) | 0.251(4) | H(32) | 0.029(9) | 0.72(1) | 0.213(9) |
| N(1) | 0.416(2) | 0.487(2) | 0.234(3) | H(41) | 0.146(9) | 0.913(9) | 0.251(9) |
| N(2) | 0.391(3) | 0.710(2) | 0.265(3) | H(42) | 0.337(9) | 0.92(1) | 0.274(8) |
| N(3) | 0.131(3) | 0.683(2) | 0.224(4) | | | | |

comparison[37,39] affords a 'highly significant' difference in the structures of the free and co-ordinated cnge.

The layer separation is almost identical in the two structures (313.1 for **1** and 312.5 pm for **2**) suggesting that the separation is determined not by the $(CuX_2^-)_n$ chain but by the packing of the cnge molecules. To accommodate the bridging halogen atoms with typical Cu···X distances the Cu–X–Cu bond angles decrease from 85.0 and 80.1° for **1** to 80.1 and 75.0° for **2**.

The structure of compound **3** is also characterised by two types of polymeric chains but joined at a common copper atom; a zigzag $(CuBr)_n$ chain is directed along the *z* axis and a buckled $[BrCu(cnge)]_n$ chain along the *y* axis. An unco-ordinated water molecule completes the structure. The $(CuBr)_n$ chain [Fig. 2(*a*)] consists of bridging bromine atoms strongly bonded to one copper (Cu··· Br 244.7 pm) and weakly bonded to the other (Cu··· Br 271.2 pm). The $[BrCu(cnge)]_n$ chain [Fig. 2(*b*)] is very similar to that in $Cu_2X_2$·cnge. The main difference is the buckling of the chain which results in a dihedral angle between adjacent cnge molecules of 8.9° (Table 6). The copper co-ordination sphere can be described as midway between distorted tetrahedral and trigonal pyramidal, the copper atom lying 41 pm above the basal plane formed by N(1), N(2) and the nearer bromine. The cnge is essentially coplanar with the basal plane of the co-ordination sphere of the copper to which it is bonded through the nitrile-nitrogen atom (dihedral angle = 0.04°). In this case, multivariate comparison[37,39] of the geometries of free and co-ordinated cnge (Table 5) shows that the differences in bond lengths are 'not significant'.

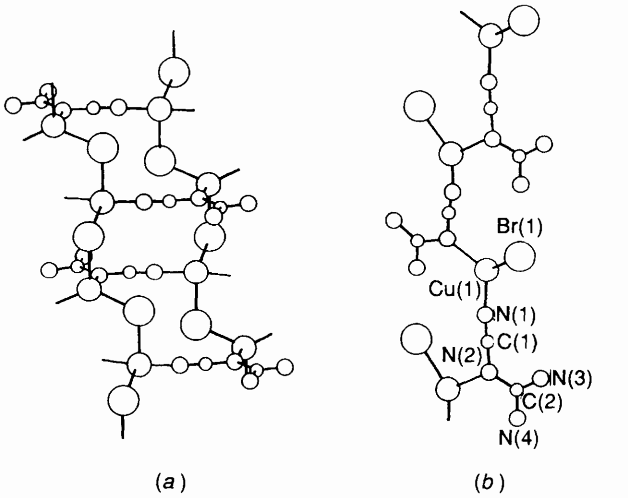


**Fig. 2** Molecular structure of CuX·cnge·$H_2O$ showing the $(CuX)_n$ (*a*) and $[XCu(cnge)]_n$ (*b*) chains

**Table 3** Interatomic distances (pm) and bond angles (°) (X = Cl or Br)

| | $Cu_2Cl_2$·cnge | $Cu_2Br_2$·cnge | CuBr·cnge·$H_2O$ |
|---|---|---|---|
| N(1)–C(1) | 110(1) | 113(1) | 117(4) |
| C(1)–N(2) | 137(1) | 133(1) | 133(4) |
| N(2)–C(2) | 139(1) | 135(1) | 138(4) |
| C(2)–N(3) | 136(1) | 135(1) | 130(4) |
| C(2)–N(4) | 127(1) | 132(1) | 132(4) |
| Cu(1)–N(1) | 181.1(6) | 190.1(9) | 193(2) |
| Cu(1)–N(2′) | 208.3(7) | 201.5(9) | 204(3) |
| Cu(1)–X(1) | 226.3(3) | 236.4(2) | 244.7(6) |
| Cu(1)–X(1′) | | | 271.2(6) |
| Cu(2)–X(2) | 231.8(2) | 242.9(1) | |
| Cu(2)–X(1) | 243.5(2) | 256.8(1) | |
| N(1)–C(1)–N(2) | 176(1) | 178(1) | 177(4) |
| C(1)–N(2)–C(2) | 117.0(8) | 117.2(8) | 116(3) |
| N(2)–C(2)–N(3) | 127.0(9) | 123.9(8) | 125(3) |
| N(2)–C(2)–N(4) | 117(1) | 117(1) | 113(3) |
| N(3)–C(2)–N(4) | 117(1) | 119(1) | 122(4) |
| N(1)–Cu(1)–N(2′) | 120.1(4) | 123.1(4) | 125(1) |
| N(1)–Cu(1)–X(1) | 127.8(3) | 127.0(3) | 120.0(7) |
| N(2′)–Cu(1)–X(1) | 112.1(2) | 109.9(3) | 104.2(8) |
| N(1)–Cu(1)–X(1′) | | | 99.8(8) |
| N(2′)–Cu(1)–X(1′) | | | 100.1(8) |
| X(2)–Cu(2)–X(2′) | 116.3(1) | 117.7(1) | |
| X(2)–Cu(2)–X(1′) | 97.4(1) | 102.4(1) | |
| X(2)–Cu(2)–X(1′) | 114.7(1) | 112.0(1) | |
| X(1)–Cu(2)–X(1′) | 97.4(1) | 110.5(1) | |
| Cu(1)–X(1)–Cu(2) | 93.8(1) | 97.5(1) | |
| Cu(2)–X(2)–Cu(2′) | 85.0(1) | 80.1(1) | |
| Cu(2)–X(1)–Cu(2′) | 80.1(1) | 75.0(1) | |
| X(1)–Cu(1)–X(1′) | | | 104.0(8) |
| Cu(1)–X(1)–Cu(1′) | | | 102.6(2) |

**Table 4** Hydrogen-bond interactions

| Interaction X–H · · · X′ | X · · · X′/ pm | X · · · H/ pm | H · · · X′/ pm | X–H–X/ ° |
|---|---|---|---|---|
| $Cu_2Cl_2$·cnge | | | | |
| N(3)–H(31) · · · Cl(2) | 314 | 79 | 260 | 128 |
| N(3)–H(32) · · · Cl($2^{I}$) | 341 | 70 | 276 | 156 |
| N(4)–H(41) · · · Cl($2^{I}$) | 339 | 82 | 266 | 149 |
| N(4)–H(41) · · · Cl($1^{II}$) | 313 | 82 | 277 | 110 |
| N(4)–H(42) · · · Cl($1^{II}$) | 313 | 80 | 277 | 110 |
| $Cu_2Br_2$·cnge | | | | |
| N(3)–H(31) · · · Br(2) | 333 | 74 | 272 | 143 |
| N(3)–H(32) · · · Br($2^{I}$) | 364 | 83 | 291 | 150 |
| N(4)–H(41) · · · Br($2^{I}$) | 340 | 69 | 274 | 158 |
| N(4)–H(41) · · · Br($1^{II}$) | 338 | 69 | 307 | 111 |
| N(4)–H(42) · · · Br($1^{II}$) | 338 | 87 | 303 | 107 |
| CuBr·cnge·$H_2O$ | | | | |
| N(3)–H(31) · · · O(1) | 289 | 100 | 203 | 142 |
| N(3)–H(32) · · · Br($1^{III}$) | 360 | 101 | 272 | 146 |
| N(4)–H(41) · · · O($1^{III}$) | 303 | 102 | 206 | 158 |
| N(4)–H(41) · · · Br($1^{IV}$) | 340 | 98 | 298 | 107 |
| N(4)–H(42) · · · Br($1^{IV}$) | 340 | 102 | 307 | 100 |
| O(1) · · · Br(1) | 319 | — | — | — |
| O(1) · · · Br($1^{V}$) | 327 | — | — | — |

Symmetry equivalents: I 1 − x, $-\frac{1}{2}$ + y, z; II x, −1 + y, z; III −x, $\frac{1}{2}$ + y, $\frac{1}{2}$ − z; IV x, 1 + y, z; V x, $\frac{1}{2}$ − y, $\frac{1}{2}$ + z. The six angles around O(1) range from 78 to 134° and average 107°.

It is interesting that the apical position of the copper(I) co-ordination sphere is occupied by a bromine atom, not the water of crystallisation, demonstrating the ability of unsaturated copper(I) to distinguish between 'soft' bromine ligands and 'hard' water ligands. The water molecule is fixed in position by approximately tetrahedrally disposed hydrogen-bonding interactions to two cnge amino-nitrogen atoms and two bromine atoms (Table 4).

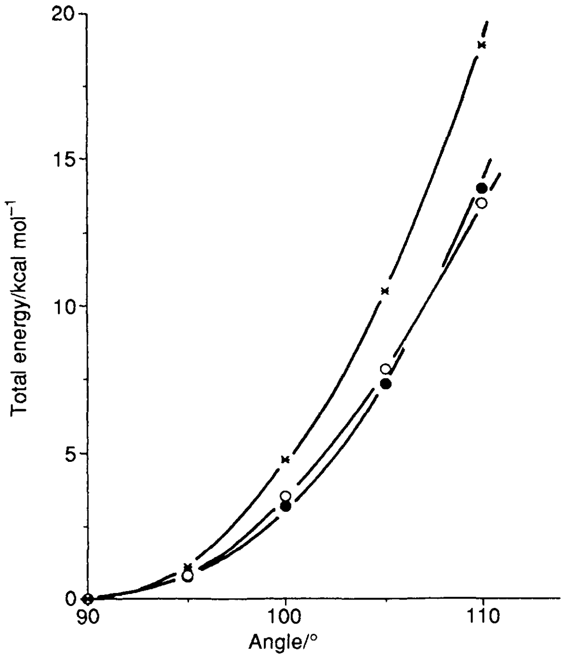


**Fig. 3** Total energy change on distortion of $CuH_3^{2-}$ (○), $CuCl_3^{2-}$ (●) and $Cu(CO)_3^+$ (✱) using copper(I) 4s, 4p and 3d orbitals

The structures of compounds **1** and **2** indicate the remarkable tendency of copper(I) to form unsaturated centres when co-ordinated by cnge. Furthermore as their preparations are completed in aqueous solution, they demonstrate that stable unsaturated copper(I) complexes with *N*-donor bases can be generated in aqueous environments. Structural analysis of **3** shows that the $[BrCu(cnge)]_n$ chains seen in **2** prevail. However, as they are no longer constrained by the presence of the perpendicular $(CuX_2^-)_n$ chains, they are no longer planar, but buckled. This buckling permits the copper(I) co-ordination sphere to expand from trigonal planar to distorted trigonal pyramidal by co-ordination of a bromine atom from an adjacent chain to the apical position. This distorted trigonal-pyramidal geometry is particularly interesting as it clearly indicates the tendency of the copper(I) centre to bind weakly a fourth co-ordinating atom at the vacant site.

(*iii*) *Trigonal* vs. *Tetrahedral* $Cu^I$, *A Theoretical Examination*.—Although copper(I) ($d^{10}$) generally forms complexes with tetrahedral geometry ($T_d$),[1,2] a number of three-co-ordinate complexes have been observed in the crystalline state.[5–10,21] Included among these are **1** and **2** which contain trigonal-planar copper(I). We now describe the results of extended-Hückel calculations undertaken, using the weighted $H_{ij}$ formulation,[40] to examine the factors controlling the choice of a trigonal-planar over a tetrahedral structure.

The change in total energy for the distortion of $Cu^IL_3$ from a planar ($D_{3h}$) to a pyramidal ($C_{3v}$) geometry **I** was calculated for L = $H^-$, $Cl^-$ or CO, representing a σ donor, π donor and π acceptor, respectively. Regular trigonal-planar structures were used for $Cu^IL_3$, using Cu · · · H 155, Cu · · · C 180, C · · · O 113 and Cu · · · Cl 230 pm. All the ligands were bent down in unison for the distortion in **I**. The parameters for copper were taken from Hoffmann and co-workers.[41] The calculations were carried out with and without the copper d block ($3d^{10}$); inclusion of the d block increases the energy changes observed on distortion but does not drastically alter the ordering of the distortions for the different ligands, L. The energy changes observed with the copper d block present are shown in Fig. 3. The trigonal-planar structure is always preferred over the pyramidal structure. The π acceptor shows the largest energy difference upon pyramidalisation followed by the π donor and σ

**Table 5** Interatomic distances (pm) and bond angles (°) in free and co-ordinated cnge

| | N(1)–C(1) | C(1)–N(2) | N(2)–C(2) | C(2)–N(3) | C(2)–N(4) | N(1)–C(1)–N(2) | C(1)–N(2)–C(2) | N(2)–C(2)–N(3) | N(2)–C(2)–N(4) | N(3)–C(2)–N(4) |
|---|---|---|---|---|---|---|---|---|---|---|
| Free cnge[a] | 117.4 | 130.7 | 134.3 | 134.4 | 133.5 | 175.1 | 118.4 | 123.8 | 117.5 | 118.7 |
| $Cu_2Cl_2$·cnge[b] | 110 | 137 | 139 | 136 | 127 | 176 | 117.0 | 127.0 | 117 | 117 |
| $Cu_2Br_2$·cnge[b] | 113 | 133 | 135 | 135 | 132 | 178 | 117.2 | 123.9 | 117 | 119 |
| CuBr·cnge·$H_2O$[b] | 117 | 133 | 138 | 130 | 132 | 177 | 116 | 125 | 113 | 122 |
| $[Cu(cnge)_2(H_2O)_2][NO_3]_2{\cdot}2H_2O$[c] | 116 | 129 | 133 | 134 | 131 | 173 | 123 | 123 | 118 | 119 |
| $[Cu_2(\mu\text{-}O_2CCH_3)_4(cnge)_2]$[d] | 114.6 | 130.0 | 132.8 | 131.8 | 133.1 | 175.1 | 117.9 | 123.7 | 116.9 | 119.4 |
| $[\{Cd_2(\mu\text{-}cnge)_2(H_2O)_4(SO_4)_2\}_n]$[e] | 114 | 130 | 134 | 134 | 132 | 173.1 | 118.8 | 122.5 | 119.4 | 118.1 |
| $[\{Cd(cnge)Cl_2\}_n]$[f] | 113.6 | 131.7 | 136.3 | 131.8 | 131.7 | 177.6 | 116.4 | 122.6 | 117.5 | 119.8 |

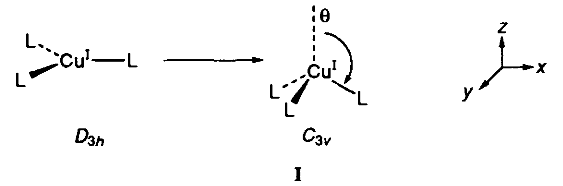
[a] Ref. 25. [b] Present work. [c] Ref. 22. [d] Ref. 24. [e] Ref. 23. [f] Ref. 38.

**Table 6** Planarities of the cnge molecule in CuBr·cnge·$H_2O$

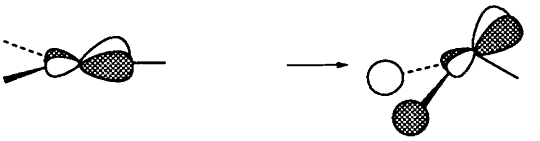
Equation of best plane: $-0.915\,06x - 0.849\,02y - 6.801\,62z = -1.236$

Deviations (pm) of atoms from plane: N(1), −2.6; C(1), 1.7; N(2), 1.7; C(2), 1.2; N(3), −2.6; N(4), 0.6

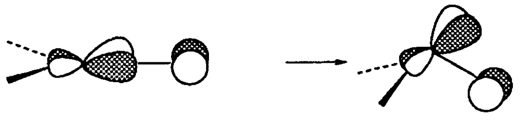
Dihedral angle between adjacent cnge molecules: 8.87°



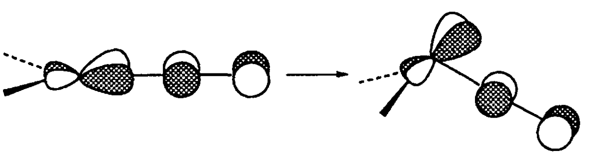
**I**



**Ia**



**Ib**



**Ic**

donor. These results suggest that the planar structure should always be favoured over a pyramidal structure.

Walsh diagrams were constructed for distortion **I**. Similar diagrams have been presented elsewhere[42] and are not included here. Their important features may be described by isolating the different interactions of the three different ligand types. The copper–ligand σ interactions disfavour the pyramidalisation of $Cu^IL_3$ mostly by increasing the antibonding interaction between the ligands and the metal occupied orbitals. This effect is especially visible in the degenerate $d_{xy}/d_{x^2-y^2}$ (e) pair making up the highest occupied molecular orbital (HOMO) [**Ia**, **Ib** and **Ic** (for $d_{xy}$) and Fig. 4] since upon pyramidalisation this degenerate pair mixes with the other e set ($d_{xz}/d_{yz}$). Ligands which are π acceptors (L = CO) raise the energy of the HOMO further on distortion due to loss of the stabilising back-bonding interactions, **Ic**, whereas π donors (L = $Cl^-$) reduce the energy of the HOMO due to loss of the π-donating interaction between the ligand and the metal, **Ib**. In Fig. 4 the HOMO of $CuCl_3^{2-}$ shows the smallest energy change, but its total energy change (Fig. 3) is similar to that of $CuH_3^{2-}$. This is because the chlorine lone pairs approach each other upon distortion causing a destabilisation.

The most striking difference between the three Walsh diagrams is the change in the lowest unoccupied molecular orbital (LUMO) ($a_1$) upon distortion (Fig. 5). For L = $H^-$ and $Cl^-$ we see a drastic drop in the energy of the LUMO upon distortion, whereas for L = CO it remains at the same energy. In the planar geometry with L = $H^-$ the LUMO is pure copper $p_z$. When L = $Cl^-$ the copper $p_z$ is *destabilised* by the chlorine $p_z$ lone pairs. For L = CO the copper $p_z$ is *stabilised* by $\pi^*_{CO}$. Upon pyramidalisation the copper $p_z$ orbital is stabilised by mixing in the antibonding combination of copper s and ligand orbitals.[43] The LUMO, which is now σ bonding between copper and the ligands, points towards the new vacant site. In the case of L = $Cl^-$ the pyramidalisation decreases also the overlap between copper $p_z$ and the chlorine $p_z$ lone pairs and this effect increases the stabilisation of the LUMO. However, for L = CO, the overlap between $p_z$ and $\pi^*_{CO}$ decreases upon pyramidalisation and this counteracts the stabilisation caused by σ interactions, and the LUMO does not change in energy.

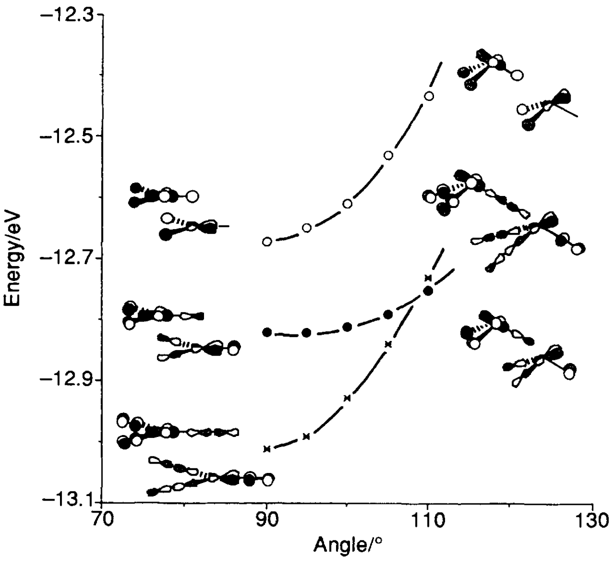


**Fig. 4** Energy changes in the HOMO on distortion of $CuH_3^{2-}$ (○), $CuCl_3^{2-}$ (●) and $Cu(CO)_3^+$ (✱) using copper(I) 4s, 4p and 3d orbitals

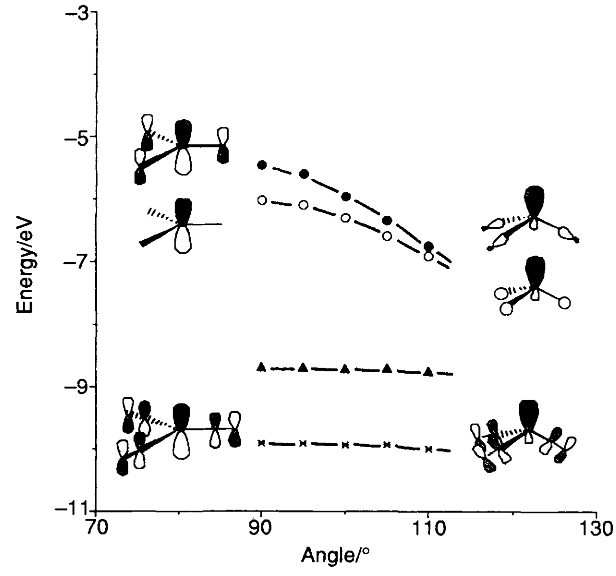


**Fig. 5** Energy changes for the LUMO of $CuH_3^{2-}$ (○), $CuCl_3^{2-}$ (●), $Cu(CO)_3^+$ (✱) and $Cu(NCH)_3^+$ (▲) using copper(I) 4s, 4p and 3d orbitals

Thus we see that distorting a planar $Cu^IL_3$ makes the LUMO more accessible for nucleophilic attack if L is a σ- or a π-donor whereas no such benefit arises for a π acceptor such as CO. This explanation can account for, in part, the observation of $[CuCl_4]^{3-}$ as a tetrahedral unit[1,2] and of $[Cu(CN)_3]^{2-}$ as a trigonal-planar species.[10] Calculations for L = NCH,[44] a preliminary model for cnge, were also carried out using Cu···N 193, N···C 117 and C···H 90 pm. The LUMO in this case behaves as a π acceptor which is unusual in the case of an *N*-donor ligand (Fig. 5). This situation arises from the closer proximity in energy of the empty π* orbital of NCH to copper $p_z$, compared to its full π orbitals. Therefore, in the case of L = NCH (and cnge) we expect a situation like L = CO (Fig. 5) and find little tendency for the $Cu^IL_3$ to distort and undergo nucleophilic attack.

(*iv*) *The Role played by an Axial Ligand*.—A number of these complexes are found with an axial ligand at long distance.[44] In order to verify the role of this ligand in determining the eventual structure of the $Cu^IL_3$ fragment we can allow a fourth ligand to approach the copper in the axial position. By recalculating the energy diagrams upon pyramidalisation in the presence of a long distant axial ligand we find a mild distortion from a planar structure.

For the systems $Cu^IL_3$ ($L = H^-$, $Cl^-$ or CO) an axial $Br^-$ was introduced at long distance (271 pm). The derived energy diagrams for $L = H^-$ are given in Fig. 6. For each ligand there is a shift in the position of the minimum towards a tetrahedral structure when the axial $Br^-$ is introduced. The precise position of the minimum depends on the ligand; for $L = Cl^-$ it occurs at above 100°, whereas for $L = H^-$ and CO it is at less than 100°. This result comes from a combination of the two effects we have analysed: an intrinsic preference for a trigonal geometry for the $Cu^IL_3$ part and increased stabilising interaction between the LUMO of $Cu^IL_3$ and the entering ligand when the copper moieties are bent. The especially low LUMO in the case of $Cl^-$ favours a larger hybridisation angle. The opposite is true in the case of CO.

The real systems $(cnge)_2CuBr$ and $[(cnge)_2CuBr \cdots Br]^-$ were examined to check our results with the experimental systems. The corresponding Walsh diagrams are much more complicated than for the $Cu^IL_3$ and $[Cu^IL_3 \cdots Br]^-$ systems, but nevertheless it is possible to trace the same features as above. The bromine and the nitrile nitrogen of cnge act as $\pi$ donors in the occupied orbitals, whilst the imino nitrogen of cnge acts more as a $\sigma$ donor. The effect of an axial bromine is similar to those above; with no axial ligand, the system prefers to be trigonal planar, but when an axial ligand is co-ordinated, even at long distance, the system prefers a small distortion towards a tetrahedron. This is consistent with the experimental observations.

## Experimental

$Cu_2Cl_2$·cnge **1**.—A deoxygenated aqueous solution containing $CuCl_2·2H_2O$ (1.70 g, 0.01 mol) and cnge (0.42 g, 0.005 mol) was treated with a three-fold excess of sodium sulfite (1.89 g, 0.015 mol). A precipitate formed immediately (yield 93%) which was removed by cannula filtration after ≈120 s. The clear filtrate was left to stand under nitrogen until after 5 d a crop of colourless crystalline blocks had developed. The crystals were recovered using standard Schlenk procedures (yield < 1%). After washing with deionised water the products were dried in vacuum.

$Cu_2Br_2$·cnge **2**.—This was prepared as for $Cu_2Cl_2$·cnge using $CuBr_2$ (2.23 g, 0.01 mol) instead of $CuCl_2·2H_2O$. Yield: precipitate 95%; colourless crystalline plates < 1%.

CuCl·cnge·$H_2O$.—A deoxygenated aqueous solution containing $CuCl_2·2H_2O$ (1.70 g, 0.01 mol) and cnge (0.84 g, 0.01 mol) was treated with a three-fold excess of sodium sulfite (1.89 g, 0.015 mol). A precipitate formed immediately (yield 85%) which was removed by cannula filtration after ≈120 s. The clear filtrate was left to stand under nitrogen until after 7 d a crop of colourless crystalline blocks had developed. The crystals were recovered using standard Schlenk procedures (yield < 1%). After washing with deionised water the products were dried in a desiccator.

CuBr·cnge·$H_2O$ **3**.—This was prepared as for CuCl·cnge·$H_2O$ using $CuBr_2$ (2.23 g, 0.01 mol) instead of $CuCl_2·2H_2O$. Yield: precipitate 87%; pale yellow crystalline blocks < 1%.

*Crystallography*.—Colourless crystals of compounds **1** and **2** and pale yellow crystals of **3** were grown from the aqueous mother-liquor remaining after filtration of the precipitates resulting from the aqueous sodium sulfite reduction of 2:1 $CuCl_2$:cnge, 2:1 $CuBr_2$:cnge and 1:1 $CuBr_2$:cnge molar ratio mixtures, respectively. Several crystals of each product were mounted in Lindemann tubes under dry nitrogen for preliminary study. Oscillation and Weissenberg photographs revealed orthorhombic cell parameters with space group either *Pbcm* (no. 57) or $Pca2_1$ (no. 29) for **1** and **2** and monoclinic cell parameters with space group $P2_1/c$ (no. 14) for **3**. X-Ray diffraction data for the refinement of cell parameters and structure determination were collected for suitable crystals using a Hilger and Watts Y290 four-circle diffractometer. For each crystal one unique set of data was collected in the range $1 < \theta < 25°$ using graphite-monochromated Mo-K$\alpha$ radiation ($\lambda$ 71.07 pm). Standard reflections were constant 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.

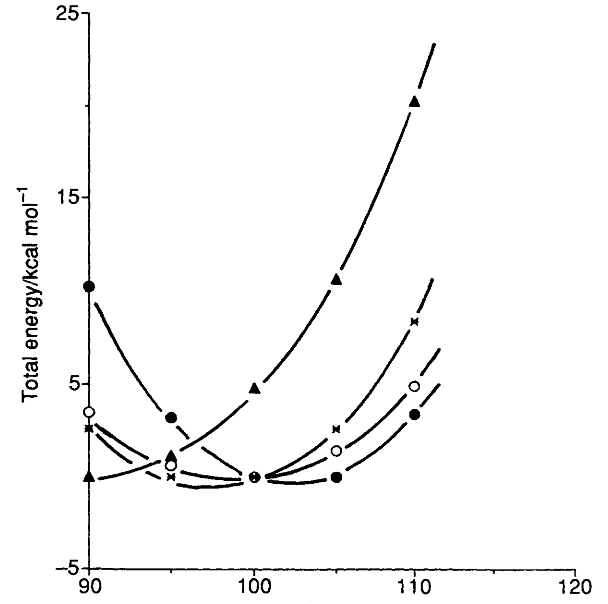


**Fig. 6** Total energy changes on introduction of a bromide ion along the $C_3$ axis of $CuH_3^{2-}$ (○), $CuCl_3^{2-}$ (●) and $Cu(CO)_3^+$ (✱); the total energy change for $Cu(CO)_3^+$, in the absence of the incoming ligand (*cf.* Fig. 3), is shown for comparison (▲)

The positions of the heavy atoms were determined by Patterson methods and those of the remaining atoms by Fourier difference syntheses using the CRYSTALS suite of programs.[45] For compounds **1** and **2** interatomic distances in the cnge moiety were corrected for libration. Full least-squares matrix refinement in space group *Pbcm* converged to $R = 0.048$ and $R' = 0.033$ for **1** and to 0.046 and 0.035 for **2**; refinement in the less-symmetrical space group $Pca2_1$ resulted in larger *R* factors. Full least-squares matrix refinement in space group $P2_1/c$ converged to $R = 0.097$ and $R' = 0.112$ for **3**; these high *R* factors are attributed to the very low intensity data set. Details of the data collection and structure solution for all three complexes are collated in Table 7.

Additional material available from the Cambridge Crystallographic Data Centre comprises thermal parameters.

## Acknowledgements

We thank the SERC for financial support (to P. H. W.) and the British Council for a grant under the British–French 'Alliance' Joint Research Programme.

**Table 7** Data collection parameters[a] for $Cu_2Cl_2$·cnge **1**, $Cu_2Br_2$·cnge **2** and CuBr·cnge·$H_2O$ **3**

| | **1** | **2** | **3** |
|---|---|---|---|
| Formula | $C_2H_4Cl_2Cu_2N_4$ | $C_2H_4Br_2Cu_2N_4$ | $C_2H_6BrCuN_4O$ |
| $M$ | 282.08 | 370.98 | 245.55 |
| Crystal system | Orthorhombic | Orthorhombic | Monoclinic |
| Space group | *Pbcm* (no. 57) | *Pbcm* (no. 57) | $P2_1/c$ (no. 14) |
| $a$/pm | 1084.8(3) | 1101.1(3) | 945.6(5) |
| $b$/pm | 1041.4(3) | 1092.5(3) | 1097.8(5) |
| $c$/pm | 626.2(2) | 625.0(2) | 753.9(5) |
| $\alpha$/° | 90 | 90 | 90 |
| $\beta$/° | 90 | 90 | 120.7(5) |
| $\gamma$/° | 90 | 90 | 90 |
| $10^{-6}U/pm^3$ | 707.9 | 751.8 | 672 |
| $\mu_{calc}/cm^{-1}$ | 67.1 | 161.4 | 90.7 |
| $D_c/g\ cm^{-3}$ | 2.65 | 3.28 | 2.42 |
| $D_m/g\ cm^{-3}$ (bromoform–hexane) | 2.64 | 3.28 | 2.40 |
| $F(000)$ | 544 | 688 | 472 |
| Crystal dimensions/mm | 0.2 × 0.2 × 0.15 | 0.3 × 0.1 × 0.01 | 0.1 × 0.1 × 0.05 |
| Reflections collected (unique) | 1058 | 989 | 1058 |
| Reflections with $F_o^2 > 3\sigma(F_o^2)$ | 711 | 645 | 615[b] |
| Number of parameters | 72 | 72 | 98 |
| Data/parameter ratio | 9.88 | 8.96 | 6.28 |
| $R = [\Sigma\|\Delta F\|/\Sigma\|\Delta F_o\|]$ | 0.048 | 0.046 | 0.097 |
| $R' = [\Sigma w(\Delta F)^2/\Sigma w(\Delta F_o)^2]$ | 0.033 | 0.035 | 0.112 |

[a] Details in common: $Z = 4$; $\theta_{max}$ 25°; scan type $\omega$–$2\theta$. [b] Reflections with $F_o^2 > 2\sigma(F_o^2)$.

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