Unusual Magnetic Chain of Copper(II) Ions in $[Cu(pepci)Br]_n$-$[PF_6]_n$ [pepci = *N*-(2-pyridylethyl)pyridine-2-carbaldimine]

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The complex $[Cu(pepci)Br]PF_6$ [pepci = *N*-(2-pyridylethyl)pyridine-2-carbaldimine] has been synthesised and characterization by X-ray crystallography shows it to contain cationic mono-μ-bromocopper(II) chains, with two crystallographically independent consecutive cations forming –Cu(pepci)– Br–Cu(pepci)–Br– units which repeat by translation to give the chain structure, and isolated PF_6^- counter ions; the ESR spectrum, showing the forbidden $\Delta M_s = 2$ transition, is indicative of interactions between copper(II) pairs, and the preliminary magnetic susceptibility data indicate a weak antiferromagnetic behaviour.

Combination of 'quasi-planar' tridentate ligands (L) and copper(II) ions in 1:1 ratio leads to the possibility of stabilizing square-planar $[Cu(L)X]^+$ moieties in solution. The stacking of these units, by following the synthetic strategy shown in equations (1) and (2), allows polynuclear entities of general

$$[Cu(L)X_2](s) \rightleftharpoons [Cu(L)X_2](aq) \rightleftharpoons [Cu(L)X]^+(aq) + X^-(aq) \quad (1)$$

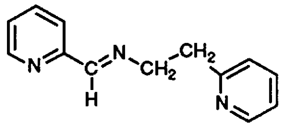
$$[Cu(L)X]^+(aq) + Y^-(aq) \rightleftharpoons \frac{1}{n}[Cu(L)X]_n[Y]_n(aq\ or\ s) \quad (2)$$

formula $[Cu(L)X]_n[Y]_n$ (X = halide or pseudohalide; Y = non-co-ordinating anion) to be obtained. The variation in rigidity of the tridentate ligands is a determining factor in the resulting geometry of these polynuclear systems. Thus the use of ligands of high rigidity leads to dimeric molecules,[1,2] while with more flexible ligands chain structures are obtained.[3,4]

To develop this synthetic strategy we studied the new more flexible ligand *N*-(2-pyridylethyl)pyridine-2-carbaldimine (pepci) and synthesised the copper(II) complex $[Cu(pepci)Br]PF_6$.

The crystal structure of $[Cu(pepci)Br]PF_6$ consists of cationic chains in which bromo groups link Cu(pepci) units through alternate short and long Cu–Br bonds. This type of complex is scarce, and its structural characteristics, to our knowledge, are unique.

The complex $[Cu(pepci)Br]PF_6$ was obtained by treating a methanol solution (10 cm^3) of $[Cu(pepci)Br_2]$ (0.05 g) (previously prepared by mixing equimolar amounts of copper bromide and the pepci ligand) with a saturated aqueous solution of potassium hexafluorophosphate. Within a few minutes a blue solid precipitated, which was filtered off and discarded. The clear blue solution yielded X-ray-quality blue needles on standing at room temperature (yield: 0.06 g) (Found: C, 31.15; H, 2.75; N, 8.26. $C_{13}H_{13}BrCuF_6N_3$ requires C, 31.20; H, 2.60; N, 8.40%).



pepci

The first crystallographic peculiarity of this complex arose in attempting to solve the crystal structure. This was accomplished with the program SIR 88,[5] which was able to handle properly the strong pseudo-translational effect present in the collected set of reflections (we were not able to determine the structure by traditional Patterson methods or with the program MULTAN[6]).

The structure[†] consists of two independent cationic chains each comprised of repeating –Cu(pepci)–Br–Cu(pepci)–Br– units (Fig. 1) [*i.e.* there are four independent Cu and Br atoms in the crystal (Fig. 2)], and separate PF_6^- anions. The pepci ligands are located on alternate sides of the chain, presumably to minimize steric factors, and are not parallel to each other. The pepci ligands themselves are not planar owing to the presence of the $-CH_2CH_2-$ groups and the two pyridine rings are inclined with dihedral angles close to 25°. In general, C–C, C=C and C=N bond lengths are close to average values except for the C(11)=N(11) distance of 1.44(3) Å. The bridging bromide occupies the basal position of a distorted square pyramid of one copper(II) atom [average $Cu-Br_{basal}$ 2.41(3) Å] and an axial position for the adjacent copper(II) environment [average $Cu-Br_{apical}$ 2.87(3) Å]. The intrachain separations Cu(1)···Cu(2) and Cu(3)···Cu(4) are 4.846(4) and 4.851(4) Å respectively, while the interchain distances, Cu(1)···Cu(3) and Cu(2)···Cu(4), are 7.58(2) and 7.59(2) Å respectively.

[†] Crystal data for $[Cu(pepci)Br]PF_6$: $M = 499.68$, orthorhombic, space group $Pc2_1b$ (standard $Pca2_1$ no. 29), $a = 7.904(3)$, $b = 24.816(3)$, $c = 34.289(4)$ Å, $D_m = 1.97(2)$, $Z = 16$, $D_c = 1.97$ g cm^{-3}, $F(000) = 3920$, $R = 7.1$ ($R' = 6.7$) for 2405 reflections with $I \geqslant 3\sigma(I)$ collected at 25 °C on an Enraf-Nonius CAD4 diffractometer, θ–2θ scan, $1.5 < 2\theta < 65°$, $w = 1/\sigma^2$.

Atomic coordinates, thermal parameters and bond lengths and angles have been deposited at the Cambridge Crystallographic Data Centre. See Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1992, Issue 1, pp. xx–xxv.

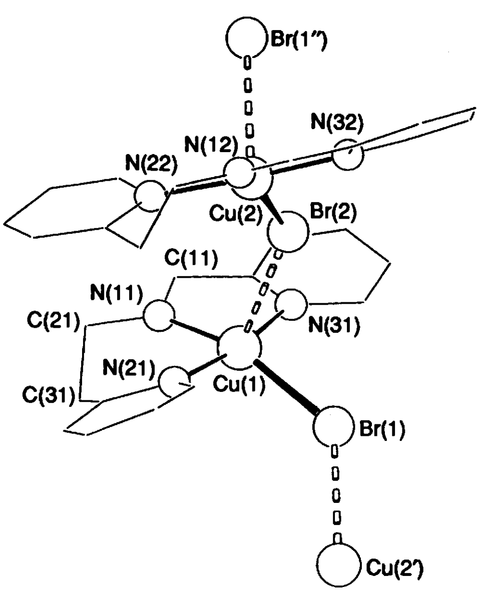


Fig. 1 View of one of the inequivalent dimeric entities which repeats to give the chain structure. Selected bond distances (Å) and angles (°) for the co-ordination polyhedra of the [Cu(pepci)Br]PF_6 compound: Cu(1)–Br(1) 2.434(3), Cu(1)–N(11) 2.02(2), Cu(1)–N(21) 2.00(1), Cu(1)–N(31) 2.00(2), Cu(1)–Br(2) 2.856(3), Cu(2)–Br(2) 2.401(3), Cu(2)–N(12) 1.95(2), Cu(2)–N(22) 2.02(1), Cu(2)–N(32) 1.97(1), Cu(2)–Br(1′) 2.866(3), Cu(3)–Br(3) 2.382(3), Cu(3)–N(13) 1.95(2), Cu(3)–N(23) 2.02(2), Cu(3)–N(33) 2.03(1), Cu(3)–Br(4) 2.871(6), Cu(4)–Br(4) 2.419(3), Cu(4)–N(14) 2.06(2), Cu(4)–N(24) 1.94(1), Cu(4)–N(34) 1.93(2), Cu(4)–Br(3′) 2.888(3), Cu(1)–Br(1)–Cu(2″) 134.0(1), Cu(1)–Br(2)–Cu(2) 134.1(1), Cu(3)–Br(3)–Cu(4″) 134.9(1), Cu(3)–Br(4)–Cu(4) 134.9(1)

The ESR spectrum of powdered samples of the compound, at 100 K, shows a broad and isotropic signal for the g tensor (g = 2.117). The linewidth of this signal (peak to peak) is *ca.* 210 G (0.0210 T). In the half-field position the forbidden $\Delta M_s = 2$ transition is also observed which can probably be explained by the existence of a dipole–dipole interaction between two consecutive crystallographically independent copper(II) ions in the chain structure. The Cu ••• Cu distance calculated from the relative intensities of the main signal and the forbidden transition[7] is *ca.* 4.6 Å, in good accord with the structural results.

Preliminary variable-temperature magnetic susceptibility data (4.2–300 K) show a slight lowering in the $\chi_m T$ values with decreasing temperature and a Weiss temperature of $\theta = -1$ K, both characteristic of a weak antiferromagnetic behaviour for the complex. Magnetic measurements below 4.2 K to allow an accurate determination of the exchange coupling constant are now in progress.

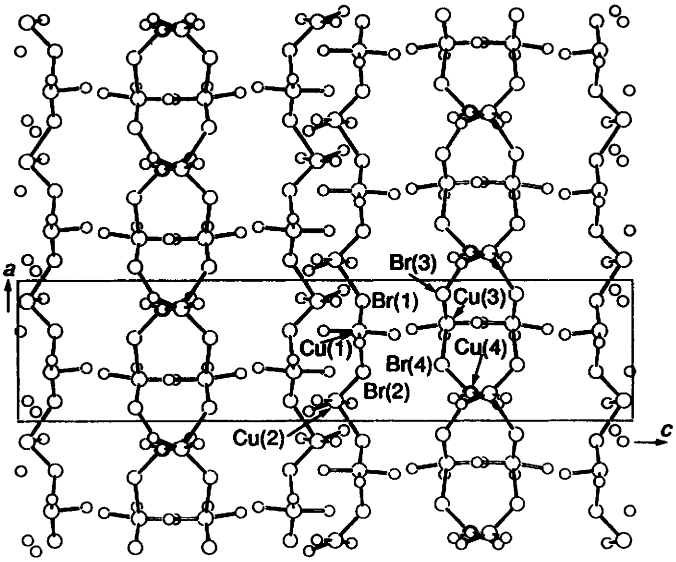


Fig. 2 Perspective view of the *ac* plane in the unit cell, showing the disposition of the two inequivalent chains and their propagation along the [100] direction. The carbon atoms are omitted for clarity

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References

1 T. Rojo, M. I. Arriortua, J. Ruiz, J. Darriet, G. Villeneuve and D. Beltrán, *J. Chem. Soc., Dalton Trans.*, 1987, 285.

2 T. Rojo, M. I. Arriortua, J. L. Mesa, R. Cortés, G. Villeneuve and D. Beltrán, *Inorg. Chim. Acta*, 1987, **134**, 59.

3 T. Rojo, J. L. Mesa, M. I. Arriortua, J. M. Savariault, J. Galy, G. Villeneuve and D. Beltrán, *Inorg. Chem.*, 1988, **27**, 3904.

4 J. V. Folgado, F. Coronado, D. Beltrán, D. Burriel, A. Fuertes and C. J. Miravitlles, *J. Chem. Soc., Dalton Trans.*, 1988, 3041.

5 M. C. Burla, M. Carralli, G. Cascarano, G. Giaccovazzo, G. Polidori, R. Spagna and D. Vitervo, SIR 88, A Direct Methods Program for the Automatic Solution of Crystal Structures, *J. Appl. Crystallogr.*, 1989, **22**, 389; E. Weller, *J. Appl. Crystallogr.*, 1989, **22**, 19.

6 P. Main, G. Germain and M. M. Woolfson, MULTAN 84. A System of Computer Programs for the Automatic Solution of Crystal Structures from X-ray Diffraction Data, Universities of York and Louvain, 1984.

7 S. S. Eaton, K. M. More, B. H. Sawant and G. R. Eaton, *J. Am. Chem. Soc.*, 1983, **105**, 6560.

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