

## X-Ray Crystal Structure of the Antiferromagnetic Binuclear Dichloro- $\mu$ -dichloro- $\mu$ -di(1,8-naphthyridine)-dicopper Complex

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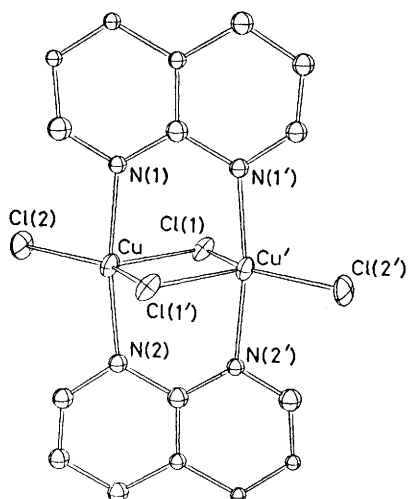
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The title compound, known to exhibit antiferromagnetic behaviour, is shown by an X-ray analysis to have two copper(II) atoms bridged, symmetrically, by two molecules of 1,8-naphthyridine and, asymmetrically, by two chlorine atoms; a terminal chlorine atom completes the five-co-ordination of each metal centre.

1,8-Naphthyridine (npthd) is commonly considered to be a potentially binucleating ligand of the carboxylate type.<sup>1</sup> However, no examples have been reported of transition-metal dimers with magnetic interactions favoured by the presence of npthd bridges. The only structural evidence for the binucleating behaviour of npthd is found in the complexes  $[\text{Ni}_2\text{Br}_2(\text{npthd})_4]\text{BPh}_4$ <sup>2</sup> and  $\text{Cu}_2\text{Cl}_3(\text{npthd})_2$ <sup>3</sup> where the metals

are formally reduced to an oxidation state of 1.5 and the magnetic moments are not temperature dependent.

Recently our attention focused on complexes of the formula  $\text{Cu}_2\text{X}_4(\text{npthd})_2$  (X = Cl or Br) reported by Emerson *et al.* in 1973.<sup>4</sup> On the basis of magnetic properties and i.r. and visible spectra they suggested a dimeric structure with both bridging and terminal chlorine atoms, with one chelating



**Figure 1.** Molecular structure of the  $\text{Cu}_2\text{Cl}_4(\text{npthd})_2$  molecule with point symmetry  $C_2$ . Important bond lengths (Å) and angles ( $^\circ$ ) for this and the second independent molecule (in square brackets) are: Cu–Cu', 2.659(4) [2.664(5)]; Cu–Cl(1), 2.667(14) [2.667(20)]; Cu–Cl(1'), 2.299(14) [2.322(18)]; Cu–Cl(2), 2.275(14) [2.253(16)]; Cu–N(1), 2.009(20) [2.046(21)]; Cu–N(1'), 2.005(22) [2.040(21)]; Cl(1)–Cu–Cl(1'), 115.7(5) [115.9(6)]; Cl(1)–Cu–Cl(2), 98.3(5) [98.7(6)]; Cl(2)–Cu–Cl(1'), 146.0(6) [145.2(7)]; N(1)–Cu–N(2), 171.1(10) [171.3(8)]; Cl(1)–Cu–N(1), 90.9(1.1) [88.7(8)]; Cl(1)–Cu–N(2), 86.4(1.1) [84.9(8)]; Cl(1')–Cu–N(1), 87.0(1.1) [85.9(8)]; Cl(1')–Cu–N(2), 86.5(1.1) [91.6(8)]; Cl(2)–Cu–N(1), 94.1(1.2) [91.1(8)]; Cl(2)–Cu–N(2), 94.6(1.2) [95.7(9)].

npthd molecule terminally completing the square-pyramidal 5-co-ordination of each metal centre. However, the *dihapto*-co-ordination proposed for npthd is quite rare.<sup>5</sup> The fluxional behaviour observed for gold<sup>6</sup> and platinum<sup>7</sup> complexes supports the view that npthd is a unidentate ligand, the chelating mode defining an energetically unfavoured transition state. Also, EHMO calculations which we are presently carrying out starting from both the *cis*<sup>8</sup> and the *trans*<sup>9</sup> models of the square planar complex  $\text{CuCl}_2(\text{npthd})_2$  provide confirmation that the observed unidentate co-ordination of npthd to copper is most favoured by energy and overlap arguments. In view of these considerations we investigated the X-ray structure of the complex  $\text{Cu}_2\text{Cl}_4(\text{npthd})_2$ .

**Crystal data:**  $\text{C}_{16}\text{H}_{12}\text{N}_4\text{Cl}_4\text{Cu}_2$ , monoclinic, space group  $C_2/c$   $a = 9.171(5)$ ,  $b = 14.931(5)$ ,  $c = 25.324(5)$  Å,  $\beta = 90.2(1)^\circ$ ,  $Z = 8$ ,  $D_c = 2.03$ ,  $D_m = 2.02$  g cm<sup>-3</sup>. Intensity measurements were collected on a Philips PW 1100 diffractometer and the structure determination and refinement were carried out using 920 unique reflections [ $I > 3\sigma(I)$ ,  $\theta < 25^\circ$ ]. The structure is affected by stacking disorder along the principal axes  $a$  and  $b$ . By adaptation of a technique recently suggested,<sup>10</sup> by which different scale factors are refined for different groups of reflections, the  $R$  factor converged to 0.059.†

There are two independent molecules in the unit cell with either  $C_2$  (Figure 1) or  $C_i$  crystallographic symmetry; however, both molecules have a higher  $2/m$  symmetry and can be considered equivalent within experimental error. The molecular structure includes two types of bridge between the copper atoms: two symmetric bridges involving npthd molecules and two asymmetric bridges involving chlorine atoms. While all

the Cu–N distances are practically equal (2.01 Å),‡ long (2.67 Å) and short (2.30 Å) Cu–Cl bridging distances may be distinguished. The Cu–Cu separation of 2.66 Å is almost identical to that found in the structure of copper acetate, 2.64 Å,<sup>11</sup> but it is longer than in the other doubly npthd-bridged copper dimer<sup>3</sup> (2.39 Å) which is known. Within the limits imposed by the bridged arrangement of the ligands there is a clear trend for the five-co-ordinate  $\text{CuN}_2\text{Cl}_2\text{Cl}$  grouping to follow the normal sense of distortion for trigonal  $\rightarrow$  square pyramidal interconversion.<sup>12</sup> At variance with the structure of the  $\text{CuCl}_2\cdot\text{S}_4\text{N}_4$  polymer,<sup>13</sup> also involving bridges formed by Cl atoms and triatomic chelate groupings (NSN), here all the Cu–N distances are remarkably short (*ca.* 2.00 Å *vs.* *ca.* 2.60 Å). Finally it is noteworthy that, whereas tetragonal pyramidal five-co-ordinate dimeric copper(II) structures with asymmetrically bridging chlorine atoms are ferromagnetic [ $2J + 6.3$  cm<sup>-1</sup> in  $\text{Cu}_2\text{Cl}_4(\text{dimethylglyoxime})_2$ ]<sup>14,15</sup> or slightly antiferromagnetic [ $2J - 7.4$  cm<sup>-1</sup> in  $\text{Cu}_2\text{Cl}_4(2\text{-picoline})_2$ ]<sup>1</sup> the present structure shows a strong antiferromagnetic coupling ( $2J - 278$  cm<sup>-1</sup>).<sup>4</sup> The presence of the two NCN bridges strongly differentiates the latter from the two former structures, as does the bridging geometry at the chlorine atoms which is commonly thought to influence the magnetic properties of this type of molecules.<sup>16</sup> The Cu–Cl–Cu angles are here as small as 64.2°, while values of 88 and 101° were found for the above ferromagnetic and antiferromagnetic compounds respectively.

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† The atomic co-ordinates for this work are available on request from the Director of the Cambridge Crystallographic Data Centre, University Chemical Laboratory, Lensfield Rd., Cambridge CB2 1EW. Any request should be accompanied by the full literature citation for this communication.

‡ For clarity the discussion refers only to the structural details of the molecule with  $C_2$  symmetry, the other molecule being practically superimposable on this one.