Inorganica Chimica Acta, *179* (1991) 1–2

Inorganica Chimica Acta
LETTER

The synthesis and X-ray structural characterisation of [(2-aminoethyl)pyridine]copper(II) azide

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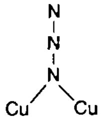
(Received October 29. 1990)

The azido ligand, N_3^-, is a versatile ligand which can bridge two metals in an end-on (μ-1,1-) fashion as in **1**, or in an end-to-end (μ-1,3) fashion as in **2**. When the metal is copper this latter bridge can either by symmetrical **3**, or non-symmetrical, **4**. The ability to form bridges leads not only to dimers (**3**, **4**) but also to polymeric species in which the chains can be built up from either the first or third nitrogen atom of the azido ligand (**5**, **6**) [1].



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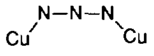

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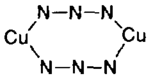

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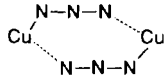

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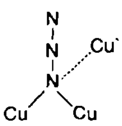

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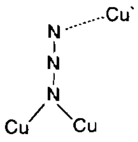

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In furtherance of studies on the binding of bridging groups at dinuclear copper(II) centres the reaction of di-μ-hydroxy-bis[(2-aminoethyl)-pyridine-dicopper(II) perchlorate with sodium azide was carried out in order to monitor the potential exchange of the bridging anions and to establish which of modes **1** or **2** was present in the product.

Di-μ-hydroxy-bis[(2-aminoethyl)-pyridine-dicopper(II) perchlorate was first prepared by reaction of 2-(2-aminoethyl)pyridine (2 mmol) and copper perchlorate (2 mmol) in methanol [2]. A deep blue solution formed immediately to which was added aqueous sodium hydroxide solution (1 mmol). On standing deep blue crystals of the product were deposited and collected. An aqueous solution of sodium azide (0.4 mmol) was then added to a solution of di-μ-hydroxy-bis[(2-aminoethyl)-pyridine-dicopper(II) perchlorate (0.2 mmol) in methanol. A green powder was first isolated and filtered off and then green crystals deposited from the filtrate upon standing for two days. The compound recovered was the title compound, the structure of which evidences that the intra-molecular hydroxy-bridges present in the starting material [3] have been broken and that the molecules are now stacked such that there are weak (μ-1,1-) interactions between adjacent molecules. A satisfactory microanalysis was obtained (Found: C, 30.92, H, 3.76, N, 41.37. Calc.: C, 31.17, H, 3.74, N, 41.54%) and two bands were observed in the IR spectrum for the azide stretch (2060 and 2020 cm^{-1}).

The crystals used for this study were recrystallised from methanol as dark green elongated plates. Crystal data for $C_7H_{10}CuN_3$, $M_r = 269.75$, monoclinic, $a = 16.45(4)$, $b = 20.32(5)$, $c = 7.057(9)$ Å, $\beta = 113.57(5)°$, $U = 2162(8)$ Å^3, $D_x = 1.657$ g cm^{-3}, $Z = 8$, space group $C2/c$ (C_{2h}^6, No. 15) (from systematic absences hkl, $h+k=2n+1$; $h0l$, $l=2n+1$). Mo Kα radiation ($\lambda = 0.71069$ Å), μ(Mo Kα) = 20.11 cm^{-1}, $F(000) = 1095.49$, final $R = 0.1149$ for 863 observed reflections, 148 parameters. A crystal having dimensions $0.73 \times 0.16 \times 0.02$ mm was used to collect X-ray data at room temperature in the range $6.5 < 2\theta > 50°$ on a Stoe Stadi-2 diffractometer by the ω-scan method. Of the 2412 reflections measured, the 863 for which $I/\sigma(I) > 4.0$ were corrected for Lorentz and polarisation effects, and for absorption by Gaussian integration methods (minimum and maximum transmission coefficients 0.70 and 0.96). The structure was solved by Patterson and Fourier techniques and refined by blocked cascade least-squares methods. Extensive geometrical constraints were applied during refinement in order to ensure that chemically bonds were of equal length. There was some evidence of disorder of carbon atoms C(6) and C(7), but no satisfactory model could be achieved: the second component appeared to be of low occupancy. In order to overcome the problem of a geometrically unsatisfactory refinement in this region,

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0020-1693/91/$3.50

more restrictive constraints were applied both to bond lengths and angles, resulting in little residual electron density in the region. Hydrogen atoms were included in calculated positions with isotropic thermal parameters related to those of the supporting atom. Refinement converged at a final $R=0.1149$, with allowance for the thermal anisotropy of all non-hydrogen atoms. Complex scattering factors were taken from the program package SHELXTL [4], as implemented on the Data General Nova 3 computer. A weighting scheme with $w^{-1}=[\sigma^2(F)+g(F)^2]$ with $g=0.00025$ was used during the latter stages of the refinement. The maximum final Δ/σ was 0.008 (mean 0.002). The final difference electron density functions showed maxima and minima of +1.36 and −1.36 e Å^{-3}.

The molecular structure is illustrated in Fig. 1, which also illustrates the interactions formed to adjacent molecules and lists bond lengths and angles with estimated standard deviations. The structure is closely related to that of diazido-2,2′-bipyridinecopper(II) [5] in which the copper is described as being square-planar with two additional long bonds (Cu–N, 2.682, 2.680 Å) leading, through semi-coordination, to polymerisation in the x direction.

The molecule comprises a four-coordinated copper(II) atom with the nitrogen atoms of the 1-(2-pyridyl)-2-aminoethane chelate occupying mutually *cis* sites. The remaining sites are occupied by the two azide ligands, which are linear (at N(4) and N(7)) but are coordinated in a bent manner (Cu–N–N 123°). In view of the need to apply constraints during refinement, a detailed discussion of the geometry would be unjustified. The terminal azide bonds are shorter than those to the bonded nitrogen atoms. The coordination geometry around the copper atom is distorted from square-planar by a tetrahedral twist of 28° (between planes defined by Cu(1), N(1), N(2) and Cu(1), N(3), N(6)). The copper coordination polyhedron is completed by short interactions, both above and below the mean plane, to the bonded azide nitrogen atoms of adjacent molecules related by the c-glide symmetry (Cu...N 2.88 and 2.66 Å), giving rise to weak polymerisation along the c axis; this is illustrated in the Figure. The azide anions are therefore present as non-symmetrical μ-1,1-bridges. The copper–copper separation is 3.78 Å.

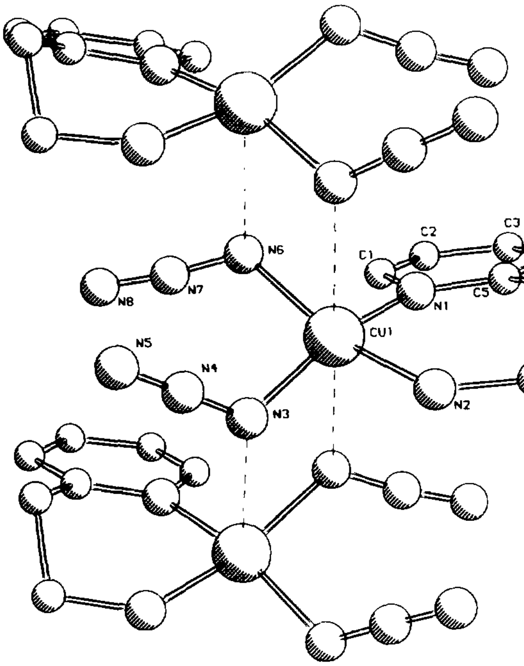

Fig. 1. The molecular structure of [(2-aminoethyl)pyridine] copper(II) showing the weak polymerisation along the c axis. Selected bond lengths: Cu(1)–N(1), 1.995(19); Cu(1)–N(2), 1.966(16); Cu(1)–N(3), 1.987(22); Cu(1)–N(6), 1.981(21); N(3)–N(4), 1.214(23); N(4)–N(5), 1.157(27); N(6)–N(7), 1.216(21); N(7)–N(8), 1.152(24). Selected bond angles: N(1)–Cu(1)–N(2), 93.6(2); N(1)–Cu(1)–N(3), 162.2(8); N(2)–Cu(1)–N(3), 87.4(8); N(1)–Cu(1)–N(6), 90.9(8); N(2)–Cu(1)–N(6), 157.3(8); N(3)–Cu(1)–N(6), 95.1(8); N(3)–N(4)–N(5), 178.2(19); N(6)–N(7)–N(8), 174.1(27).

Supplementary material

Tables of atomic coordinates, bond lengths and angles, thermal parameters, and structure factors are available from the authors on request.

Acknowledgements

We thank the Department of Education, Northern Ireland for an award (to C.H.McL.) and the SERC for funds towards purchase of the diffractomer.

References

1 I. Bkouche-Waksman, M.-L. Boillot, O. Kahn and S. Sikorov, *Inorg. Chem.*, *23* (1984) 4454, and refs. therein.

2 C. H. McLean, *Ph.D. Thesis*, University of Sheffield, 1985.

3 R. Krohmer, M. Maaser, K. Stanger and E. Uhlig, *Z. Anorg. Allg. Chem.*, *354* (1967) 242.

4 G. M. Sheldrick, *SHELXTL*, Revision 4, system for crystal structure solution and refinement, University of Göttingen, F.R.G., 1983.

5 G. W. Bushnall and M. A. Khan, *Can. J. Chem.*, *52* (1974) 3125.