A Novel Type of Copper(II) Dimers with Tetradentate Schiff Bases: *X*-Ray Crystal Structure and Magnetic Properties of Bis-μ-[*N*,*N*′-ethylenebis(pyrrol-2-ylmethyleneaminato)]-dicopper(II)

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The 1:1 complex of copper(II) with *N*,*N*′-ethylenebis(pyrrol-2-ylmethyleneamine) in benzene-inclusion crystals forms a novel copper(II) dimer in which each of the two interwined Schiff bases binds two copper atoms with a separation of 3.29 Å and with a strong antiferromagnetic interaction of J −61.2 cm^{-1} as shown by *X*-ray structural analysis and by magnetic susceptibility measurements.

The 1 : 1 complex of copper(II) with *N*,*N*′-ethylenebis(pyrrol-2-ylmethyleneamine), a tetradentate Schiff base, was believed to be a square-planar complex, on the basis of various spectroscopic results[1,2] and a preliminary *X*-ray analysis.[3] We report here that this complex forms a crystalline copper(II) dimer of a novel structural type with a strong antiferromagnetic interaction.

Crystals of this complex from various solvents fall into a variety of crystal systems, depending on the solvent included; all the crystals lose included solvent molecules easily in air. Tetragonal-bipyramidal crystals obtained from benzene were studied here.

Crystal data: $[Cu(C_{12}H_{12}N_4)]\cdot 1.5C_6H_6$, orthorhombic, space group *Fddd*, $a = 23.561(3)$, $b = 16.723(2)$, $c = 19.818(3)$ Å,

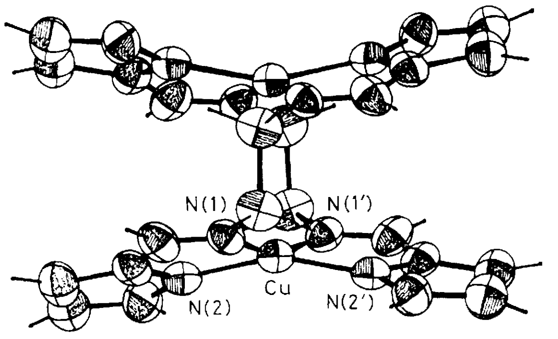

Figure 1. ORTEP drawing (30% probability ellipsoids) and atomic numbering scheme for the title complex $[Cu(C_{12}H_{12}N_4)]_2$.

$U = 7808.51(2)$ Å^3, $Z = 16$, $D_c = 1.337$ g cm^{-3}, $F(000) = 2751$, $\lambda(\text{Mo-}K_\alpha) = 0.71069$ Å, $\mu(\text{Mo-}K_\alpha) = 14.28$ cm^{-1}. The crystals were rather imperfect. Intensities were measured on a Rigaku AFC-5 diffractometer ($2\theta < 50°$) using a crystal of dimensions $0.2 \times 0.2 \times 0.3$ mm^3 which was coated with gum arabic to prevent evaporation of included benzene molecules. No corrections were made for absorption. The final R factor is 8.9% for 1267 reflections with $F_o > 2\sigma(F_o)$ of 1635 measured reflections.†

As shown in Figure 1, the complex consists of dimeric units $[Cu(C_{12}H_{12}N_4)]_2$, in which each of the two Schiff bases functions, not as the usual tetradentate ligand but as a bis(bidentate) one; each copper atom is bonded to two pyrrole nitrogens [N(2) and N(2′)] and two imino nitrogens [N(1) and N(1′)] from two different (primed and unprimed) ligands with intertwined conformations. This dimeric complex has, as a whole, crystallographically imposed D_2 symmetry (point symmetry 222). The co-ordination geometry around the copper atom is a flattened tetrahedron, as indicated by the atom deviations [N(1) $+0.37$, N(2) -0.37 Å] and by the angle of 36.9° between the two pyrrole ring planes. The pyrrole ring and its methyleneamine group are essentially coplanar. It is characteristic of this dimer that the two Cu–N bonds and N–Cu–N angles are both significantly different [Cu–N(1) 1.976, Cu–N(2) 1.925 Å and N(1)–Cu–N(2) 84.4, N(1′)–Cu–N(2′) 99.7, N(1)–Cu–N(1′) 158.3, N(2)–Cu–N(2′) 157.9°]. The bond lengths and angles in the ligand are in good agreement with those of bis(pyrrol-2-ylmethyleneaminato)copper(II).[4] In this dimer, the two copper atoms are apparently bridged by two ethylene di-imine groups so as to form a ten-membered ring which involves significantly short interatomic distances [Cu–Cu 3.29, N(1)–N(1) 2.94, Cu–N(1) 3.50 Å].

Another interesting feature is the inclusion of benzene molecules in the vacant space as guests to achieve a close-packed crystal. These benzene molecules seem to bind loosely to the host complexes from all sides. The reason why the present complex does not form a planar complex but a novel dimer instead may be that the two pyrrole nitrogens in the tetradentate ligand are sterically difficult to accommodate in the square-planar positions of CuN_4-co-ordination, as indicated by space-filling molecular models. The same type of dimeric structure might also be found for other complexes with tetradentate ligands, sterically similar to the present one.

The magnetic susceptibilities of the complex in gum arabic-coated crystals (Figure 2) and in benzene-free powders (prepared by heating the benzene-inclusion crystals at *ca.* 50 °C *in vacuo*) were determined by the Faraday method over the temperature range 4.2 to 300 K, and the data were approximated by the Bleaney–Bowers equation (Figure 2). The best least-square fits to the equation gave J values of -61.2 (crystals) and -55.6 cm^{-1} (benzene-free powders). These $|J|$ values are remarkably large for binuclear copper(II) complexes of the type which have no explicit spin–spin interaction pathways (*e.g.* carboxy, halogen, oxo, and related bridges).

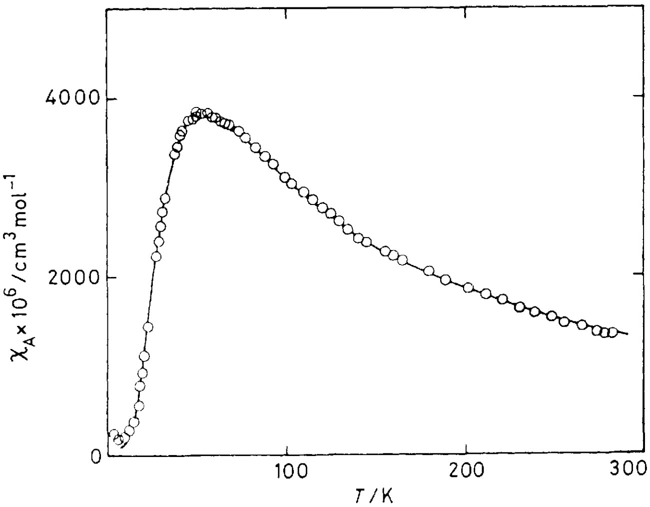

Figure 2. Calculated (——) and experimental (○) magnetic data for the title complex in benzene-inclusion crystals (coated with gum arabic). The equation of the calculated curve is $\chi_A = (Ng^2\beta^2/3kT)[1 + \exp(-J/kT)/3]^{-1} + N\alpha$, with $J = -61.2$ cm^{-1}, $g = 2.10$, and $N\alpha = 60 \times 10^{-6}$ cm^3 mol^{-1}.

These unique data on both spin exchange interaction and dimeric structure are important for a practical understanding of spin exchange mechanisms, since spin exchange couplings in dimeric or binuclear metal complexes are of current interest in co-ordination and bio-inorganic chemistry.[5] The strong antiferromagnetic interaction of J -61.2 cm^{-1} for the present dimer may be explained in terms of a superexchange mechanism, because its Cu–Cu distance of 3.29 Å is too long for the J value to be explained by a direct spin exchange coupling.[6] We point out a possibility of there being a superexchange pathway along Cu–N(1)–N(1)–Cu in the dimer, since the N(1)–N(1) distance of 2.94 Å is a little shorter than twice the van der Waals' radius of nitrogen and is short enough for an effective electronic interaction between the nitrogen atoms.

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