Structure of the Linear Trinuclear Copper Complex, Dichlorotetrakis-(di-2-pyridylamido)tricopper

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The synthesis and X-ray crystal structure of a nitrogen-bridged linear trinuclear copper complex $[Cu_3(dpa)_4Cl_2]$ {dpa = di-2-pyridylamido, $[(C_5H_4)_2N]^-$}, with extremely short Cu–Cu bond distances [2.4712(4) Å] and tridentate dipyridylamido ligands in a novel *syn–syn* conformation are reported.

Spin interactions in paramagnetic multinuclear copper(II) clusters and chains have received considerable attention. Most of the recent work has focused on dinuclear copper complexes and alternating copper-halide chains. Trinuclear copper complexes are not as common, and most of these contain triangular arrays of copper atoms. To date, all the linear copper trinuclear complexes contain either oxygen[1–3] or chloride[4–6] bridges and have copper–copper distances greater than 3 Å. We report here the synthesis and structure of a nitrogen-bridged linear trinuclear copper(II) complex with extremely short copper–copper distances [2.4712(4) Å] and novel *syn–syn* conformation for the tridentate di-2-pyridylamido ligand (dpa).

The conformation of the dipyridylamido ligand in the trinuclear complex is significantly different from that observed for other dipyridylamido complexes. The deprotonated form of dipyridylamine is known to form bidentate complexes with metals, such as Pd,[7,8] and Cu and Ni.[9] A trinuclear Ni dipyridylamido chloride complex with the stoichiometry $Ni_3L_4Cl_2$ has been prepared; however, it was postulated that a central nickel atom was coordinated to two chloride ions and the amido nitrogen atoms.[9] Metal complexes with dipyridylamine usually contain the ligand in an *anti–anti* configuration, where *anti–anti* refers to the relation of the pyridyl nitrogens to the amine hydrogen. By use of similar nomenclature, the solid-state structure of dipyridylamine, the free ligand, consists of dimers in the *syn–anti* conformation. The current trinuclear complex is the first example of a dipyridylamido ligand in a *syn–syn* conformation. The ligand is nonplanar with an average dihedral angle between the pyridyl rings of 47.1(2)°.

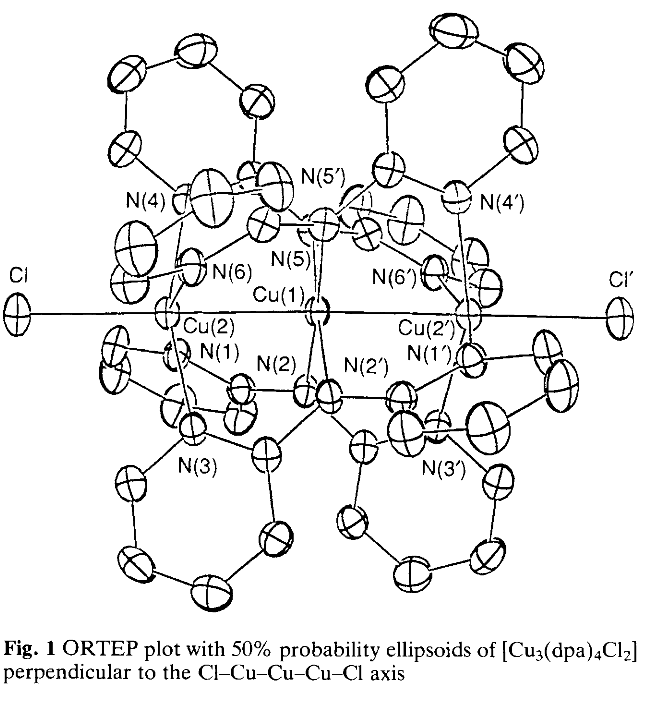

Fig. 1 ORTEP plot with 50% probability ellipsoids of $[Cu_3(dpa)_4Cl_2]$ perpendicular to the Cl–Cu–Cu–Cu–Cl axis

The complex was prepared by the slow oxidation in air at room temperature of bis(di-2-pyridylamino)copper(I) chloride[10] in acetonitrile. Dark purple crystals precipitated in 1–2 days in 31% yield based on copper.†

The structure of $[Cu_3(dpa)_4Cl_2]$ is shown in ORTEP plots in Fig. 1 (perpendicular to the Cl–Cu–Cu–Cu–Cl axis) and Fig. 2 (along the copper–chlorine axis).‡ The three Cu^{II} ions and the two chloride ions are collinear, and the molecule has crystallographic twofold symmetry. The *syn–syn* conformation of the four dipyridylamido ligands allows each nitrogen atom to be coordinated to a different copper atom. The copper–copper distance [2.4712(4) Å] is within 0.1 Å of the shortest known copper–copper distance (2.38 Å) observed for the mixed valent Cu^I–Cu^{II} complex with chlorine and 4-methyl-1,8-naphthyridine.[11] Each copper atom is in an

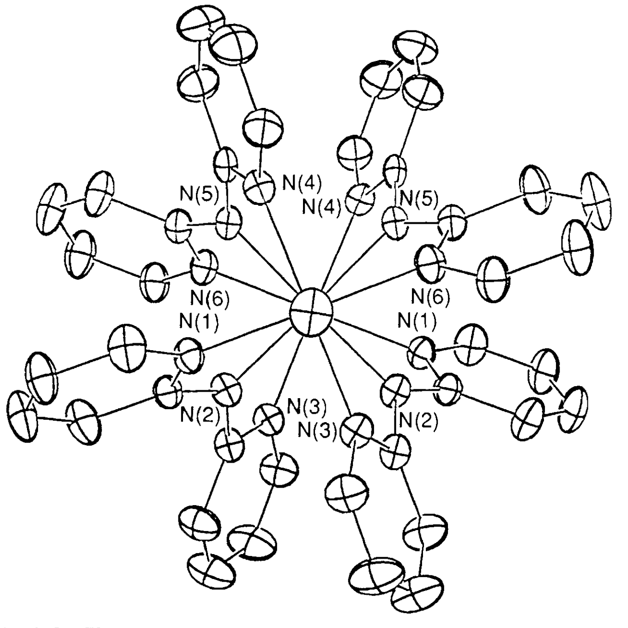

Fig. 2 ORTEP plot with 50% probability ellipsoids of $[Cu_3(dpa)_4Cl_2]$ along the Cl–Cu–Cu–Cu–Cl axis

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† Found: C, 52.7; H, 3.9; Cu, 20; N, 18.4. $C_{40}H_{32}Cl_2Cu_3N_{12}$ requires C, 51.0; H, 3.4; Cu, 20.2; N, 17.8%.

‡ *Crystal data* for $C_{40}H_{32}Cl_2Cu_3N_{12}$, M = 942.31, orthorhombic, space group $Pnn2$, a = 12.892(2), b = 14.083(2), c = 11.186(2) Å, V = 2031.0 Å^3, Z = 2, D_c = 1.54 g cm^{-3}, D_m = 1.58 g cm^{-3}, λ(Mo-Kα) = 0.71073 Å, μ = 17.4 cm^{-1}, $F(000)$ = 954. The data, corrected for absorption and decay, were collected on an Enraf-Nonius CAD4 diffractometer. The structure was solved by use of Patterson and Fourier methods. 1873 reflections having intensities greater than 3σ were used in the refinement of 267 parameters. The refinement converged with R = 0.028 and R_w = 0.041; (Δ/σ) = 0.01. All calculations were performed on a VAX11/750 computer using SDP/VAX.[13] Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Notice to Authors, Issue No. 1.

octahedral environment with the two end copper atoms slightly displaced from the plane of the nitrogen atoms.

The oxidation of the metal centre results in the deprotonation of the dipyridylamine ligand at the amine nitrogen. The mechanism for the reaction most likely involves the formation of a dioxygen–copper(I) adduct, with dioxygen present as the superoxide, O_2^-.[12] Substantial rearrangement of the coordination sphere around the copper occurs during the reaction. At least one Cu–N bond per ligand must be broken, and two ligands must be displaced. The ligand must also undergo rotation of both pyridyl rings around the pyridyl–amine nitrogen bond to the *syn–syn* conformation, which allows all three nitrogens to coordinate to the linear array of copper atoms.

Preliminary magnetic susceptibility measurements show a room temperature susceptibility/Cu atom of 1.00×10^{-3} cgs units (cgs $\times 4\pi \times 10^{-6}$ m^3 cm^{-3} = SI unit). The temperature dependence of the magnetic susceptibility down to 90 K suggests antiferromagnetic coupling between adjacent copper atoms; however, determination of the coupling constants awaits acquisition of data down to liquid helium temperatures.

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