Structure and ^1H N.M.R. Spectrum of a Binuclear Copper(I) Complex with Non-bridging and Bridging 2-Vinylpyridine Ligands (vpy), $[Cu_2(\mu\text{-vpy})_2(vpy)_2](ClO_4)_2$

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The dimeric copper(I) complex $[Cu_2(\mu\text{-vpy})_2(vpy)_2](ClO_4)_2$ (vpy = 2-vinylpyridine) containing bridging and non-bridging vpy has been synthesized and characterized crystallographically; the C=C distance in the co-ordinated vinyl group is slightly longer than those found in unco-ordinated vpy.

The synthesis, molecular structures, and bonding modes of copper(I) alkene complexes have been the subject of considerable research in recent years.[1—3] In particular binuclear copper(I) alkene complexes have been of interest in connection with the synthesis of copper(I) clusters and the development of novel catalysts.[4] Our interest in this area arose from the proposed role of copper in the binding of the plant hormone ethylene to its receptor site.[1,2] Bis(diphenylphosphino)methane, allyl and acetate groups, sulphur-containing ligands, and halides have all been used as bridging ligands in Cu^I complexes.[5] We have synthesized the new binuclear copper(I) alkene complex $[Cu_2(\mu\text{-vpy})_2\ (vpy)_2](ClO_4)_2$ (**1**) in which two vpy ligands are co-ordinated to the copper ions as bridging ligands.

A solution of vpy (0.5 mmol) in methanol (2 ml) was added to tetrakis(acetonitrile)copper(I) perchlorate (0.25 mmol) under nitrogen. The solution was sealed in a glass tube and left at −20 °C. After 3 days, yellow-white crystals of (**1**)† suitable for *X*-ray diffraction studies were obtained.

The molecular structure of (**1**) is shown in Figure 1.‡ In (**1**), the two copper atoms are bridged in a 'head to tail' mode by two vpy ligands, bonding through the pyridine nitrogen and the C=C moiety of the vinyl group, to form an eight-membered ring. This is the first report of a metal complex involving bridging vpy molecules. The copper atoms are three-co-ordinate, each metal atom being bonded to the pyridine nitrogen of the non-bridging and bridging vpy molecules and also to the C=C moiety of the bridging vpy molecule. The perchlorate anions interact weakly with the copper atoms, the distances Cu(1) · · · O(3) and Cu(2) · · · O(7) being 2.820(10) and 2.773(16) Å, respectively. Cu(2) lies at a distance of 0.10 Å from the plane defined by N(21), N(31), C(17), and C(18),

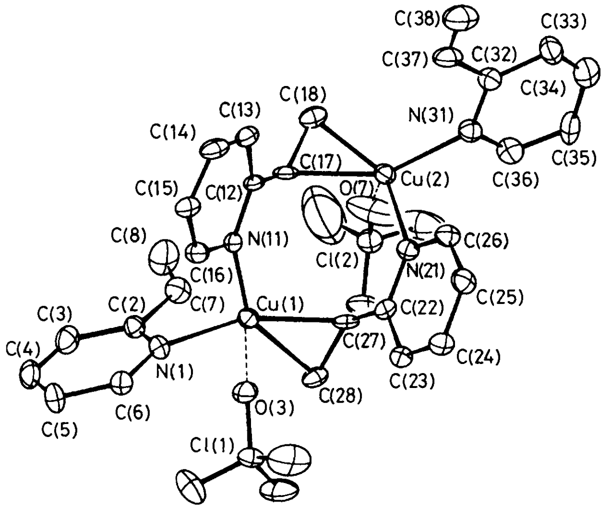

Figure 1. Structure of $[Cu_2(\mu\text{-vpy})_2(vpy)_2](ClO_4)_2$ (**1**) showing 20% probability thermal elipsoids. Selected bond distances (Å) and angles (°): Cu(1)–N(1) 1.988(9), Cu(1)–N(11) 1.981(9), Cu(1)–C(27) 2.044(13), Cu(1)–C(28) 1.998(13), Cu(2)–N(21) 2.008(10), Cu(2)–N(31) 1.988(11), Cu(2)–C(17) 2.040(12), Cu(2)–C(18) 2.031(13), C(7)–C(8) 1.307(23), C(17)–C(18) 1.368(17), C(27)–C(28) 1.358(16), C(37)–C(38) 1.319(23); N(1)–Cu(1)–N(11) 104.4(4), N(1)–Cu(1)–C(28) 109.6(5), N(11)–Cu(1)–C(27) 108.4(4), C(27)–Cu(1)–C(28) 39.2(4).

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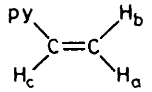
† (**1**) is air-sensitive and thermally unstable.

‡ *Crystal data* for (**1**): $C_{28}H_{28}Cu_2N_4Cl_2O_8$, M = 746.5, monoclinic, space group $P2_1/n$, a = 31.059(16), b = 10.696(2), c = 9.455(2) Å, β = 96.08(3)°, U = 3123.3 Å^3, Z = 4, D_c = 1.587 g cm^{-3}, μ(Cu-K_α) = 15 cm^{-1}, crystal dimensions 0.2 × 0.2 × 0.2 mm. Intensity data in the range $2\theta < 120°$ were collected by the ω–2θ scan technique using a Rigaku AFC-5B automated diffractometer. The structure was solved by a direct method (MULTAN 78) and was refined using least-square techniques. The final R and R_w values were 0.089 and 0.083, respectively, for 3174 unique reflection with $F_o > 3\sigma(F_o)$. Atomic co-ordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Notice to Authors, Issue No. 1.

Table 1. ^{1}H n.m.r. chemical shifts of free vpy and co-ordinated vpy in $[Cu_2(\mu\text{-vpy})_2(vpy)_2](ClO_4)_2$ (CD_3OD) at −55 °C.[a]



	Chemical shift, δ		
	H$_a$	H$_b$	H$_c$
Free vpy	5.56	6.21	6.82
Co-ordinated vpy	5.21	5.73	7.03
Δδ[b]	−0.35	−0.48	0.21

[a] δ in p.p.m. relative to Me_4Si. [b] Δδ = change in chemical shift on co-ordination.

positioned towards the ClO_4^- anion.§ The co-ordination geometry around each copper atom is distorted trigonal planar, with dihedral angles between the planes defined by Cu(1), N(11), N(1) and Cu(1), C(28), C(27) and that of Cu(2), N(21), N(31) and Cu(2), C(17), C(18) being 25.1 and 7.6°, respectively. The relatively long Cu · · · Cu distance of 4.085(3) Å precludes any metal–metal interactions. The Cu–N(pyridine) distances for bridging vpy [1.981(9), 2.008(10) Å] are essentially the same as those for non-bridging vpy [1.988(9), 1.988(11) Å] and lie within the range of those reported for three-co-ordinate copper–ethylene complexes; 1.963(2) Å for $[Cu\{NH(py)_2\}(C_2H_4)]ClO_4$ (py = pyridine),[1] 1.972(6)—2.032(2) Å for $[Cu(bpy)(C_2H_4)]ClO_4$ (bpy = 2,2′-bipyridine),[2] and 2.002(18)—2.004(9) Å for $[Cu(phen)(C_2H_4)]ClO_4$ (phen = 1,10-phenanthroline).[2] The C=C moiety of the vinyl group is coplanar with the pyridine ring in non-bridging vpy, whereas the co-ordinated C=C moiety is twisted *ca.* 8° out of the plane of the pyridine ring. The Cu–C distances of the olefinic carbons display asymmetry, with slightly longer bond lengths for the inner carbons than for the terminal carbons.¶ Similar asymmetry has been observed in the Pt–C distances of platinum complexes[6] with η^2-styrene ligands analogous to η^2-vpy.

The co-ordinated olefinic C=C distances of 1.358(16) and 1.368(17) Å lie at the lower end of the range reported for platinum–η^2-styrene complexes [1.360(11)—1.53(3) Å].[6] No direct comparison between η^2-bound styrene ligands and free styrene ligands has been made since the structure of the ligand itself is unknown. For complex (**1**) such a comparison is possible since it contains both co-ordinated and non-co-ordinated olefinic C=C bonds. The C=C distances of the former are found to be slightly longer than those for the latter [1.319(23) and 1.307(23) Å], whereas no significant differences in the C=C distances have been found between copper(I) ethylene complexes and free ethylene.

The ^{1}H n.m.r. signals of bridging and non-bridging vpy molecules could not be independently observed even at −55 °C, and averaged signals were obtained, indicating rapid chemical exchange between the bridging and non-bridging vpy molecules. Table 1 shows the chemical shifts for the olefinic protons in free and co-ordinated vpy. The signals due to the terminal protons shift upfield on co-ordination, whereas the inner proton H$_c$ shifts downfield. This is in agreement with the non-equivalence of the Cu–C (olefinic carbon) distances.

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§ The deviation of Cu(1) cannot be calculated because the dihedral angle between the planes formed by N(1), N(11) and Cu(1), and by C(27), C(28) and Cu(1) is very large (25.1°).

¶ Inner carbon–copper atom bond lengths: Cu(1)–C(27) and Cu(2)–C(17) 2.044(13) and 2.040(12) Å, respectively. Terminal carbon–copper atom bond lengths: Cu(1)–C(28) and Cu(2)–C(18) 1.998(13) and 2.031(13) Å, respectively.