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Structure, characterisation and dynamics of copper(I) complexes of 2,6-bis(3,5-dimethylpyrazol-1-ylmethyl)pyridine

Palanichamy Manikandan, Babu Varghese and Periakaruppan T. Manoharan*

Department of Chemistry, Indian Institute of Technology, Madras 600 036, India

Two mononuclear copper(I) complexes of a tripodal ligand, 2,6-bis(3,5-dimethylpyrazol-1-ylmethyl)pyridine (L), have been prepared, $[CuL(ClO_4)]\cdot CH_2Cl_2$ **1** and $[CuL(PPh_3)]ClO_4$ **2**. A new route to L is also proposed. The crystal structures of both complexes have been determined. In **1** the perchlorate is bonded through one of its oxygens with a distance of 2.426(3) Å. In **2** the perchlorate ion is thermally disordered. A variable-temperature NMR study of both complexes revealed that the methylene carbon of **2** is chiral at low temperatures. Carbon monoxide formed a terminal adduct with **1**.

Synthesis of copper(I) complexes is of great interest to bioinorganic chemists[1–4] since they can be used to mimic the reduced state of 'type III copper' active site of proteins like haemocyanin and tyrosinase.[5–9] Also, since these dinuclear copper proteins have characteristic reactions with CO[10,11] [deoxyhaemocyanin binds only 1 mol of CO per dinuclear copper(I) species] the reaction of model copper(I) complexes with CO assumes importance. Research groups led by Sorrel[12,13] and others[14–18] have carried out a systematic study on the interaction of CO with co-ordinatively saturated copper(I) complexes. The syntheses of such complexes and their reactions with gases like CO and O_2 could provide a deep insight into the chemical and electronic properties of copper proteins. A number of copper(I) complexes with different co-ordination environments and co-ordination numbers have been reported.[19–24] The co-ordination number of univalent metal ions is greatly influenced by the chemical nature of the ligands and the geometry they impose. The imidazoles of histidine residues are known to occupy the active site of haemocyanins and many other metalloproteins.[25,26] Recently there have been attempts to mimic the active site of type III copper-containing proteins by making copper complexes of imidazole,[21,27] pyridine,[28–30] pyrazole,[31–33] and benzimadazole[34–36] derivatives.

This paper reports the synthesis of copper(I) complexes with a tripodal ligand made up of three heterocyclic nitrogen-donor atoms, and their structures and reactions with carbon monoxide and triphenylphosphine. One of these complexes has a geometry similar to that of the CuB site of deoxyhaemocyanin,[37] although it absorbs carbon monoxide in contrast to the observed property of CuB. Monodentate tertiary phosphines form a number of mononuclear copper(I) complexes with different stoichiometries and structures.[38,39]

Experimental

Materials

Commercially available reagent-grade quality chemicals and solvents were used. 3,5-Dimethylpyrazole and pyridine-2,6 dimethanol were obtained from Aldrich Chemical Company and NaH from Fluka. Commercially available argon and nitrogen gases were purified and dried by passing through P_4O_{10}, oxygen scavenger and 4 Å molecular sieve columns. The oxygen scavenger[40] was frequently reactivated by passing H_2 at 380 °C and the molecular sieve column was reactivated at 400 °C under vacuum or under a nitrogen atmosphere. The purity and dryness of CO were assured by passing it through P_4O_{10}, concentrated H_2SO_4, and KOH columns. Solvents were dried and distilled from appropriate drying agents just prior to use.[41] Methanol was distilled from $Mg(OMe)_2$. Commercially available diethyl ether was first dried with $CaCl_2$ (fused) and subsequently distilled from sodium. Dichloromethane was purified as follows: commercial grade dichloromethane was stirred with concentrated H_2SO_4 in the dark for several days. After removing the acid layer, the dichloromethane was washed with distilled water, K_2CO_3–KOH and again with distilled water and finally distilled from CaH_2. Acetonitrile was refluxed and distilled from CaH_2. All the solvents were distilled under Ar or N_2. The preparation and handling of air-sensitive compounds were carried out by adapting standard Schlenk techniques.[40] Solvents and solutions were deoxygenated by either repeated vacuum–purge cycles (Ar) or by bubbling with Ar. The samples were stored in an argon atmosphere. Samples for IR and NMR studies were prepared in an argon atmosphere. All column chromatographic purifications of the ligand were carried out using 60–120 mesh silica gel.

Physical measurements

The purity check and characterisation of the ligand and complexes were performed using techniques like TLC, NMR, IR and mass spectrometries. Infrared spectra were obtained on a Bruker IFS 66v-FTIR spectrometer, ^1H, ^{13}C and ^{31}P NMR spectra on a JEOL-GSX 400 spectrometer with shifts reported as δ values (in ppm) downfield from an internal standard of $SiMe_4$ for ^1H and ^{13}C and external H_3PO_4 for ^{31}P. X-Band EPR measurements were done on a Varian E-112 spectrometer in frozen CH_2Cl_2 solution at 77 K or in powder samples. Elemental analysis was performed using a Heraeus CHN-O rapid analyser. Electrochemical experiments were carried out on a BAS-100 A cyclic voltmeter using a platinum working electrode and acetonitrile as solvent. Tetraethylammonium perchlorate was the supporting electrolyte. All potentials were recorded at 298 K *vs.* a Ag–AgCl electrode.

Preparations

2,6-Bis(3,5-dimethylpyrazol-1-ylmethyl)pyridine (L). Compound L was prepared either by a earlier method[42] or as follows. Under Ar, 3,5-dimethylpyrazole (9.6 g, 0.11 mol) was added to a suspension of NaH (2.6 g, 0.11 mol) in dry dimethylformamide (100 cm^3). The solution was stirred at 60 °C for 30 min. 2,6-Bis(chloromethyl)pyridine (9.295 g, 0.055 mol) was then added at 60 °C. Stirring was continued for 24 h. The solution was then evaporated to dryness at reduced pressure and the residue treated with chloroform (3 × 50 cm^3). The

combined organic portion was washed with water and NaCl-saturated water (50 cm^3) and then dried in anhydrous Na_2SO_4. The filtered solution was purified by column chromatography on 60–200 mesh silica gel with ethyl acetate–hexane (60:40) as the eluent. Yield 80–82%. NMR ($CDCl_3$, 298 K): ^1H, δ 2.1 (6 H, s, CH_3), 2.15 (6 H, s, CH_3), 5.22 (4 H, s, CH_2), 5.78 (2 H, s, CH of pyrazolyl), 6.58 (2 H, d, CH of pyridine), 7.44 (4 H, t, CH of pyridine); ^{13}C, δ 10.97 (CH_3), 13.43 (CH_3), 54.12 (CH_2), 105.60 (CH of pyrazolyl), 119.41 (CH of pyridine), 138.05 (CH of pyridine), 139.71 (C of pyrazolyl), 147.99 (C of pyrazolyl) and 156.96 (C of pyridine).

[CuL(ClO_4)]·CH_2Cl_2 1. Under Ar, a dry and degassed dichloromethane solution (10 cm^3) of L (295 mg, 1 mmol) was added to $[Cu(MeCN)_4]ClO_4$[43] (327 mg, 1 mmol) with stirring. The reaction was immediate. The colourless reaction mixture turned yellow. It was then allowed to stir for 1 h. Dry and degassed hexane was then added until the product precipitated. The product was filtered off and recrystallised from dichloromethane–hexane (1:3) as light greenish yellow needle-like crystals. Yield 94% (Found: C, 39.95; H, 4.30; N, 13.00. Calc. for $C_{18}H_{23}Cl_3CuN_5O_4$: C, 39.80; H, 4.25; N, 12.90%). NMR ($CDCl_3$, 298 K): ^1H, δ 2.27 (6 H, s, CH_3), 2.33 (6 H, s, CH_3), 5.23 (4 H, s, CH_2), 5.25 (2 H, s, CH_2Cl_2), 5.95 (2 H, s, CH of pyridine), 7.57 (2 H, d, CH of pyridine) and 7.77 (1 H, t, CH of pyridine); ^{13}C, δ 11.52 (CH_3), 14.63 (CH_3), 51.18 (CH_2), 53.43 (CH_2Cl_2), 106.34 (CH of pyrazolyl), 123.87 (CH of pyridine), 140.19 (CH of pyridine), 143.58 (C of pyrazolyl), 150.61 (C of pyrazolyl) and 152.70 (C of pyridine).

[CuL(PPh_3)]ClO_4 2. This complex can be prepared either by mixing **1** and PPh_3 in 1:1 ratio or as follows. A dry and degassed CH_2Cl_2 (15 cm^3) solution of L (295 mg, 1 mmol) and PPh_3 (262.3 mg, 1 mmol) was added dropwise to $[Cu(MeCN)_4]ClO_4$ (295 mg, 1 mmol) with constant stirring under Ar. The solution was then allowed to stir for 1–2 h. A faint yellow microcrystalline product was collected after the addition of dry and degassed hexane (45 cm^3). It was washed with dry diethyl ether and recrystallised from dichloromethane–hexane (1:3) as faint yellow crystals. Yield 96% (Found: C, 58.25; H, 5.20; N, 10.05. Calc. for $C_{35}H_{36}ClCuN_5O_4P$: C, 58.35; H, 5.05; N, 9.70%). NMR ($CDCl_3$, 298 K): ^1H, δ 2.08 (6 H, s, CH_3), 2.30 (6 H, s, CH_3), 4.6–5.4 (4 H, br, CH_2), 5.8 (2 H, s, CH of pyrazolyl), 7.15 (6 H, t, Ph), 7.22 (3 H, t, Ph), 7.28 (6 H, d, Ph), 7.72 (2 H, d, CH of pyridine) and 7.88 (1 H, t, CH of pyridine); ^{13}C, δ 11.22 (CH_3), 15.15 (CH_3), 51.73 (CH_2), 106.33 (CH of pyrazolyl), 124.89 (CH of pyridine), 128.82 (Ph), 129.99 (Ph), 132.84 (Ph), 133.18 (Ph), 140.59 (CH of pyridine), 141.87 (C of pyrazolyl), 149.06 (C of pyrazolyl) and 153.11 (Ph); ^{31}P-$\{^1H\}$, δ −7.382.

[CuL(CO)]ClO_4. This complex can be prepared either by passing CO into CH_2Cl_2 solution of **1** for 10 min or by addition of L (29.5 mg, 0.1 mmol) and $[Cu(MeCN)_4]ClO_4$ (32.7 mg, 0.1 mmol) to CO-saturated dichloromethane (5 cm^3). The solution was used for IR measurements: 2097.6 cm^{-1} (CO). NMR (CD_2Cl_2, 298 K): ^1H, δ 2.25 (6 H, s, CH_3), 2.44 (6 H, s, CH_3), 5.31 (4 H, s, CH_2), 6.06 (2 H, s, CH), 7.75 (2 H, d, CH) and 8.09 (1 H, t, CH); ^{13}C, δ 11.45 (CH_3), 15.03 (CH_3), 106.50 (CH of pyrazolyl), 124.69 (CH of pyridine), 140.94 (CH of pyridine), 143.30 (C of pyrazolyl), 150.58 (C of pyrazolyl), 153.25 (C of pyridine) and 172.09 (CO).

Crystallography

Dichloromethane–hexane (1:3) solutions of compounds **1** and **2** under Ar at room temperature yielded needle-shaped light greenish yellow and rectangular faint yellow crystals respectively. Crystals with approximate sizes of 0.2 × 0.2 × 0.3 mm were inserted into 0.3 mm diameter Lindemann capillary tubes along with their mother-liquor. The sealed tubes were mounted on an Enraf-Nonius CAD-4 diffractometer equipped with a graphite-monochromated Mo-Kα X-ray source (λ 0.710 73 Å). The unit-cell parameters were obtained using the method of short vectors followed by least-squares refinement of 25 reflections with $15 < \theta < 20°$. Two check reflection intensities monitored every hour showed less than 3% variation during the data collection. This ensured the stability of the crystals in their mother-liquor. After Lorentz and polarisation correction, empirical absorption corrections for both compounds were done using ψ-scan data. Table 1 shows the experimental crystallographic data.

Structure determination and refinement. Space group $P\bar{1}$ could be assigned to compound **1** using crystallographic E statistics while **2** showed systematic absences for space group $P2_1$. Both structures were solved by direct methods using the SHELXS 86[44] computer program and refined using MolEN.[45] Compound **1** was refined to $R(F) = 0.039$ and $R' = 0.037$ with anisotropic parameters for all non-hydrogen atoms and isotropic parameters for hydrogen atoms and using 3588 unique reflections with $I > 2.5\sigma(I)$. All the hydrogen atoms were located in a Fourier-difference map. Compound **2** was refined to $R(F) = 0.039$, $R' = 0.05$ using 2986 unique reflections with $I > 2.5\sigma(I)$. Oxygens of the ClO_4 moiety were found to be disordered. Eight peaks from the Fourier-difference map satisfying bond-distance criteria with Cl were chosen as oxygens and their fractional occupancies, positional co-ordinates and isotropic thermal parameters were refined. The sum of the fractional occupancies of the oxygens was constrained to be 4 (*cf.* Table 4). All other non-hydrogen atoms were refined with anisotropic thermal parameters. Methylene hydrogens were obtained using the Fourier-difference map while all other hydrogen atoms were fixed geometrically. The final Fourier-difference maps were featureless for both compounds.

Variable-temperature NMR measurements

Temperature-dependent ^1H NMR measurements were performed on a JEOL-GSX 400 spectrometer with a variable-temperature controller. The spectra of **1** and **2** were recorded in $CDCl_3$ over the range 213–328 K at intervals of 10–20 K. Since complex **1** is very sensitive to air, the sample was prepared in an argon atmosphere and then carefully sealed with a Suba-seal rubber septum and parafilm to prevent aerial oxidation.

Results and Discussion

Crystal structure

Table 1 summarises the experimental crystal data for compounds **1** and **2**, Tables 2 and 3 give fractional atomic co-ordinates of non-hydrogen atoms and Tables 4 and 5 give selected bond distances and angles. Figs. 1 and 2 show ORTEP[46] diagrams of the molecules of **1** and **2** respectively. In **1** the Cu^I is co-ordinated to four donor atoms of which three are nitrogens N(3) and N(5) from pyrazole rings and N(1) from pyridine and the fourth [O(2)], albeit somewhat remote, is from the perchlorate ion. The Cu–O(2) distance of 2.426(3) Å is characteristic of a weak bond[39] and this type of weakly co-ordinated copper(I) perchlorate complex is uncommon. With the inclusion of atom O(2), the geometry around the Cu is a highly distorted tetrahedron and can be described as distorted trigonal-planar co-ordination if atom O(2) is excluded. A reference[47,48] must be made here to the reactivity and solution behaviour of complexes of CuL^+ which seem to be essentially independent of the anion. For example, ν(CO) of carbon monoxide adducts of CuL(ClO_4), CuL(PF_6) and CuLCl is

Table 1 Crystal data for complexes **1** and **2**

	1 $[CuL(ClO_4)]\cdot CH_2Cl_2$	**2** $[CuL(PPh_3)]ClO_4$
Chemical formula	$C_{18}H_{23}Cl_3CuN_5O_4$	$C_{35}H_{36}ClCuN_5O_4P$
M	543.32	720.675
T/K	298	298
Space group	$P\bar{1}$	$P2_1$
Crystal system	Triclinic	Monoclinic
Z	2	2
a/Å	8.245(2)	10.153(2)
b/Å	12.387(1)	14.807(3)
c/Å	13.063(1)	11.615(3)
α/°	66.32(1)	—
β/°	75.23(1)	98.35(2)
γ/°	71.38(1)	—
U/Å^3	1145.6(4)	1728.2(6)
$F(000)$	556	748
D_c/g cm^{-3}	1.5748	1.3847
μ/cm^{-1}	13.35	7.992
No. reflections	4285	3358
No. unique reflections	3588	2986
No. parameters refined	428	444
Data/parameter ratio	8.38	6.73
Largest peak/e Å^{-3}	0.12	0.19
R^a	0.039	0.039
R'^b	0.037	0.05
Maximum, minimum transmission factors	99.965, 88.539	99.967, 90.027

^{a} $R = \Sigma[|F_o| - |F_c|/\Sigma|F_o|]$. ^{b} $R' = [\Sigma w(|F_o| - |F_c|)^2/\Sigma w|F_o|^2]^{\frac{1}{2}}$, $w = 1/[\sigma^2(F_o) + g(F_o)^2]$, $g = 0.001$.

Table 2 Atomic coordinates for compound **1**

Atom	x	y	z
Cu	0.340 71(3)	0.132 21(2)	0.682 83(2)
Cl(1)	0.008 75(6)	0.330 69(4)	0.795 22(4)
Cl(2)	0.435 2(1)	0.455 83(7)	0.898 18(7)
Cl(3)	0.140 5(2)	0.662 2(1)	0.837 5(1)
O(1)	−0.166 2(4)	0.344 2(3)	0.849 4(4)
O(2)	0.066 4(3)	0.214 0(2)	0.780 9(3)
O(3)	0.013 1(6)	0.422 7(3)	0.685 5(3)
O(4)	0.118 3(6)	0.337 4(4)	0.857 6(4)
N(1)	0.471 3(2)	0.275 2(1)	0.608 3(1)
N(2)	0.609 4(2)	0.065 1(1)	0.816 3(1)
N(3)	0.470 7(2)	0.033 2(1)	0.808 0(1)
N(4)	0.273 7(2)	0.250 4(1)	0.452 1(1)
N(5)	0.268 5(2)	0.147 7(2)	0.546 2(1)
C(1)	0.460 7(3)	0.340 1(2)	0.498 3(2)
C(2)	0.594 3(4)	0.388 6(2)	0.425 4(2)
C(3)	0.746 5(4)	0.366 3(2)	0.467 0(2)
C(4)	0.757 3(3)	0.298 9(2)	0.578 9(2)
C(5)	0.615 4(2)	0.256 8(2)	0.648 0(2)
C(6)	0.289 4(3)	0.359 5(2)	0.463 0(2)
C(7)	0.611 8(3)	0.193 7(2)	0.774 4(2)
C(8)	0.257 3(3)	0.234 5(2)	0.359 4(2)
C(9)	0.242 0(3)	0.117 1(2)	0.393 3(2)
C(10)	0.248 6(3)	0.066 6(2)	0.509 0(2)
C(11)	0.255 2(4)	0.332 0(2)	0.246 1(2)
C(12)	0.242 5(5)	−0.060 0(2)	0.587 7(3)
C(13)	0.709 5(2)	−0.029 6(2)	0.888 5(2)
C(14)	0.636 0(3)	−0.125 5(2)	0.925 6(2)
C(15)	0.489 2(2)	−0.084 0(2)	0.873 8(2)
C(16)	0.870 5(3)	−0.023 8(3)	0.915 9(3)
C(17)	0.361 2(3)	−0.151 4(2)	0.883 6(3)
C(18)	0.222 7(5)	0.524 2(4)	0.940 6(3)

always 2097.6 cm^{-1}. Also, the PPh_3 adducts of all these three complexes show the same dynamic NMR pattern (see below). In addition, the displacements of Cu with respect to the mean plane N(1)N(3)N(5) of the ligand in **1** and **2**, *viz.* 0.395(0) and 0.939(0) Å, reveals the three- and four- co-ordinate behaviours.

The bond distances Cu–N(1) 2.131(2), Cu–N(3) 1.942(2), Cu–N(5) 1.942(2) Å and the bond angles N(1)–Cu–N(3) 98.33(7), N(1)–Cu–N(5) 97.26(8), N(3)–Cu–N(5) 148.74(8)° of complex **1** compare well with those of one of the active sites, CuB, of *Limulus polyphemous* deoxyhaemocyanin,[37] especially

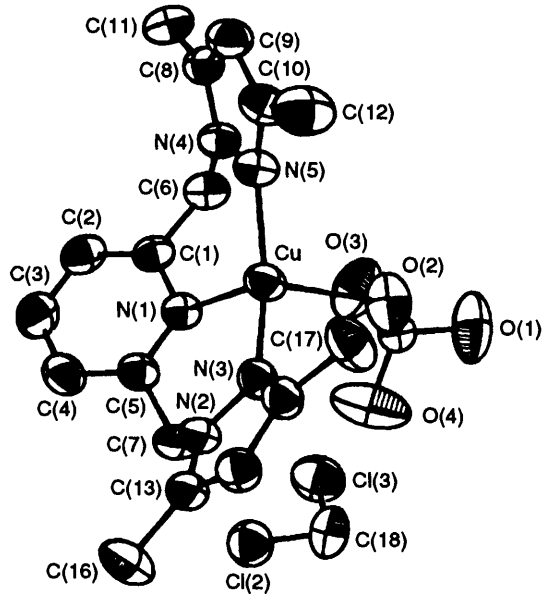

Fig. 1 An ORTEP diagram of the $[CuL(ClO_4)]\cdot CH_2Cl_2$ with the atom labelling scheme. Hydrogen atoms are omitted for clarity. Ellipsoids are drawn at the 50% probability level

the most unique largest angle, namely N(E328)–CuB–N(E364) 142° (Fig. 3). This resemblance of geometries between **1** and the active site CuB shows that **1** is a good mimic for one of the copper(I) sites of deoxyhaemocyanin. The six-membered chelation rings, CuN(3)N(2)C(7)C(5)N(1) and CuN(5)N(4)-C(6)C(1)N(1), assume distorted-chair conformations. No evidence exists for any alteration of the resonance patterns in the pyridine and pyrazole rings. The Cl–O distances in the perchlorate moiety are normal except for Cl–O(2) which has a value of 1.443(3) Å,[49] slightly longer than the other distances [Cl(1)–O(1) 1.425(3), Cl(1)–O(3) 1.429(3), Cl(1)–O(4) 1.401(6)]. This elongation may be due to its weak bonding with Cu. The unit cell of this compound is stabilised by the presence of one solvent molecule per complex.

Compound **2** consists of a $CuL(PPh_3)$ cation and a perchlorate counter ion. It crystallises in space group $P2_1$ with

Table 3 Atomic coordinates for compound **2**

Atom	*x*	*y*	*z*	Atom	*x*	*y*	*z*
Cu	0.491 05(5)	0.286	0.708 32(4)	C(13)	0.330 3(5)	0.466 7(3)	0.597 1(4)
Cl	−0.146 3(2)	0.297 7(1)	0.200 2(1)	C(14)	0.219 3(5)	0.425 9(4)	0.535 3(5)
P	0.400 8(1)	0.418 83(8)	0.736 0(1)	C(15)	0.168 5(6)	0.453 5(5)	0.422 6(5)
O(1)[a]	−0.070(1)	0.227 4(9)	0.166(1)	C(16)	0.231 8(7)	0.521 3(5)	0.373 1(5)
O(3)[b]	−0.278(1)	0.305(1)	0.149(1)	C(17)	0.343 2(8)	0.564 0(5)	0.430 8(5)
O(4)[c]	−0.234(2)	0.241(2)	0.266(2)	C(18)	0.392 3(6)	0.535 9(4)	0.543 5(4)
O(5)[d]	−0.147(2)	0.301(2)	0.319(2)	C(19)	0.570 3(5)	0.122 5(4)	0.857 3(4)
O(6)[e]	−0.089(1)	0.380(1)	0.213(1)	C(20)	0.573 1(6)	0.032 1(4)	0.881 9(5)
O(7)[f]	−0.115(2)	0.362(2)	0.292(2)	C(21)	0.464 4(8)	−0.021 8(4)	0.838 5(6)
O(8)[g]	−0.005(3)	0.292(3)	0.190(2)	C(22)	0.356 4(6)	0.018 2(4)	0.772 0(5)
O(2)[a]	−0.216 0	0.337 8	0.092 9	C(23)	0.360 8(5)	0.111 1(4)	0.750 6(4)
N(1)	0.465 7(4)	0.162 8(3)	0.791 3(3)	C(24)	0.683 1(5)	0.185 0(4)	0.905 2(4)
N(2)	0.756 3(4)	0.219 6(3)	0.815 8(3)	C(25)	0.888 9(5)	0.215 9(4)	0.813 7(5)
N(3)	0.695 3(4)	0.276 5(3)	0.731 4(3)	C(26)	0.911 6(5)	0.273 1(5)	0.725 9(5)
N(4)	0.271 8(4)	0.183 2(3)	0.566 3(4)	C(27)	0.793 0(5)	0.309 0(4)	0.679 0(5)
N(5)	0.382 9(4)	0.231 6(3)	0.553 6(3)	C(28)	0.979 7(6)	0.159 6(6)	0.893 6(6)
C(1)	0.508 2(4)	0.507 1(3)	0.809 6(4)	C(29)	0.765 4(7)	0.379 2(6)	0.586 0(8)
C(2)	0.632 2(5)	0.482 4(4)	0.867 2(5)	C(30)	0.244 8(5)	0.159 8(4)	0.682 5(5)
C(3)	0.712 0(5)	0.545 8(5)	0.932 9(5)	C(31)	0.375 9(6)	0.245 0(4)	0.439 4(5)
C(4)	0.668 1(5)	0.632 7(4)	0.939 6(5)	C(32)	0.261 9(8)	0.205 3(5)	0.381 3(5)
C(5)	0.545 7(6)	0.658 3(4)	0.882 9(5)	C(33)	0.195 1(6)	0.166 2(5)	0.463 8(5)
C(6)	0.464 8(5)	0.595 4(3)	0.817 7(4)	C(34)	0.480 3(8)	0.297 5(7)	0.393 3(5)
C(7)	0.261 6(5)	0.421 1(3)	0.820 3(4)	C(35)	0.064 4(8)	0.118 5(7)	0.454 1(7)
C(8)	0.264 7(5)	0.360 9(4)	0.911 3(5)	H(241)	0.661 0	0.236 6	0.941 1
C(9)	0.165 2(6)	0.364 3(4)	0.983 4(5)	H(242)	0.738 4	0.165 3	0.959 0
C(10)	0.065 4(6)	0.425 8(5)	0.963 8(5)	H(301)	0.168 1	0.120 0	0.680 4
C(11)	0.061 1(6)	0.485 3(5)	0.872 7(6)	H(302)	0.222 9	0.225 8	0.717 5
C(12)	0.158 9(5)	0.483 5(4)	0.799 7(5)				

Occupancies: [a] 0.5. [b] 0.55. [c] 0.75. [d] 0.51. [e] 0.665. [f] 0.265. [g] 0.25.

Table 4 Selected bond distances (Å) and angles (°) for compound **1**

Cu–O(2)	2.426(3)	Cu–N(1)	2.131(2)
Cu–N(3)	1.942(2)	Cu–N(5)	1.942(2)
Cl(1)–O(4)	1.401(6)		
N(1)–Cu–N(3)	98.33(7)	N(1)–Cu–N(5)	97.26(8)
N(3)–Cu–N(5)	148.74(8)	O(2)–Cu–N(3)	101.02(9)
O(2)–Cu–N(1)	105.62(7)	O(2)–Cu–N(5)	100.62(10)
C(1)–N(1)–C(5)	119.0(2)		

Numbers in parentheses are estimated standard deviations in the least significant digits.

Table 5 Selected bond distances (Å) and angles (°) for compound **2**

Cu–P	2.212(1)	Cu–N(1)	2.097(4)
Cu–N(3)	2.057(4)	Cu–N(5)	2.125(4)
P–Cu–N(1)	128.7(1)	P–Cu–N(3)	118.2(1)
P–Cu–N(5)	106.7(1)	N(1)–Cu–N(3)	93.9(2)
N(1)–Cu–N(5)	88.6(2)	N(3)–Cu–N(5)	118.1(2)
C(19)–N(1)–C(23)	117.7(5)		

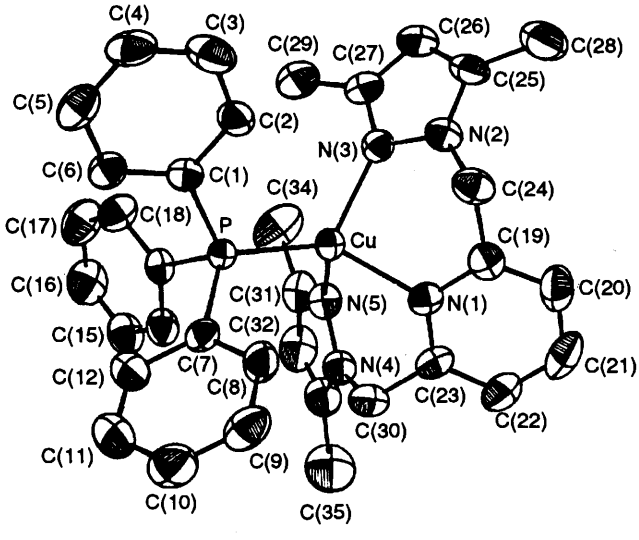

Fig. 2 An ORTEP diagram of the $[CuL(PPh_3)]ClO_4$ with the atom labelling scheme. The perchlorate ion and all hydrogen atoms are omitted for clarity. Ellipsoids as in Fig. 1

two molecules per unit cell. Whereas the copper is weakly co-ordinated to perchlorate in **1** it is directly bonded to phosphorus of triphenylphosphine in **2**. Compounds **1** and **2** differ considerably in the co-ordination geometry around copper(I). The main differences are: (1) angle N(3)–Cu–N(5) in **2** is only 118.1(2)° while it is 148.74(8)° in **1**; (2) angles N(1)–Cu–N(3) and N(1)–Cu–N(5) in **1** are 98.33(7) and 97.26(8)° while in **2** they are 93.9(2) and 88.6(2)° respectively; (3) distances Cu–N(1), Cu–N(3) and Cu–N(5) are 2.097(4), 2.057(4) and 2.125(4) Å in **2** while they are 2.131(2), 1.942(2) and 1.942(2) in **1**; (4) the chelation rings CuN(1)C(19)C(24)N(2)N(3) and CuN(1)C(23)C(30)N(4)N(5) in **2** assume a boat-like structure as opposed to the chair-like conformation in **1**.

The Cu–P bond distance [2.212(1) Å] is somewhat less than that found in most Cu^{I}–P complexes.[50–52] No evidence exists for any alteration in the planarity of the pyridine, pyrazole and phenyl rings. After geometrical fixing and refining of all hydrogen atoms except those belonging to methylene groups, a Fourier-difference map showed the hydrogen positions corresponding to C(24) and C(30) with distances C(24)–H(241) 0.914, C(24)–H(242) 0.830, C(30)–H(301) 0.973 and C(30)–H(302) 1.093 Å. The C–H bond distances of hydrogen pairs in each methylene group show differences which are probably consistent the chirality of these two carbon atoms as evidenced by the NMR results (see below). The perchlorate ion is disordered in such a way that there are eight positions for four oxygen atoms with partial occupancies.[53]

Reaction with carbon monoxide

The IR spectrum of a dichloromethane solution of complex **1** obtained by passing carbon monoxide for more than 10 min

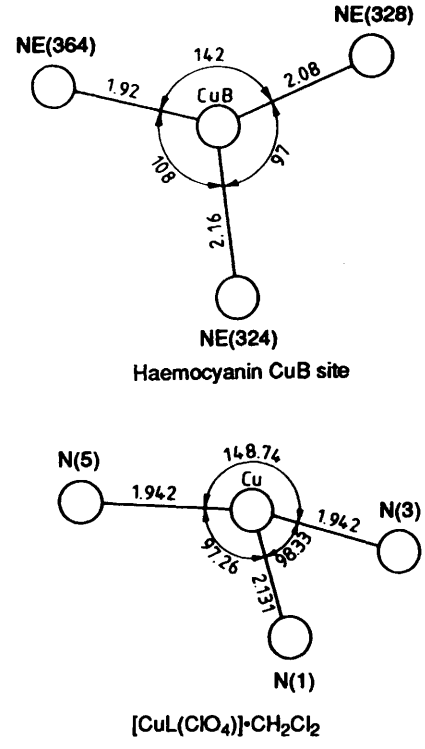

Fig. 3 Comparative geometries of the CuB site of deoxyhaemocyanin and Cu^{I} of $[CuL(ClO_4)]\cdot CH_2Cl_2$. Distances in Å, angles in °

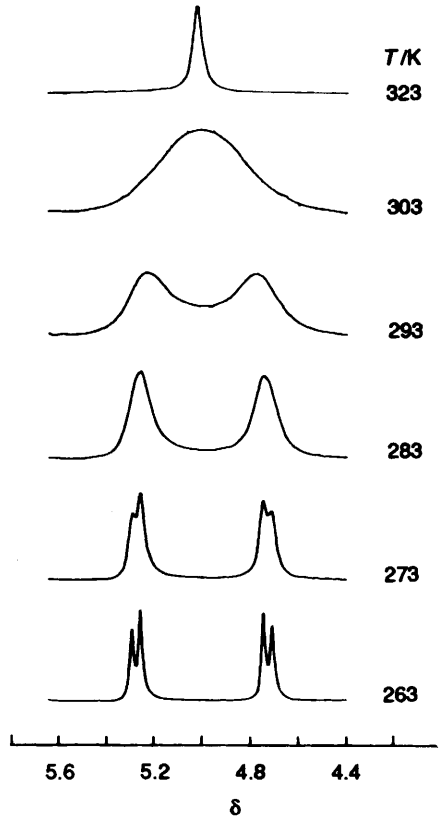

Fig. 4 Variable-temperature ^1H NMR spectra (400 MHz) of methylene protons of $[CuL(PPh_3)]ClO_4$ dissolved in $CDCl_3$

with constant stirring gives a ν(CO) stretching frequency at 2097.6 cm^{-1}, indicating that CO binds to Cu^{I} in a terminal fashion. The addition of CO is totally reversible. The adduct can be decarbonylated by purging with argon gas. Formation of the adduct was confirmed by ^{13}C NMR spectroscopy. The ^1H NMR signals are sharp and the chemical shifts of most protons shift with respect to those of **1**. Although the copper(I) centres in deoxyhaemocyanin are co-ordinated to three histidines, only the CuA site is suspected to bind CO and not CuB. The latter has one of its three bond angles (142°) much larger than any of the N–Cu–N angles in the CuA site. Interestingly, compound **1**, in spite of being structurally similar to the CuB site, absorbs CO. Sorrel and Jameson[11,12] linked this tendency of 'large angle' co-ordination to the very weak uptake of CO. Absorption of CO by compound **1** thus suggests the probable involvement of some dynamics and consequent conformational change in proteins after the uptake of the first molecule of CO.

NMR spectra and the chiral centre in complex 2

Both the compounds **1** and **2** are diamagnetic due to the presence of d^{10} Cu^{I} as testified by the lack of EPR signals both in the solid and solution. The room-temperature (296.5 K) NMR spectral behaviours of both complexes corresponding to the CuL moiety are essentially the same except in one aspect. There are two close broad signals corresponding to the methylene protons of complex **2** instead of a singlet as expected (as in the case of **1**) and hence it was decided to perform a variable-temperature experiment on this region for **2**. Fig. 4 shows the corresponding spectra. The two close signals observed at room temperature merge into a broad singlet at higher temperatures. Exchange narrowing at high temperatures reveals the equivalence of the two protons of the methylene group due to dynamic exchange. As the temperature is lowered the signals gradually separate into two less broad ones and finally become two sharp lines. The chemical shifts of these peaks change until the temperature is lowered to 263 K. The signals at 263 K resemble an AB quartet. Below this temperature there is no change either in the chemical shift or spectral features. This NMR study thus clearly indicates that the methylene carbon is chiral[54,55] at low temperatures. The chirality of the methylene group may be due to the inequivalence of the protons of the methylene group. The two protons located at apical positions of a boat-like conformation may be subjected to differing contributions from ring currents or shieldings due to the pyrazole and pyridine groups, especially at lower temperatures where the molecular motion is slowed on the NMR time-scale. The other part of the NMR spectrum of **2** is almost independent of temperature. The spectrum of **1** shows a sharp singlet corresponding to the methylene group. It is not clear at present why no chiral behaviour of the methylene carbon was exhibited by **1**. However, it is surmised that the restricted motion of the Cu–PPh_3 bond could play a role in the chiral behaviour in **2**. Some experiments performed with substituted triphenylphosphines and other phosphine derivatives indicate the importance of the fourth ligand in the dynamic process.[56]

A cyclic voltammogram of compound **1** reveals a quasi-reversible one-electron oxidation of the copper(I) ion at $E_{\frac{1}{2}}$ = 0.52 V *vs.* Ag–AgCl with a peak-to-peak separation of 152.5 mV. The ratio of I_a/I_c is 0.64:1 at scan rate 100 mV s^{-1} suggesting that there is some degradation of the complex upon oxidation. Compound **2** undergoes irreversible oxidation in acetonitrile medium. The cyclic voltammogram indicates that the oxidised species undergoes chemical decomposition, presumably due to loss of the triphenylphosphine molecule since it is not likely to co-ordinate to the copper(II) oxidised species. Further EPR studies of the oxidised species are in progress.[56]

Acknowledgements

P. M. thanks the Council of Scientific and Industrial Research (CSIR), New Delhi, India for a fellowship. We thank Dr. K. C. Santhosh for his kind help in the synthetic work. The Regional Sophisticated Instrumentation Centre, Indian Institute of Technology Madras is thanked for all instrumental facilities. This work was financially supported by the Department of Science and Technology, Government of India, New Delhi by a grant (SP/S1/47/90) awarded to P. T. M.

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Received 11*th September* 1995; *Paper* 5/06012E