Preparation and *X*-Ray Crystal Structure † of the Complex μ-Chloro-bis[bis(imidazole)copper(I)] Chloride

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The title complex, $[Cu_2Cl(Him)_4]Cl$, has been prepared from copper(I) chloride and imidazole (Him) in acetonitrile solution. It crystallises in the trigonal space group $P3_221$, with $a = 8.546(1)$, $c = 21.370(3)$ Å, and $Z = 3$. The trigonally co-ordinated Cu atoms are joined by a Cl bridge [Cu–Cl 2.564(2) Å, mean Cu–N 1.904(5) Å, Cu–Cl–Cu 95.5(1)°, Cu ··· Cu 3.797(3) Å]. The Cl^- anion lies between the two hinged Cu co-ordination planes, with Cu ··· Cl 3.134(2) Å. $[Cu_2Cl(Him)_4]Cl$ reacts readily and irreversibly with dioxygen in solution; in the solid state, only surface reaction occurs, although the molecular structure is similar to the active centre proposed for hemocyanin proteins.

The active centre of the hemocyanin proteins, responsible for the reversible binding of dioxygen in molluscs and arthropods,[1–3] is now generally agreed [4–7] to consist of a pair of copper atoms, each bound to the protein by ligation of at least two imidazole groups and linked together *via* another atom, probably oxygen, from a protein residue. The deoxy-forms of these proteins contain copper(I) atoms, and the binding of an O_2 molecule results in a μ-peroxo-group linking two antiferromagnetically coupled copper(II) centres. Two research groups have reported copper *K*-edge extended *X*-ray absorption fine structure (EXAFS) data for the oxy- and deoxy-forms of hemocyanin from *Busycon canaliculatum*[5] and *Megathura crenulata*.[6,7] The interpretations of the EXAFS data are in agreement for the oxy-form of these proteins, for which a $Cu^{II} \cdots Cu^{II}$ separation of *ca.* 3.6 Å is suggested, but differ for the deoxy-forms, for which Spiro and co-workers [5] suggest a $Cu^{I} \cdots Cu^{I}$ separation of *ca.* 3.4 Å, whereas Co and Hodgson [7] obtained no evidence for a copper–copper interaction within 4 Å. More recent EXAFS measurements on the deoxy-form of hemocyanin derived from *Busycon* and from two other arthropod species support the proposal of a Cu ··· Cu separation of 3.4—3.5 Å in all three.[8]

In the course of studies of copper–imidazole (Him) comcomplexes,[9–11] we have prepared $[Cu_2Cl(Him)_4]Cl$, the cation of which has a structural similarity to the active site proposed [4–6] for the hemocyanin proteins.

Experimental

All solution manipulations were carried out in a purified dinitrogen atmosphere. Solvents were dried and degassed before use.

Preparation of μ-*Chloro-bis*[*bis*(*imidazole*)*copper*(I)] *Chloride*, $[Cu_2Cl(Him)_4]Cl$.—Copper(I) chloride (4.1 g, 41 mmol) was added to a stirred solution of imidazole (11.2 g, 165 mmol) in acetonitrile (50 cm³). A small amount of white solid was removed by filtration, and the pale yellow solution was reduced in volume and cooled to −20 °C for 18 h. The colourless crystals obtained were washed with diethyl ether and dried *in vacuo*. A second crop of crystals was obtained by further volume reduction and cooling. Yield *ca.* 9 g (60%) (Found: C, 31.0; H, 3.4; Cl, 16.8; Cu, 25.0; N, 23.3. $C_{12}H_{16}Cl_2Cu_2N_8$ requires C, 30.6; H, 3.4; Cl, 15.1; Cu, 27.0; N, 23.8%).

Crystal Structure Determination.—Crystal data. $C_{12}H_{16}Cl_2Cu_2N_8$, $M = 470.3$, trigonal, space group $P3_221$, $a = 8.546(1)$, $c = 21.370(3)$ Å, $U = 1\,351.6$ Å³, $Z = 3$, $D_c = 1.733$ g cm⁻³, $F(000) = 708$, $\mu = 26.78$ cm⁻¹ for Mo-K_α radiation, $\lambda = 0.710\,69$ Å.

3 846 Profile-fitted [12] intensities from a crystal of size 0.75 × 0.58 × 0.50 mm were measured in the range $7 < 2\theta < 60°$ on a Stoe-Siemens AED diffractometer. Because the space group is polar, the data included a full set of Friedel pairs. Cell parameters were refined from 2θ measurements of 30 reflections centred at $\pm\omega$. Empirical absorption corrections were based on 205 azimuthal scan measurements: transmission factors ranged from 0.32 to 0.38. Of 2 623 unique reflections, 2 124 with $F > 4\sigma(F)$ were used for the structure determination.

The structure was solved by direct methods and refined to $R = \Sigma|\Delta|/\Sigma|F_o| = 0.054$, $R' = (\Sigma w\Delta^2/\Sigma wF_o^2)^{\frac{1}{2}} = 0.074$, with $w^{-1} = \sigma^2(F) + 0.0005F^2$. Hydrogen atoms (located in a difference synthesis) were constrained to give C–H = N–H = 0.96 Å on external angle bisectors of the imidazole rings, $U(H) = 1.2U_{eq}(C)$ or $1.2U_{eq}(N)$. Carbon and nitrogen atoms were clearly distinguished by the thermal parameters when all were refined as C. Non-hydrogen atoms were refined with anisotropic thermal parameters. The crystal polarity (and hence the choice between $P3_121$ and $P3_221$) was established by refinement of the η parameter,[13] for which a value of +0.95(5) was obtained; refinement in $P3_121$ (without the η parameter) resulted in much higher residuals: $R = 0.064$, $R' = 0.098$. A final difference synthesis showed no peaks higher than 0.45 e Å⁻³. Final atomic co-ordinates and bond lengths and angles are presented in Tables 1 and 2 respectively.

Discussion

The title compound consists of a $[Cu_2Cl(Him)_4]^+$ cation, together with a Cl^- anion. A crystallographic two-fold

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† *Supplementary data available* (No. SUP 56009, 16 pp.): H-atom co-ordinates, thermal parameters, structure factors. See Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1984, Issue 1, pp. xvii—xix.

Table 1. Atomic co-ordinates ($\times 10^4$)

Atom	*x*	*y*	*z*
Cu	1 385(1)	2 258(1)	4 165(1)
Cl(1)	−195(2)	−195(2)	5 000
Cl(2)	4 739(2)	4 739(2)	5 000
N(11)	367(6)	3 776(6)	4 256(2)
C(12)	−1 200(9)	3 335(10)	4 524(3)
N(13)	−1 434(9)	4 794(11)	4 540(3)
C(14)	7(10)	6 161(10)	4 290(4)
C(15)	1 102(10)	5 542(8)	4 101(4)
N(21)	2 687(5)	1 337(5)	3 720(2)
C(22)	2 715(9)	976(7)	3 112(2)
N(23)	3 959(7)	547(6)	2 995(2)
C(24)	4 782(11)	621(13)	3 533(3)
C(25)	3 986(9)	1 077(9)	3 970(3)

Table 2. Bond lengths (Å) and angles (°)

Cu–Cl(1)	2.564(2)	Cu–N(11)	1.899(6)
Cu–N(21)	1.908(5)	N(11)–C(12)	1.326(9)
N(11)–C(15)	1.354(8)	C(12)–N(13)	1.357(14)
N(13)–C(14)	1.315(9)	C(14)–C(15)	1.346(14)
N(21)–C(22)	1.338(6)	N(21)–C(25)	1.347(10)
C(22)–N(23)	1.310(11)	N(23)–C(24)	1.334(10)
C(24)–C(25)	1.324(13)		
Cl(1)–Cu–N(11)	104.7(1)	Cl(1)–Cu–N(21)	100.8(1)
N(11)–Cu–N(21)	153.4(2)	Cu–Cl(1)–Cu′	95.5(1)
Cu–N(11)–C(12)	126.4(5)	Cu–N(11)–C(15)	128.3(5)
C(12)–N(11)–C(15)	105.2(7)	N(11)–C(12)–N(13)	110.0(6)
C(12)–N(13)–C(14)	107.6(8)	N(13)–C(14)–C(15)	107.4(8)
N(11)–C(15)–C(14)	109.8(6)	Cu–N(21)–C(22)	131.3(5)
Cu–N(21)–C(25)	124.6(4)	C(22)–N(21)–C(25)	103.7(6)
N(21)–C(22)–N(23)	111.1(6)	C(22)–N(23)–C(24)	107.7(7)
N(23)–C(24)–C(25)	106.6(9)	N(21)–C(25)–C(24)	110.8(6)

Cu′ is generated by the symmetry operation *y*, *x*, 1 − *z* (two-fold rotation axis)

rotation axis passes through the bridging Cl atom and the $\mathrm{Cl^-}$ anion. Each of the two Cu atoms is trigonally co-ordinated by two imidazole ligands and by the Cl bridge: the deviation of Cu from the $\mathrm{N_2Cl}$ co-ordination plane is 0.109 Å towards the chloride anion. This lies 3.134(2) Å above the Cu atom, the Cu ··· Cl line making an angle of 2.6° with the $\mathrm{N_2Cl}$ plane normal. Thus the anion is located between the two hinged Cu co-ordination planes (Figure 1). In addition, each anion in the structure forms hydrogen bonds [Cl ··· N 3.167(4) and 3.393(4) Å] with four N–H groups of neighbouring cations (Figure 2).

The T-shaped $\mathrm{Cu^I}$ co-ordination geometry is similar to that observed in some complexes of pyrazole-derived multidentate ligands, but there is a greater deviation from linearity in the N–Cu–N group.[14] At 3.797(3) Å, the Cu ··· Cu separation cannot be considered to involve any direct bonding;[15] this is in contrast with the chlorine-bridged gold(I) complex

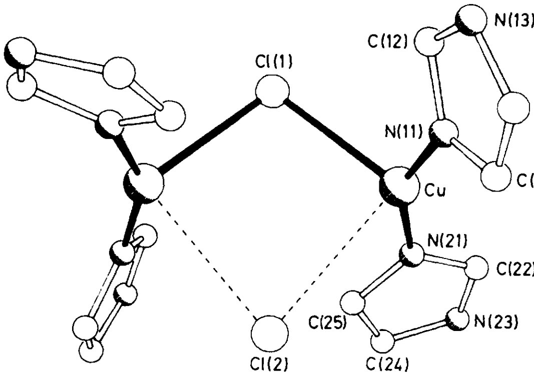

Figure 1. The structure of $[\mathrm{Cu_2Cl(Him)_4}]\mathrm{Cl}$, showing the labelling scheme for the independent atoms

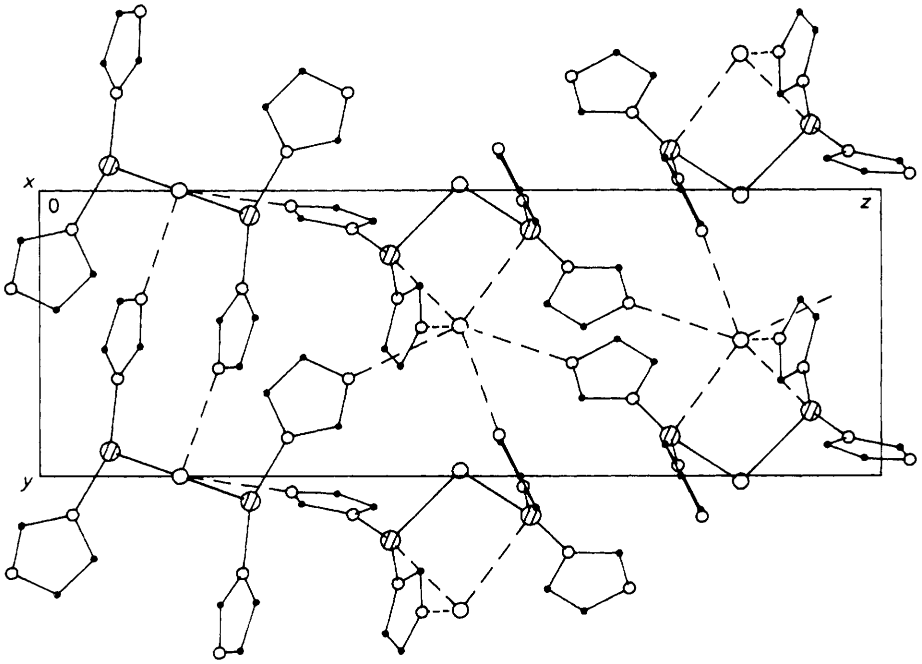

Figure 2. The crystal packing seen in projection along the *a* axis; Cl ··· Cu and Cl ··· N distances <3.4 Å are shown as dashed lines for the anions

$[Au_2(PPh_3)_2Cl]^+$, for which Au···Au is 3.085(2) and 3.035(2) Å in two crystallographically independent ions, and the corresponding Au–Cl–Au angles are 82.7(2) and 80.7(2)°, indicating direct weak Au–Au bonding.[16]

Although structures of many Cu^{II}–imidazole complexes are known (a long list was obtained by searching the Cambridge Crystallographic Data Centre files), no simple Cu^{I}–imidazole complexes have been crystallographically characterised and reported, despite the large number of Cu^{I}–imidazole complexes studied by other physical techniques.[17] However, we have recently determined the structure of tetrakis(*N*-methylimidazole)copper(I) perchlorate,[11] and the Cu–N bond length of 2.054(2) Å in this tetrahedral complex is rather longer than those [1.899(6) and 1.908(5) Å] in the title compound. Complexes of Cu^{I} with benzimidazole-containing multidentate ligands have Cu–N bond lengths similar to those found in the title compound (1.910—1.918 Å) [18,19] or, in the case of a two-co-ordinate Cu^{I} atom, rather shorter Cu–N bonds (1.869 and 1.876 Å).[20] The Cu–N bond lengths in the present structure are similar to values obtained from the EXAFS studies of the oxy- (1.96 or 2.01 Å) and deoxy-forms (1.95 Å) of hemocyanin.[5–8]

The cation structure resembles the active centre of the hemocyanin proteins, suggested from the EXAFS data,[5,6] but with a chlorine rather than an oxygen atom bridge, and hence a rather larger Cu···Cu separation. Thus far, we have been unable to achieve any reversible dioxygen uptake by the title complex. Solutions of $[Cu_2Cl(Him)_4]Cl$ in MeCN have a molar conductance consistent with the ionic formulation proposed above; such solutions are extremely sensitive to reaction with dioxygen, but the conversions which take place do not appear to be simple or reversible. Crystals acquire a clear blue surface when exposed to air; this does not noticeably affect the *X*-ray diffraction pattern, suggesting a surface reaction, but it cannot be reversed *in vacuo*. Even long exposure of the crystals to dioxygen under pressure does not produce a bulk reaction. Therefore, although the cation geometry appears to be suitable for dioxygen uptake, it is possible that the necessary co-ordination site is blocked by the chloride anion in the solid state. This restriction does not seem to exist in solution; however, the subsequent reaction with dioxygen has not yet been controlled.

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