X-Ray Structures and Magnetism of Azido-bridged Mixed-ligand Binuclear Copper(II) Complexes. Model Complexes of the Type III Copper Protein Centre†

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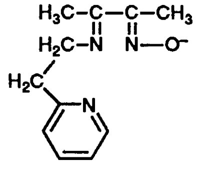
The structures of the binuclear copper(II) complexes $[CuL(N_3)Cu(bipy)][ClO_4]_2$ (**1**) and $[CuL(N_3)Cu(pmdt)][ClO_4]_2$ (**2**) [L = a Schiff base derived from 2,3-butanedione 2-oxime and 2-(2-aminoethyl)pyridine, bipy = 2,2′-bipyridine, pmdt = *N,N,N′,N″,N″*-pentamethyldiethylenetriamine)] have been determined by *X*-ray analysis. The geometry around Cu(2) in (**2**) is a square pyramid with N(4) at the apical position, while the other copper environment is essentially square planar though each Cu^{II} is semi-co-ordinated by ClO_4^- above and/or below a co-ordination plane. For both complexes two Cu^{II} ions antiferromagnetically couple with a singlet–triplet separation of $2J = -520$ cm^{-1} for (**1**) and -296 cm^{-1} for (**2**), where *J* denotes the exchange integral defined by the Hamiltonian $\mathcal{H} = -2JS_1.S_2$. Complexes (**1**) and (**2**) are e.s.r.-silent in the solid state at room temperature. In (**1**) the two co-ordination planes are nearly coplanar and the two Cu^{II} couple through N_3^- and the oxime portion (NO^-) of the ligand L. Geometrical considerations indicate that in (**2**) the magnetic interaction through the N(4) atom is negligibly small. The observed coupling is mainly through the N–O$^-$ bond of L. It is concluded that in the native type III copper protein two magnetic orbitals on two Cu^{II} are nearly coplanar and two unpaired electrons exchange extensively to give diamagnetic behaviour.

The active centre of type III copper proteins *e.g.* haemocyanin and tyrosinase forms a binuclear copper complex. Though the two coppers are in the II oxidation state they have a strong antiferromagnetic interaction and consequently the proteins exhibit diamagnetic behaviour. Loehr and co-workers[1] showed that in the active site of oxyhaemocyanin, O_2^{2-} bridges two Cu^{2+} to give $Cu^{II}–O_2^{2-}–Cu^{II}$. Each copper(II) is additionally co-ordinated by three imidazole nitrogens of histidines[2] and bridged by an unidentified ligand X.[3] The co-ordination around each copper(II) is identical in the arthropodous haemocyanin, while in molluscan haemocyanin the co-ordination is mutually different.[3,4] In the context of these investigations we prepared two mixed-ligand binuclear copper(II) complexes in which the co-ordination around each copper(II) is different but for both a strong antiferromagnetic interaction is observed. The relation between the structures and magnetism of the complexes is discussed.

Experimental

Preparation of the Copper(II) *Complexes*.—$[CuL(N_3)Cu(bipy)][ClO_4]_2$ (**1**) was prepared by the same procedure as that for $[CuL(N_3)Cu(bipy)][NO_3]_2·1.5H_2O$[5] using $Cu(ClO_4)_2·6H_2O$ instead of $Cu(NO_3)_2·3H_2O$ (Found: C, 34.70; H, 3.35; N, 14.60. Calc. for $C_{21}H_{22}Cl_2Cu_2N_8O_9$: C, 34.60; H, 3.05; N, 15.40%). The preparation of $[CuL(N_3)Cu(pmdt)][ClO_4]_2$ (**2**) (pmdt = *NN,N′,N″,N″*-pentamethyldiethylenetriamine) has been previously described.[5] Magnetic susceptibilities at room temperature were determined using the Gouy method, those over the range from liquid-nitrogen temperature to room temperature were measured using a Faraday apparatus designed by one of us (W. M.) and calibrated by $CuSO_4·5H_2O$. Powder *X*-band e.s.r. spectra at room temperature were recorded at 9.5 GHz, modulation amplitude 6.3 G (6.3×10^{-4} T), and modulation frequency 100 kHz with a JEOL JES-FE1X spectrometer.



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X-Ray Data Collection.—The dark green crystals chosen for data collection and lattice constant determination had dimensions of 0.50 × 0.33 × 0.15 mm for complex (**1**) and 0.55 × 0.30 × 0.15 mm for (**2**). They were mounted in an arbitrary orientation on a Philips PW1100 automated diffractometer. The PW1100 program obtained 20 centred reflections in the range $2 < \theta < 9°$, $-60 < \chi < 60°$, and $0 < \varphi < 120°$ for (**1**) and (**2**) and orientation matrices, and then identified the triclinic cell for both crystals. The space group $P\bar{1}$ was assumed throughout the structure analyses. The unit-cell dimensions with standard deviations were derived from a least-squares fit from the angular positions of 21 centred reflections in the range $15 < 2\theta < 25°$ for (**1**) and 19 for (**2**). Crystal data and details of data collection and structure refinements are given in Table 1. The intensity data were collected at room temperature by the use of graphite-monochromated Mo-K_α radiation ($\lambda = 0.710\,69$ Å). During each data collection the intensities of three standard reflections were monitored every 4 h. The

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† *Supplementary data available:* see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1990, Issue 1, pp. xix—xxii.

Table 1. Summary of crystal data and details of data collection and structure refinement for $[CuL(N_3)Cu(bipy)][ClO_4]_2$ (**1**) and $[CuL(N_3)Cu(pmdt)][ClO_4]_2$ (**2**)*

	(1)	(2)
Formula	$C_{21}H_{22}Cl_2Cu_2N_9O_9$	$C_{20}H_{37}Cl_2Cu_2N_9O_9$
M	728.5	745.7
a/Å	20.86(3)	16.880(8)
b/Å	15.028(16)	11.488(4)
c/Å	9.466(9)	8.769(2)
α/°	105.35(9)	106.04(2)
β/°	95.86(11)	83.78(2)
γ/°	94.98(8)	95.99(3)
Z	4	2
D_m/g cm^{-3}	1.69	1.52
D_c/g cm^{-3}	1.71	1.53
U/Å^3	2 826.7(52)	1 619.8(10)
$F(000)$	1 472	768
μ(Mo-K_α)/cm^{-1}	18.2	15.9
$2\theta_{max.}$/°	46	50
w	$[\sigma^2(F_o) + 0.008F_o^2]^{-1}$	$[\sigma^2(F_o) + 0.009F_o^2]^{-1}$
Maximum shift/error for last cycle	0.4	0.3
Residual electron density/e Å^{-3}	1.8	0.9
No. of reflections [$F > 3\sigma(F_o)$]	3 356	2 753
R [$R' = (\Sigma w\Delta F^2/\Sigma wF_o^2)^{\frac{1}{2}}$]	0.080 [0.120]	0.082 [0.119]

* Details in common: triclinic, space group $P\bar{1}$; ω scan mode; scan rate 0.05° s^{-1}; scan range 2.0 + 0.4 tan θ°; background time 10 s.

Table 2. Atomic co-ordinates with standard deviations for $[CuL(N_3)Cu(bipy)][ClO_4]_2$ (**1**)

Atom	x	y	z	Atom	x	y	z
Cu(1)	0.930 06(12)	0.299 25(17)	1.035 03(28)	Cu(1′)	0.539 59(11)	−0.302 54(16)	0.949 91(28)
Cu(2)	0.818 22(11)	0.129 50(16)	0.845 75(26)	Cu(2′)	0.673 89(11)	−0.147 43(17)	1.045 90(29)
N(1)	1.016 9(8)	0.331 2(11)	0.976 3(18)	N(1′)	0.528 0(8)	−0.426 9(10)	0.803 8(17)
N(2)	0.937 0(9)	0.414 6(11)	1.190 9(18)	N(2′)	0.457 2(9)	−0.321 5(11)	1.038 2(18)
N(3)	0.841 2(7)	0.285 0(10)	1.088 6(15)	N(3′)	0.549 2(7)	−0.192 6(11)	1.119 9(18)
N(4)	0.912 2(7)	0.169 8(10)	0.908 0(17)	N(4′)	0.616 2(7)	−0.247 2(11)	0.892 1(16)
N(5)	0.952 9(7)	0.118 0(11)	0.897 4(19)	N(5′)	0.621 9(8)	−0.260 1(12)	0.765 1(19)
N(6)	0.990 4(10)	0.072 4(13)	0.868 1(25)	N(6′)	0.622 8(11)	−0.275 6(14)	0.637 9(21)
N(7)	0.726 9(7)	0.058 4(10)	0.819 7(17)	N(7′)	0.720 7(7)	−0.028 7(11)	1.174 6(17)
N(8)	0.826 5(7)	0.036 8(10)	0.657 9(17)	N(8′)	0.759 4(7)	−0.148 6(11)	0.958 9(18)
C(1)	1.025 6(9)	0.294 4(14)	0.844 7(26)	C(1′)	0.581 4(12)	−0.465 8(14)	0.749 8(24)
C(2)	1.081 0(11)	0.307 9(15)	0.785 8(25)	C(2′)	0.573 2(13)	−0.551 5(15)	0.654 0(24)
C(3)	1.135 3(10)	0.361 4(18)	0.877 3(27)	C(3′)	0.514 1(13)	−0.593 3(14)	0.600 8(23)
C(4)	1.125 8(10)	0.398 2(15)	1.014 8(29)	C(4′)	0.459 7(12)	−0.560 3(15)	0.647 4(24)
C(5)	1.065 2(10)	0.386 3(14)	1.075 7(24)	C(5′)	0.466 9(11)	−0.473 1(14)	0.749 7(24)
C(6)	1.054 8(12)	0.428 6(16)	1.225 7(27)	C(6′)	0.408 6(10)	−0.427 9(13)	0.804 8(24)
C(7)	0.997 0(11)	0.478 8(14)	1.240 7(24)	C(7′)	0.408 2(9)	−0.403 6(14)	0.964 9(22)
C(8)	0.883 8(11)	0.422 9(13)	1.253 3(20)	C(8′)	0.445 9(10)	−0.257 7(13)	1.147 8(22)
C(9)	0.870 7(14)	0.505 1(16)	1.381 9(26)	C(9′)	0.388 6(9)	−0.253 1(15)	1.227 7(27)
C(10)	0.829 6(9)	0.350 7(13)	1.188 1(19)	C(10′)	0.505 6(9)	−0.185 4(14)	1.205 1(22)
C(11)	0.759 2(11)	0.351 9(16)	1.240 5(26)	C(11′)	0.510 2(12)	−0.108 7(17)	1.342 7(27)
C(12)	0.684 5(9)	0.071 4(13)	0.903 9(21)	C(12′)	0.694 6(11)	0.030 6(13)	1.290 0(23)
C(13)	0.623 3(10)	0.013 6(14)	0.874 1(24)	C(13′)	0.733 2(10)	0.113 3(14)	1.375 2(24)
C(14)	0.612 3(10)	−0.052 3(16)	0.759 5(25)	C(14′)	0.792 6(11)	0.135 9(13)	1.348 3(23)
C(15)	0.660 5(11)	−0.073 5(13)	0.654 8(24)	C(15′)	0.816 9(10)	0.078 4(13)	1.230 1(23)
C(16)	0.719 9(9)	−0.016 2(12)	0.696 6(22)	C(16′)	0.778 0(9)	−0.006 6(13)	1.151 5(19)
C(17)	0.775 6(9)	−0.031 9(12)	0.613 1(21)	C(17′)	0.800 5(8)	−0.071 8(13)	1.025 8(22)
C(18)	0.775 6(11)	−0.101 5(13)	0.489 0(26)	C(18′)	0.859 9(10)	−0.064 6(14)	0.979 7(24)
C(19)	0.829 2(11)	−0.109 5(14)	0.413 6(25)	C(19′)	0.877 5(12)	−0.132 0(18)	0.864 8(29)
C(20)	0.882 2(12)	−0.040 5(17)	0.458 6(23)	C(20′)	0.828 1(13)	−0.210 4(17)	0.803 1(28)
C(21)	0.878 6(9)	0.031 0(15)	0.580 4(24)	C(21′)	0.774 7(10)	−0.213 8(15)	0.853 6(26)
O(1)	0.797 7(6)	0.213 9(9)	1.018 1(15)	O(1′)	0.601 2(6)	−0.128 1(9)	1.156 4(16)
Cl(1)	0.813 6(3)	0.337 2(4)	0.748 0(7)	Cl(1′)	0.683 8(3)	−0.335 8(5)	1.192 0(8)
O(11)	0.876 9(7)	0.360 6(11)	0.831 4(16)	O(11′)	0.623 8(7)	−0.365 4(10)	1.120 3(19)
O(12)	0.795 8(8)	0.235 7(10)	0.705 1(16)	O(12′)	0.717 2(7)	−0.261 4(10)	1.158 8(16)
O(13)	0.771 2(8)	0.381 9(11)	0.841 8(20)	O(13′)	0.717 0(9)	−0.387 8(16)	1.250 0(35)
O(14)	0.813 6(9)	0.367 6(11)	0.623 2(19)	O(14′)	0.659 0(15)	−0.286 6(27)	1.334 9(31)
Cl(2)	0.987 5(3)	0.228 1(5)	1.392 9(7)	Cl(2′)	0.433 4(3)	−0.184 1(5)	0.736 1(8)
O(21)	0.966 8(8)	0.201 3(12)	1.232 1(17)	O(21′)	0.485 9(7)	−0.236 4(10)	0.745 8(19)
O(22)	1.056 2(9)	0.253 8(16)	1.420 5(21)	O(22′)	0.407 9(22)	−0.196 2(41)	0.608 6(30)
O(23)	0.957 4(14)	0.311 5(20)	1.457 9(24)	O(23′)	0.458 5(17)	−0.092 8(18)	0.780 5(67)
O(24)	0.972 1(12)	0.157 5(15)	1.455 9(23)	O(24′)	0.388 7(10)	−0.192 3(13)	0.825 6(22)

compounds remained stable. The intensities were corrected for Lorentz-polarization effects,[6] but not for absorption.

Structure solution and refinement. The program SHELXS 86[7] gave partial structures including Cu and Cl atoms for both crystals. Least-squares refinements followed by Fourier difference syntheses revealed the positions of all non-hydrogen atoms. Hydrogen atoms were placed at idealized positions (C–H 0.96 Å) and most were confirmed in a Fourier difference synthesis. In the final cycles of refinement the hydrogen atoms were included with a common isotropic thermal parameter $B = 6.0$ Å^2, but their parameters were not refined. The function minimized was $\Sigma w(F_o - |F_c|)^2$. All oxygen atoms of ClO_4^- for (2) were isotropically refined. The atomic scattering factors for Cu, Cl, O, N, C, and H atoms were taken from ref. 8, with corrections for anomalous scattering ($\Delta f'$) for Cu and Cl. Atomic co-ordinates for non-hydrogen atoms are given in Tables 2 and 3. The computer programs used in the calculations were RSLC-3, HBLS-IV, RSSFR-5, and DAPH.[9] Figures 1 and 2 were drawn by the use of ORTEP.[10] Calculations were performed on a HITAC M 660 K computer at Osaka City University.

Additional material available from the Cambridge Crystallographic Data Centre comprises H-atom co-ordinates, thermal parameters, and remaining bond lengths and angles.

Results and Discussion

The complex $[CuL(N_3)Cu(bipy)][ClO_4]_2$ crystallizes in the triclinic cell with $Z = 4$. There are two crystallographically independent complexes, one denoted as (1) and the other (1′), but their structures are similar. Perspective views of the complex cations of (1) and (2) are shown in Figures 1 and 2. In the cations of (1) and (1′) ligand L co-ordinates to Cu(1)[Cu(1′)], the NO^- portion of L and N_3^- bridges Cu(1)[Cu(1′)] and Cu(2)[Cu(2′)], and bipy chelates Cu(2)[Cu(2′)]. Atom Cu(1)[Cu(1′)] has six-co-ordination involving 4N from L and N_3^- and 2O from ClO_4^- above and below the 4N co-ordination plane, while Cu(2)[Cu(2′)] is five-co-ordinate with 3N and O from L, N_3^-, and bipy and O from ClO_4^- above the N_3O co-ordination plane. The [N(1),N(2),N(3),N(4)], [O(1),N(4),N(7),N(8)], [N(1′),N(2′),N(3′),N(4′)], and [O(1′),N(4′),N(7′),N(8′)] groups form tetrahedrally distorted planes, the largest deviation from planarity being 0.22 Å for N(4). The angles between [N(1),N(2),N(3),N(4)] and [O(1),N(4),N(7),N(8)] and [N(1′),N(2′),N(3′),N(4′)] and [O(1′),N(4′),N(7′),N(8′)] are 18.5 and 14.6° respectively.

The binuclear complex cation of (2) is similar to those of (1) and (1′) except that Cu(2) is chelated by tridentate pmdt instead of bipy. Each copper has a five-co-ordination. The arrangement of N(1), N(2), N(3), and N(4) atoms about Cu(1) is planar, the maximum deviation from planarity being 0.14 Å for Cu(1). A perchlorate ion approaches Cu(1) below the 4N co-ordination plane. The geometry about Cu(2) is square pyramidal with N(4) at the apical position and O(1), N(7), N(8), and N(9) at the basal ones; Cu(2) deviates by 0.41 Å from the basal plane. The [N(1),N(2),N(3),N(4)] and [O(1),N(7),N(8),N(9)] planes make an angle of 68.8°.

A perchlorate ion semi-co-ordinates the Cu atoms of (1) and (1′), and Cu(1) of (2). The Cu–O bond lengths range from 2.380(17) to 2.76(3) Å. The other Cu–N and Cu–O bond lengths are normal. The bridging angles of N_3^-, Cu–N(N_3^-)–Cu, are 112.6(8)° for (1), 117.9(9)° for (1′), and 112.4(5)° for (2), which are larger than those previously reported.[11–13] Selected bond lengths and angles are summarized in Tables 4 and 5.

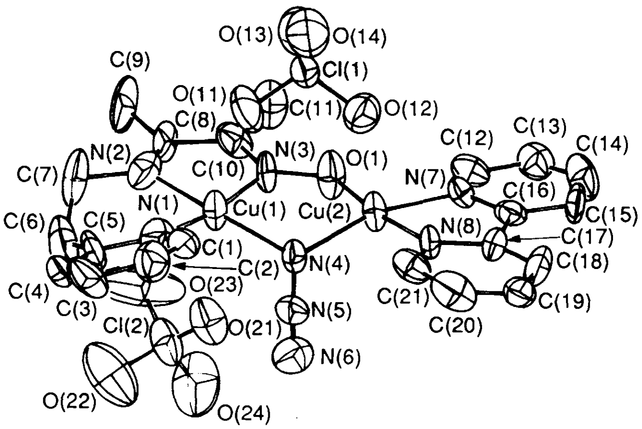

Figure 1. A view of the complex $[CuL(N_3)Cu(bipy)][ClO_4]_2$ (1) with the numbering scheme. The same numbering scheme is applied to complex (1′) using primes

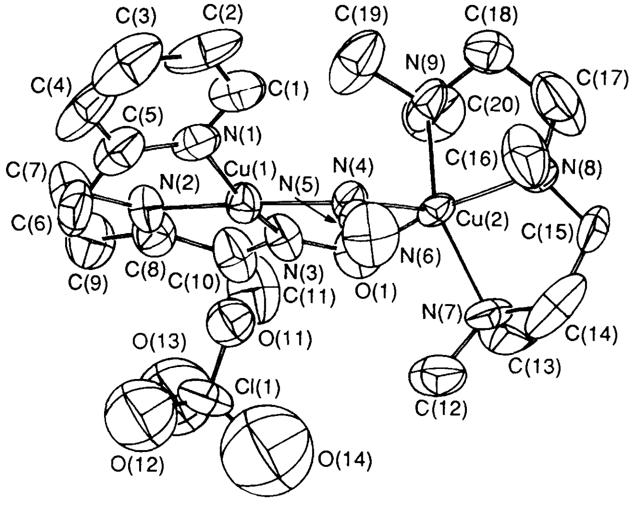

Figure 2. A view of the complex $[CuL(N_3)Cu(pmdt)][ClO_4]_2$ (2)

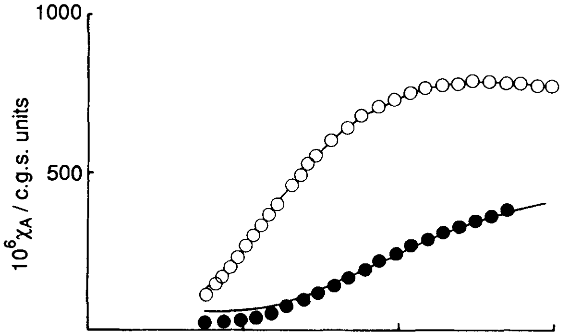

Figure 3. Temperature dependence of the magnetic susceptibilities of complexes (1) (●) and (2) (○). The solid lines show theoretical susceptibilities calculated from the Bleaney–Bowers equation $\chi_A = (N\beta^2g^2/3kT)[1 + 1/3\exp(-2J/kT)]^{-1} + N\alpha$ with $g = 2.05$, $2J = -520$ cm^{-1}, and $N\alpha = 60 \times 10^{-6}$ c.g.s. units for (1) and $g = 2.02$, $2J = -296$ cm^{-1}, and $N\alpha = 60 \times 10^{-6}$ c.g.s. units for (2) (c.g.s. = S.I. × $10^6/4\pi$)

The structures and magnetism of binuclear copper(II) complexes, in which two copper(II) ions are bridged by both N_3^- and another ligand, have attracted considerable attention in connection with those of the binuclear copper(II) site of type III copper proteins. Some complexes have been structurally characterized and the relevance of the results to these proteins discussed.[14–18] Among those there have been only three examples of antiferromagnetically coupled binuclear copper(II)

Table 3. Atomic co-ordinates with standard deviations for $[CuL(N_3)Cu(pmdt)][ClO_4]_2$ (**2**)

Atom	*x*	*y*	*z*
Cu(1)	0.197 66(10)	0.484 28(13)	0.260 60(18)
Cu(2)	0.310 07(8)	0.241 96(13)	0.221 10(15)
Cl(1)	0.296 9(3)	0.619 9(4)	0.968 5(5)
Cl(2) *	0.5	0	0.5
Cl(3) *	0.020 1(5)	0.973 6(8)	0.704 4(12)
N(1)	0.080 0(6)	0.476 2(11)	0.229 9(13)
N(2)	0.202 3(8)	0.651 1(9)	0.400 1(14)
N(3)	0.302 3(7)	0.494 1(9)	0.350 1(12)
N(4)	0.212 9(6)	0.314 8(9)	0.140 7(11)
N(5)	0.187 8(6)	0.277 6(9)	0.008 7(12)
N(6)	0.164 2(9)	0.242 8(12)	−0.111 9(14)
N(7)	0.406 4(6)	0.221 1(10)	0.054 4(12)
N(8)	0.292 8(6)	0.057 8(10)	0.138 1(12)
N(9)	0.260 1(7)	0.221 8(11)	0.436 0(12)
O(1)	0.353 0(6)	0.406 5(8)	0.312 2(11)
C(1)	0.035 5(8)	0.373 3(15)	0.214 2(17)
C(2)	−0.043 5(9)	0.371 5(19)	0.192 5(19)
C(3)	−0.074 1(9)	0.477 8(21)	0.193 1(19)
C(4)	−0.033 6(10)	0.577 0(20)	0.218 8(19)
C(5)	0.044 8(10)	0.579 6(16)	0.234 4(17)
C(6)	0.096 5(11)	0.694 4(16)	0.254 4(21)
C(7)	0.136 2(13)	0.729 9(15)	0.411 8(24)
C(8)	0.264 6(10)	0.686 8(13)	0.473 8(17)
C(9)	0.281 4(12)	0.808 3(14)	0.584 1(20)
C(10)	0.328 1(10)	0.597 4(12)	0.433 5(16)
C(11)	0.407 4(12)	0.623 4(15)	0.490 7(22)
C(12)	0.411 8(10)	0.312 8(17)	−0.042 8(20)
C(13)	0.477 3(8)	0.239 5(17)	0.142 6(23)
C(14)	0.398 4(10)	0.099 5(19)	−0.045 1(20)
C(15)	0.362 9(9)	0.012 1(13)	0.050 0(18)
C(16)	0.222 8(11)	0.022 9(14)	0.033 9(24)
C(17)	0.280 9(14)	0.012 9(15)	0.283 6(23)
C(18)	0.223 0(12)	0.089 7(16)	0.406 8(21)
C(19)	0.193 4(11)	0.291 3(19)	0.507 8(17)
C(20)	0.323 6(12)	0.256 6(19)	0.552 9(18)
O(11)	0.240(1)	0.537(1)	1.018(1)
O(12)	0.262(1)	0.704(2)	0.925(2)
O(13)	0.330(1)	0.697(2)	1.097(3)
O(14)	0.353(2)	0.556(3)	0.847(3)
O(21) *	0.499(2)	−0.065(2)	0.613(3)
O(22) *	0.473(3)	0.113(4)	0.560(4)
O(23) *	0.453(2)	−0.061(3)	0.381(4)
O(24) *	0.584(2)	−0.001(2)	0.423(3)
O(31) *	−0.025(2)	0.880(3)	0.649(4)
O(32) *	0.085(2)	0.951(3)	0.750(4)
O(33) *	−0.029(3)	1.041(5)	0.813(6)
O(34) *	0.040(3)	1.039(5)	0.614(6)

* Site occupation factor 0.5.

Table 4. Selected interatomic distances (Å) and angles (°) for complex (**1**)

Cu(1) · · · Cu(2)	3.295(4)	Cu(1′) · · · Cu(2′)	3.367(4)
Cu(1)–N(1)	2.004(17)	Cu(1′)–N(1′)	1.987(16)
Cu(1)–N(2)	1.940(18)	Cu(1′)–N(2′)	2.017(19)
Cu(1)–N(3)	1.980(15)	Cu(1′)–N(3′)	1.956(17)
Cu(1)–N(4)	1.979(16)	Cu(1′)–N(4′)	1.932(17)
Cu(1)–O(11)	2.545(16)	Cu(1′)–O(11′)	2.664(16)
Cu(1)–O(21)	2.76(3)	Cu(1′)–O(21′)	2.60(2)
Cu(2)–N(4)	1.981(16)	Cu(2′)–N(4′)	1.998(17)
Cu(2)–N(7)	2.060(16)	Cu(2′)–N(7′)	1.981(16)
Cu(2)–N(8)	1.981(17)	Cu(2′)–N(8′)	2.039(17)
Cu(2)–O(1)	1.895(14)	Cu(2′)–O(1′)	1.927(16)
Cu(2)–O(12)	2.380(17)	Cu(2′)–O(12′)	2.436(18)
N(1)–Cu(1)–N(2)	93.0(8)	N(1′)–Cu(1′)–N(2′)	95.8(7)
N(1)–Cu(1)–N(3)	171.8(7)	N(1′)–Cu(1′)–N(3′)	169.7(7)
N(1)–Cu(1)–N(4)	98.0(7)	N(1′)–Cu(1′)–N(4′)	99.9(7)
N(1)–Cu(1)–O(11)	89.1(6)	N(1′)–Cu(1′)–O(11′)	88.8(6)
N(1)–Cu(1)–O(21)	99.5(7)	N(1′)–Cu(1′)–O(21′)	88.6(7)
N(2)–Cu(1)–N(3)	82.3(7)	N(2′)–Cu(1′)–N(3′)	78.3(8)
N(2)–Cu(1)–N(4)	166.7(7)	N(2′)–Cu(1′)–N(4′)	163.4(8)
N(2)–Cu(1)–O(11)	96.2(7)	N(2′)–Cu(1′)–O(11′)	101.1(7)
N(2)–Cu(1)–O(21)	92.3(8)	N(2′)–Cu(1′)–O(21′)	95.1(7)
N(3)–Cu(1)–N(4)	87.6(7)	N(3′)–Cu(1′)–N(4′)	86.9(7)
N(3)–Cu(1)–O(11)	84.7(6)	N(3′)–Cu(1′)–O(11′)	84.2(6)
N(3)–Cu(1)–O(21)	87.5(7)	N(3′)–Cu(1′)–O(21′)	100.2(7)
N(4)–Cu(1)–O(11)	91.5(6)	N(4′)–Cu(1′)–O(11′)	84.6(6)
N(4)–Cu(1)–O(21)	78.6(7)	N(4′)–Cu(1′)–O(21′)	80.2(7)
O(11)–Cu(1)–O(21)	167.6(6)	O(11′)–Cu(1′)–O(21′)	163.8(6)
N(4)–Cu(2)–N(7)	161.7(7)	N(4′)–Cu(2′)–N(7′)	166.3(7)
N(4)–Cu(2)–N(8)	96.9(6)	N(4′)–Cu(2′)–N(8′)	102.2(7)
N(4)–Cu(2)–O(1)	91.0(7)	N(4′)–Cu(2′)–O(1′)	88.1(7)
N(4)–Cu(2)–O(12)	98.8(6)	N(4′)–Cu(2′)–O(12′)	91.3(7)
N(7)–Cu(2)–N(8)	83.7(7)	N(7′)–Cu(2′)–N(8′)	80.2(7)
N(7)–Cu(2)–O(1)	88.8(6)	N(7′)–Cu(2′)–O(1′)	89.7(7)
N(7)–Cu(2)–O(12)	99.5(6)	N(7′)–Cu(2′)–O(12′)	102.4(7)
N(8)–Cu(2)–O(1)	172.1(7)	N(8′)–Cu(2′)–O(1′)	169.7(7)
N(8)–Cu(2)–O(12)	87.8(7)	N(8′)–Cu(2′)–O(12′)	83.8(7)
O(1)–Cu(2)–O(12)	90.8(6)	O(1′)–Cu(2′)–O(12′)	96.6(7)
Cu(1)–N(4)–Cu(2)	112.6(8)	Cu(1′)–N(4′)–Cu(2′)	117.9(9)
Cu(1)–N(3)–O(1)	122.7(12)	Cu(1′)–N(3′)–O(1′)	123.6(13)
Cu(2)–O(1)–N(3)	118.4(11)	Cu(2′)–O(1′)–N(3′)	119.1(12)

complexes with an end-on type N_3^- bridge.[14,17,18] In our model complexes (**1**) and (**2**) the NO^- portion of the ligand L and an end-on N_3^- bridge two copper(II) ions forming mixed-ligand binuclear copper(II) complexes. Complexes (**1**) and (**2**) are new members of such complexes. The room-temperature magnetic moments $\mu_{eff.}$, of (**1**) and (**2**) are 0.99 and 1.34, respectively. The temperature dependences of the magnetic susceptibilities are given in Figure 3. In both complexes two copper(II) ions antiferromagnetically couple with the singlet–triplet separations $2J = -520\ cm^{-1}$ for (**1**) and $-296\ cm^{-1}$ for (**2**). The crystals of these complexes are e.s.r.-silent at room temperature. This result can be rationalized if it is assumed that the ground state of each Cu^{II} has a $d_{x^2-y^2}$ configuration, taking the geometry around each Cu^{II} into account and that the two Cu^{II} strongly couple through the NO^- portion of L and N_3^-. The stronger antiferromagnetic interaction in (**1**) is due to the fact that the co-ordination geometry around each Cu^{II} is planar and the NO^- portion of L and N_3^- bridge the two co-ordination planes resulting in their coplanarity. In (**1**) the magnetic interaction through the NO^- portion of L would be larger than that through N_3^- because binuclear copper(II) complexes with oximate NO^- bridges generally exhibit rather strong antiferromagnetism.[19–21] Kahn[22] indicates that in planar di-μ-azido-copper(II) dimers orthogonality occurs for $Cu-N(N_3^-)-Cu$ angles around 103° and antiferromagnetism is dominant when this angle is greater than 103°. On this basis, a smaller antiferromagnetic contribution through the N_3^- bridge would be expected from the $Cu-N(N_3^-)-Cu$ angles of 112.6(8) and 117.9(9)° for (**1**) and (**1′**).

The geometry around Cu(2) in complex (**2**) is square pyramidal, while the environment of Cu(1) is essentially square planar, though Cu(1) is semi-co-ordinated by ClO_4^- below the co-ordination plane. Atom N(4) is shared by one of the square-planar co-ordination sites around Cu(1) and the apical position of the square pyramid around Cu(2). As the geometrical situation in (**2**) makes it impossible for the two unpaired electrons to exchange through the N(4) atom, the coupling resulting from the end-on N_3^- bridge with the Cu(1)–N(4)–Cu(2) angle of 112.4(5)° would be negligibly small or weakly

Table 5. Selected interatomic distances (Å) and angles (°) for complex (**2**)

Cu(1) ··· Cu(2)	3.449(3)	Cu(2)–N(4)	2.179(10)
Cu(1)–O(11$^{\mathrm{I}}$)	2.39(1)	Cu(2)–N(7)	2.052(11)
Cu(1)–N(1)	2.023(13)	Cu(2)–N(8)	2.039(11)
Cu(1)–N(2)	1.967(13)	Cu(2)–N(9)	2.043(13)
Cu(1)–N(3)	1.990(12)	Cu(2)–O(1)	1.935(10)
Cu(1)–N(4)	1.969(10)		
N(1)–Cu(1)–N(2)	95.1(5)	N(4)–Cu(2)–N(9)	101.1(5)
N(1)–Cu(1)–N(3)	164.7(5)	N(4)–Cu(2)–O(1)	89.0(4)
N(1)–Cu(1)–N(4)	95.8(5)	N(7)–Cu(2)–N(8)	83.6(5)
N(2)–Cu(1)–N(3)	79.0(5)	N(7)–Cu(2)–N(9)	148.1(5)
N(2)–Cu(1)–N(4)	168.3(5)	N(7)–Cu(2)–O(1)	88.6(4)
N(3)–Cu(1)–N(4)	89.4(5)	N(8)–Cu(2)–N(9)	86.8(5)
N(1)–Cu(1)–O(11$^{\mathrm{I}}$)	94.1(5)	N(8)–Cu(2)–O(1)	165.0(4)
N(2)–Cu(1)–O(11$^{\mathrm{I}}$)	96.6(5)	N(9)–Cu(2)–O(1)	93.2(5)
N(3)–Cu(1)–O(11$^{\mathrm{I}}$)	100.5(4)	Cu(1)–N(4)–Cu(2)	112.4(5)
N(4)–Cu(1)–O(11$^{\mathrm{I}}$)	86.7(4)	Cu(1)–N(3)–O(1)	125.6(8)
N(4)–Cu(2)–N(7)	110.9(4)	Cu(2)–O(1)–N(3)	117.5(8)
N(4)–Cu(2)–N(8)	105.8(4)		

Symmetry operation: I *x*, *y*, − 1 + *z*.

ferromagnetic. This conclusion is consistent with our previous finding for $[\mathrm{Cu_2L^1{}_2(N_3)_2}][\mathrm{ClO_4}]_2$[23] [$\mathrm{L^1}$ = 1-(imidazol-4-yl)-2-(2-pyridylmethyleneaminoethane], where an end-on $\mathrm{N_3^-}$ bridges one of the square-planar co-ordination sites and an apical position of the square pyramid with a Cu–N($\mathrm{N_3^-}$)–Cu angle of 96.7(2)° and ferromagnetic coupling. Consequently the coupling in (**2**) is mainly obtained through the N–O$^-$ bond of L. The angle (68.8°) between the co-ordination and basal planes in (**2**) is generated by rotation around O(1)–Cu(2)–N(8) bonds. The rotation has a serious effect on the coupling between the magnetic orbitals of Cu(1) and Cu(2) through the N–O$^-$ bond. The observed coupling $J = -148$ cm^{-1} in (**2**) is much smaller than that ($J = -260$ cm^{-1}) in (**1**).

In the binuclear copper(II) site of molluscan oxyhaemocyanin the geometry around each copper(II) is slightly different and may be a distorted square pyramid with $\mathrm{N_3OX}$ (N is an imidazole nitrogen and the bridging ligand X has not been identified).[3,4] It is concluded that in the active site of the native oxyhaemocyanin two basal planes around copper(II) ions are nearly coplanar and two magnetic orbitals strongly antiferromagnetically couple through the bridging ligands to give a diamagnetic behaviour.

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