The Structure of a Dinuclear Copper(I) Complex of a Schiff-base Ligand containing a Copper–Copper Bond†

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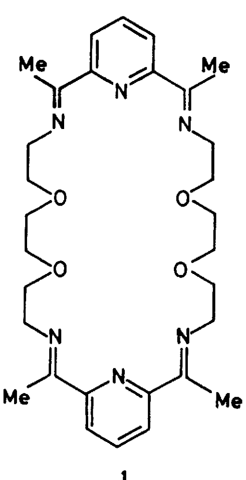
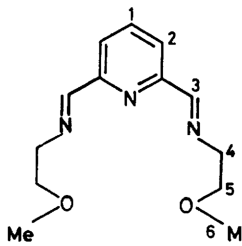
The copper(I) complex $[Cu_2L^2_2][ClO_4]_2 \cdot H_2O$ [L^2 = 2,6-di(2′-methoxyethyliminomethyl)pyridine] has been prepared by reaction of $[Cu(MeCN)_4][ClO_4]$ with the open-chain Schiff base 'N_3O_2' ligand L^2 derived from the condensation of one molecule of 2,6-diformylpyridine with two molecules of 1-amino-2-methoxyethane. Crystals of $[Cu_2L^2_2][ClO_4]_2 \cdot H_2O$ are monoclinic with a = 20.221(8), b = 16.239(7), c = 11.345(8) Å, β = 102.2(1)°, Z = 4, and space group $P2_1/n$. In the dimeric cation the two copper atoms are directly linked by a Cu–Cu bond of length 2.626(1) Å. In contrast to other metal complexes of pyridyldi-imine ligands the inequivalent copper atoms in the present structure are not bonded to all three nitrogen atoms of the same trimethine group and, moreover, all four imine groups are severely twisted out-of-plane with respect to their respective pyridine rings. Each copper atom is strongly bonded to two imino-nitrogen atoms, one from each ligand molecule. Cu(1) is also weakly bound to two ether oxygens, one from each ligand. The remaining two ether oxygen atoms are not co-ordinated. An unusual feature of the structure is that the pyridine nitrogen atoms appear to act as (asymmetric) bridges between the metal centres [Cu(1)–N, 2.693(6), 2.676(6) Å; Cu(2)–N, 2.237(6), 2.204(6) Å]. I.r. and ^1H n.m.r. spectra in CD_3CN of the free ligand and complex are compared. Evidence from electronic spectra suggests that the integrity of the dimeric unit is largely retained in solution.

We have recently described[1] the structures of some dicopper(II) complexes of the binucleating ligand L^1 (and related macrocycles[2]) containing two trimethine 'N_3' donor sets. While the planar (conjugated) trimethine group is well suited to co-ordination to Cu^{II} at three corners of an approximate square plane, the fourth position being occupied by other available monodentate or bridging ligand, it is less well adapted to co-ordination to Cu^I which, having a filled *d*-shell electron configuration prefers a non-orthogonal disposition of metal–ligand bonds.[3] The structure of the previously prepared[1] dicopper(I) complex $[Cu_2L^1][ClO_4]_2 \cdot H_2O$ was therefore of interest. Unfortunately, crystals of this complex suitable for *X*-ray analysis were not obtained. We report here the structure of the dimeric complex $[Cu_2L^2_2][ClO_4]_2 \cdot H_2O$ in which the ligand L^2 is the acyclic Schiff base equivalent to 'one-half' of the binucleating ligand L^1, but derived from 2,6-diformylpyridine rather than 2,6-diacetylpyridine.



L^1



L^2

Experimental

Preparation of the Ligand L^2 *and its Dicopper*(I) *Complex.*—The ligand L^2 was prepared by condensation of 2,6-diformylpyridine[4] (0.02 mol) with 1-amino-2-methoxyethane (Aldrich) (0.048 mol) in dry benzene (50 cm³) over molecular sieves at room temperature. After 3 d the solution was filtered and the benzene removed by rotary evaporation to yield a yellow oil in near quantitative yield. The product was characterised by mass spectra ($P^+ = m/e$ 249), i.r. and ^1H n.m.r. spectra, and chemical analysis. I.r. bands: 3 050, 2 970, 2 870, 1 632, 1 580, 1 560, 1 450, 1 120, and 680 cm⁻¹. ^1H N.m.r. data (CD_3CN): δ 3.30 (s, CH_3), δ ≃ 3.7 (m, methylene protons), δ ≃ 7.9 (m, pyridine protons), δ 8.34 (s, imine protons) in the relative intensity ratio of 6:8:3:2 (see Table 1) (Found: C, 61.2; H, 7.5; N, 16.4. Calc. for $C_{13}H_{19}N_3O_2$: C, 62.6; H, 7.7; N, 16.8%).

The complex $[Cu_2L^2_2][ClO_4]_2 \cdot H_2O$ (1) was prepared by reaction of L^2 (0.002 mol) with $[Cu(MeCN)_4][ClO_4]$ (0.002 mol) in ethanol (40 cm³) at room temperature under O_2-free conditions. The resulting dark red-brown solution was reduced in volume under a stream of N_2 until the product separated as dark brown microcrystals in *ca.* 55% yield. Recrystallisation from dry O_2-free methanol afforded large well-formed crystals suitable for *X*-ray analysis (Found: C, 37.4; H, 4.7; N, 10.2. Calc. for $[Cu_2L^2_2][ClO_4]_2 \cdot H_2O$: C, 37.1; H, 4.8; N, 10.0%).

Crystal Data for (1).—$C_{26}H_{40}Cl_2Cu_2N_6O_{13}$, M = 842.6, monoclinic, space group $P2_1/n$, a = 20.221(8), b = 16.239(7), c = 11.345(8) Å, β = 102.2(1)°, U = 3 640.8 Å³, D_m = 1.54 g

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† *Supplementary data available* (No. SUP 56250, 11 pp.): thermal parameters, hydrogen atom positions, dimensions for perchlorate anions. See Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1985, Issue 1, pp. xvii—xix. Structure factors are available from the editorial office.

Table 1. Hydrogen-1 n.m.r. data* (δ/p.p.m.) for the ligand L^2 and complex (**1**) in CD_3CN

Compound	H^1	H^2	H^3	H^4	H^5	H^6
L^2	7.89 (m)	7.95 (m)	8.34 (s)	3.76 (m)	3.65 (m)	3.30 (s)
$[Cu_2L^2{}_2][ClO_4]_2\cdot H_2O$	8.11 (m)	8.11 (m)	8.54 (s)	3.80 (t)	3.48 (t)	3.08 (s)

* The atom-numbering scheme is that indicated in the structure of L^2.

Table 2. Atomic co-ordinates ($\times 10^4$) for (**1**) with estimated standard deviations in parentheses. Population parameters (*P*) are given for the perchlorate and water oxygen atoms.

Atom	*x*	*y*	*z*	*P*
Cu(1)	3 577.1(4)	2 587.8(5)	1 676(1)	
Cu(2)	4 556.3(4)	2 562.0(5)	479(1)	
C(1A)	7 192(6)	2 002(8)	860(13)	
O(2A)	6 548(5)	2 269(6)	439(7)	
C(3A)	6 291(5)	2 825(6)	1 214(12)	
C(4A)	5 970(5)	2 437(6)	2 069(9)	
N(5A)	5 351(3)	2 036(4)	1 525(6)	
C(6A)	5 318(5)	1 268(5)	1 739(8)	
C(7A)	4 676(4)	856(5)	1 258(7)	
N(8A)	4 147(3)	1 311(3)	744(5)	
C(9A)	3 560(4)	957(5)	279(6)	
C(10A)	2 986(4)	1 492(5)	−192(7)	
N(11A)	2 948(3)	2 190(4)	265(5)	
C(12A)	2 367(5)	2 725(6)	−192(9)	
C(13A)	2 162(6)	3 210(9)	646(14)	
O(14A)	2 531(5)	3 441(7)	1 566(10)	
C(15A)	2 417(8)	4 029(9)	2 240(14)	
C(17A)	4 630(5)	−27(5)	1 270(10)	
C(18A)	4 036(6)	−380(6)	755(11)	
C(19A)	3 497(5)	88(5)	211(9)	
C(1B)	5 770(5)	2 601(7)	−3 029(11)	
O(2B)	5 148(3)	2 847(3)	−2 757(5)	
C(3B)	4 757(5)	2 210(4)	−2 425(7)	
C(4B)	4 111(4)	2 566(4)	−2 259(6)	
N(5B)	4 206(3)	3 029(3)	−1 146(4)	
C(6B)	4 033(4)	3 791(4)	−1 190(6)	
C(7B)	4 116(4)	4 255(4)	−73(7)	
N(8B)	4 286(3)	3 814(3)	964(5)	
C(9B)	4 392(4)	4 215(4)	2 003(7)	
C(10B)	4 460(4)	3 710(5)	3 116(7)	
N(11B)	4 165(3)	3 031(4)	3 079(5)	
C(12B)	4 235(6)	2 561(6)	4 204(7)	
C(13B)	3 625(7)	2 193(7)	4 292(8)	
O(14B)	3 347(5)	1 713(5)	3 283(7)	
C(15B)	2 698(6)	1 376(9)	3 176(11)	
C(17B)	4 093(6)	5 098(5)	−51(9)	
C(18B)	4 231(6)	5 511(6)	1 034(10)	
C(19B)	4 403(5)	5 074(5)	2 081(9)	
Cl(2)	3 144(1)	273(1)	6 663(2)	
O(21)	3 505(19)	−68(22)	5 795(37)	0.35
O(22)	2 708(13)	−380(16)	6 916(23)	0.35
O(23)	3 695(12)	466(14)	7 780(21)	0.35
O(24)	2 799(12)	936(16)	6 301(27)	0.35
O(31)	2 730(25)	392(23)	5 424(35)	0.35
O(32)	2 788(14)	963(15)	7 035(27)	0.35
O(33)	3 051(13)	−483(11)	7 170(21)	0.35
O(34)	3 706(17)	372(20)	6 260(33)	0.50
O(41)	3 847(18)	519(21)	7 277(42)	0.15
O(42)	3 225(19)	−583(20)	6 641(35)	0.15
O(43)	2 586(34)	487(43)	7 223(59)	0.15
O(44)	3 327(39)	234(42)	5 450(53)	0.15
O(51)	2 439(45)	302(48)	5 836(73)	0.15
O(52)	3 385(30)	−252(36)	7 700(49)	0.15
O(53)	3 173(35)	956(37)	7 470(53)	0.15
Cl(1)	1 285(1)	216(1)	9 462(2)	
O(61)	1 059(13)	524(15)	8 264(20)	0.40
O(62)	1 546(20)	747(21)	10 388(29)	0.40
O(63)	653(9)	−46(15)	9 664(20)	0.40
O(64)	1 757(12)	−416(15)	9 270(22)	0.40
O(71)	1 008(15)	915(16)	9 836(25)	0.30
O(72)	838(13)	−444(14)	9 211(20)	0.30
O(73)	1 554(14)	360(20)	8 391(22)	0.30
O(74)	1 930(11)	72(20)	10 190(26)	0.30
O(81)	1 311(14)	715(14)	8 572(19)	0.30
O(82)	1 829(13)	486(18)	10 539(20)	0.30
O(83)	740(11)	389(18)	10 111(21)	0.30
O(84)	1 351(19)	−658(13)	9 417(24)	0.30
O(200)	5 250(31)	858(31)	4 643(47)	0.50
O(300)	4 597(23)	128(36)	4 496(41)	0.50

cm^{-3}, $Z = 4$, $D_c = 1.54$, $F(000) = 1\,736$, Mo-K_α radiation, $\lambda = 0.7107$ Å, $\mu = 14.3\ cm^{-1}$.

A crystal (0.2 × 0.3 × 0.4 mm) prepared as described above was mounted on a Stoe STADI 2 diffractometer and data were collected *via* variable-width ω scan. Background counts were 20 s and the scan rate of 0.033° s^{-1} was applied to a width of (1.5 + sin μ/tan θ). 6 990 Independent data were measured with a $2\theta_{max.}$ of 50° of which 2 950 with $I > 2.5\sigma(I)$ were used in subsequent calculations. Absorption and extinction corrections were not applied. The positions of the copper atoms were determined from a Patterson function and Fourier methods were used to complete the structure determination. The structure was refined by full-matrix least-squares methods using SHELX 76.[5] The final *R* value was 0.055 ($R' = 0.061$). The weighting scheme was chosen to give equivalent values of $w\Delta^2$ over ranges of F_o and $(\sin\theta)/\lambda$; this was $w = 1/[\sigma^2(F) + 0.003\ F^2]$ with $\sigma(F)$ taken from counting statistics. The Cu, Cl, O, N, and C atoms were refined anisotropically. Hydrogen atoms bonded to carbon were placed in tetrahedral or trigonal positions. Their thermal parameters were allowed to refine but those on the same atom were constrained to be equivalent. The perchlorate ions were both disordered. For Cl(1) four rigid groups were refined with occupancies 0.35, 0.35, 0.15, and 0.15 and for Cl(2) three groups with occupancies 0.40, 0.30, and 0.30, respectively. In addition, there were two sites for the water molecules [O(200), O(300)] each with 0.5 occupancy.

Scattering factors were taken from International Tables.[6] Calculations were made using SHELX 76 on the CDC 7600 computer at the University of Manchester Computer Centre. Atomic co-ordinates are given in Table 2, interatomic distances and angles in Table 3, and least-squares planes in Table 4. In

Table 3. Molecular dimensions: distances (Å), angles (°)

Cu(1)–Cu(2)	2.626(1)	Cu(2)–N(5A)	1.979(6)
Cu(1)–N(11A)	1.933(5)	Cu(2)–N(8A)	2.237(6)
Cu(1)–N(11B)	1.914(5)	Cu(2)–N(5B)	1.980(5)
Cu(1)–O(14A)	2.510(11)	Cu(2)–N(8B)	2.204(6)
Cu(1)–O(14B)	2.432(8)		
Cu(1) ••• N(8A)	2.693(6)		
Cu(1) ••• N(8B)	2.676(6)		
Cu(2)–Cu(1)–N(11A)	90.19(19)	Cu(1)–Cu(2)–N(5A)	107.58(20)
Cu(2)–Cu(1)–N(11B)	91.89(20)	Cu(1)–Cu(2)–N(8A)	66.70(16)
N(11A)–Cu(1)–N(11B)	176.72(27)	N(5A)–Cu(2)–N(8A)	78.69(23)
N(11A)–Cu(1)–O(14A)	75.1(3)	Cu(1)–Cu(2)–N(5B)	108.42(17)
N(11A)–Cu(1)–O(14B)	103.1(3)	N(5A)–Cu(2)–N(5B)	143.91(26)
N(11B)–Cu(1)–O(14A)	101.7(3)	N(8A)–Cu(2)–N(5B)	113.80(20)
N(11B)–Cu(1)–O(14B)	77.3(3)	Cu(1)–Cu(2)–N(8B)	66.63(16)
O(14A)–Cu(1)–O(14B)	93.8(3)	N(5A)–Cu(2)–N(8B)	117.46(23)
Cu(2)–Cu(1)–O(14A)	134.64(26)	N(8A)–Cu(2)–N(8B)	133.30(23)
Cu(2)–Cu(1)–O(14B)	131.52(22)	N(5B)–Cu(2)–N(8B)	79.67(21)

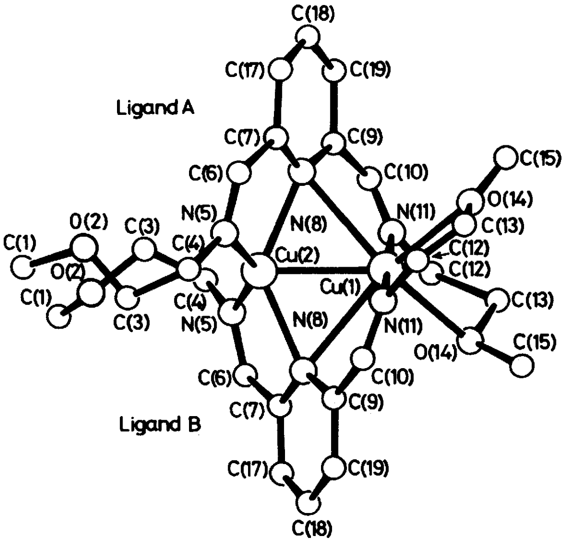


Figure. The structure of the dinuclear cation $[Cu_2L^2{}_2]^{2+}$ in (**1**)

the final cycle of refinement no shift was greater than 0.1σ. The final difference Fourier map showed no significant features. The structure is shown in the Figure.

Other Physical Measurements.—I.r. spectra were measured as KBr discs and/or paraffin mulls using a Perkin-Elmer 598 instrument. ^1H N.m.r. spectra were recorded using a Bruker WM250 instrument and u.v.–visible spectra using a Unicam SP700 spectrophotometer. Electrical conductances in MeCN solutions (10^{-3} mol dm^{-3}) at 25 °C were measured with a resistance/capacitance bridge between bright Pt electrodes in a cell of cell constant 0.037.

Results and Discussion

The asymmetric unit of the complex (**1**) contains discrete $[Cu_2L^2{}_2]^{2+}$ cations, two disordered perchlorate anions, and a disordered water molecule. The structure of the cation is shown in the Figure together with the atomic numbering scheme. The two copper atoms are directly linked by a Cu–Cu bond of length 2.626(1) Å but they have very different environments. The cation does, however, have approximate C_2 symmetry with the two-fold axis coincident with the Cu–Cu bond.

Table 4. Least-squares planes for (**1**) (distances from the planes are given in Å)

Plane 1: Pyridine ring A

N(5A)* −0.31, C(6A)* −0.09, C(7A) −0.00, N(8A) −0.02, C(9A) 0.03, C(17A) 0.01, C(18A) 0.01, C(19A) −0.03, C(12A)* 0.78, C(10A)* 0.11, N(11A)* 0.68, C(4A)* −0.29, Cu(1)* 1.62, Cu(2)* −0.64

Plane 2: Pyridine ring B

N(5B)* −0.41, C(6B)* −0.10, C(7B) 0.00, N(8B) −0.02, C(9B) 0.03, C(10B)* 0.23, N(11B)* 0.85, C(4B)* −0.49, C(17B) 0.00, C(18B) 0.00, C(19B) −0.02, C(12B)* 1.06, Cu(1)* 1.66, Cu(2)* −0.63

Plane 3: Cu(1) −0.07, Cu(2) −0.11, N(8A) 0.08, N(8B) 0.11

Plane 4: Cu(1), O(14A), O(14B) 0.00

Angles between planes (°): 1 and 2, 59.2; 3 and 4, 43.5

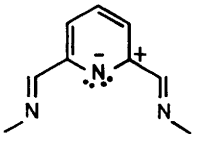
* Atoms not contributing to the plane.

The Cu(1) atom is strongly bound to one imino-nitrogen of each ligand molecule [Cu(1)–N(11A) 1.933(5), Cu(1)–N(11B) 1.914(5) Å], these being mutually *trans* [N(11A)–Cu(1)–N(11B) 176.7(3)°] and also perpendicular to the Cu(1)–Cu(2) bond [Cu–Cu–N 90.2(2), 91.9(2)]. In addition, Cu(1) is weakly bound to two ether oxygen atoms, one from each ligand molecule, at 2.510(11) Å for O(14A) and 2.432(8) Å for O(14B). There are also weak interactions with the pyridine nitrogen atoms N(8A) and N(8B) at 2.693(6) and 2.676(6) Å, respectively. If these atoms are included in the co-ordination sphere then the geometry around Cu(1) is that of a distorted, axially compressed, pentagonal bipyramid in which Cu(2), O(14A), O(14B), N(8A), and N(8B) make up the pentagonal girdle while N(11A) and N(11B) occupy the axial positions.

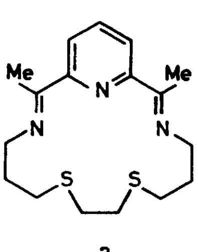
The geometry around Cu(2) is completely different. Cu(2) is strongly bonded to the remaining two imino-nitrogens N(5A) and N(5B) of the two ligand molecules at 1.979(6) and 1.980(5) Å, and also, less strongly, to the two pyridine nitrogen atoms N(8A) and N(8B) at 2.237(6) and 2.204(6) Å, as well as to Cu(1). The arrangement of the five donor atoms around Cu(2) is very irregular. The Cu–Cu bond intersects the N(8A)–Cu(2)–N(8B) angle of 133.3(2)° while the N(5A)–Cu(2)–N(5B) angle is 143.9(3)°. The two planes N(8A),N(8B),Cu(1),Cu(2) and N(5A),Cu(2),N(5B) intersect at an angle of 59.2°. The ether oxygen atoms O(2A) and O(2B) are not co-ordinated.

A most unusual feature of the structure is the apparent interaction of each of the two pyridine nitrogen atoms with two Cu^I atoms; in effect, the pyridine nitrogens are acting as bridging atoms between the metal centres. An associated feature not previously observed in other complexes containing the pyridyldi-imine chromophore is the non-planarity of the trimethine groups. All four C=N groups are twisted out of plane with their respective pyridine rings. The N(5) atoms are displaced from the pyridine ring plane by −0.31, −0.41 Å, while for N(11) the displacement is even greater at 0.68, 0.85 Å. The torsion angles N(8)–C(7)–C(6)–N(5) and N(8)–C(9)–C(10)–C(11) are −7.1° and −30.6° in ligand A and −9.0 and −28.9° in ligand B. The two different degrees of twist of the C=N groups out of plane with the pyridine ring are reflected in two distinct ν(C=N) stretching frequencies in the i.r. spectrum, *viz.* 1 645 and 1 625 cm^{-1}.

These structural abnormalities suggest the participation of Valence Bond structures such as (**I**) which allow for a bifunctional (bridging) role on the part of the pyridine nitrogen



(I)



L^3

together with some loss of conjugation with the imino-groups. A probable contributory reason for the unusual structure may be the unsuitability of the planar trimethine chromophore as a tridentate chelating group to Cu(1) which, having a filled *d* shell, is well known to favour a tetrahedral disposition of donor atoms.[3]

Even in the Cu^I complex of the macrocyclic 'N_3S_2' ligand L^3, where the cyclic array of donor atoms within a relatively small ring virtually forces trimethine group co-ordination upon the (single) Cu^I ion, there is considerable distortion as evidenced by one unusually long Cu–N(imino) bond at 2.519(25) Å.[7]

There are two positions for the water molecule both of which were refined with an occupancy of 0.5. They cannot coexist, as the O(200) ··· O(300) distance is 1.87 Å. Also, the O(300) ··· O(300) distance across the centre of symmetry at $(\frac{1}{2}, 0, \frac{1}{2})$ is 1.83 Å. There are several close contacts between the perchlorate anions and other anions or indeed cations. The shortest is O(53) ··· C(19A) $(x, y, 1 + z)$ 2.86 Å but we doubt whether this is significant because of the disorder in the perchlorate anions.

Solution Properties of Complex (**1**).—The electronic spectrum of the solid consists of a broad absorption between 33 000 and 15 000 cm^{-1} with features at 30 000, 28 600, and 21 600 cm^{-1}. In acetonitrile solution, in which the dimeric complex behaves as a uni-divalent electrolyte (Λ_m = 264 cm^2 mol^{-1} in 10^{-3} mol dm^{-3} solution) there is a colour change from dark brown to red and the electronic spectrum now consists of three well resolved bands at 31 300, 27 500, and 21 500 cm^{-1}. The highest energy band is also shown by the free ligand and is therefore assigned to a $\pi \longrightarrow \pi^*$ transition of the trimethine moiety of the ligand. The lower energy bands may be due to metal to ligand charge-transfer transitions and possibly also to a transition involving the Cu–Cu bond. It was also observed that the intensity of the lowest energy band is somewhat concentration dependent, becoming relatively less intense in dilute solution. This observation would be consistent with a concentration-dependent dimer $\rightleftharpoons$ monomer equilibrium involving dissociation of the metal–metal bond. The complex is stable to aerobic oxidation in acetonitrile solution but slowly oxidises in methanol as judged by the development of a greenish turbidity.

Hydrogen-1 n.m.r. data for the complex and the free ligand are in Table 1. There is a close correspondence in chemical shift and profile in the two spectra. The most significant differences are for the protons on the two carbon atoms flanking the ether oxygens, *viz.* the H^5 protons and H^6 protons have shifted upfield on co-ordination by 0.17 and 0.22 p.p.m. respectively. This would be consistent with at least partial ether group co-ordination in MeCN solution. Since a rapid exchange of co-ordinated and unco-ordinated ether groups would be expected only single time-averaged resonances are seen. Moreover, the n.m.r. data indicate that the Cu(1) and Cu(2) atoms are equivalent on the n.m.r. time-scale.

Conclusions

The structure of the complex cation $[Cu_2L^2{}_2]^{2+}$ differs from all previously determined structures[1,2] of complexes containing the trimethine pyridyldi-imine co-ordinating group in that each metal ion is bonded to only two of the three trimethine nitrogen atoms of each ligand molecule. The second imino-nitrogen is bonded to the second Cu^I atom so that each ligand molecule acts as a bridge between the two metal ions. In order to adapt to this unusual co-ordination mode the imine groups are twisted out-of-plane with the pyridine rings. In addition, each pyridine nitrogen atom appears to have a bifunctional co-ordinating role being bonded, albeit weakly and asymmetrically, to both Cu^I atoms.

As noted above the reason for the unusual structure of $[Cu_2L^2{}_2][ClO_4]_2 \cdot H_2O$ may be the reluctance of the d^{10} ion to accommodate to the planar tridentate pyridyldi-imine group. However, there is no evidence that trimethine group distortion is a general phenomenon in Cu^I complexes of this class. It does not occur in the Cu^I complex of macrocycle L^3 presumably because of the cyclic, less flexible nature of the ligand. For the same reasons it is considered unlikely to occur in the di-copper(I) complex of the binucleating macrocycle L^1. Indeed, the observation of a single ν(C=N) vibration in the i.r. spectrum of this complex[1] would argue for retention of trimethine group planarity in this case.

References

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Received 22*nd October* 1984; *Paper* 4/1799