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A Binuclear Copper(II) Complex of the Schiff Base Derived from 1,1′-(2,6-Pyridyl)-bis-1,3-butanedione and 3-Amino-1-propanol

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Abstract

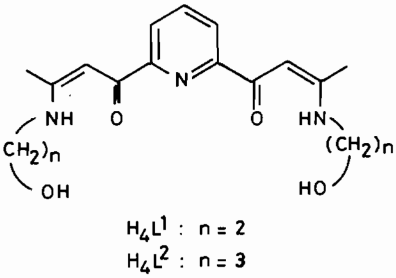
The reaction of $Cu(ClO_4)_2\cdot6H_2O$ with the Schiff base derived from 1,1′-(2,6-pyridyl)-bis-1,3-butanedione and 3-amino-1-propanol, (H_4L^2), yields the complex $Cu(H_4L^2)(ClO_4)_2\cdot H_2O$. The crystal structure of this complex is triclinic, $R = 0.0521$, 5602 reflections. The species is dimeric leading to a binuclear copper(II) complex in which the well-separated (8.93 Å intramolecular and 5.46 Å intermolecular) copper(II) atoms are in distorted square pyramidal geometries.

Introduction

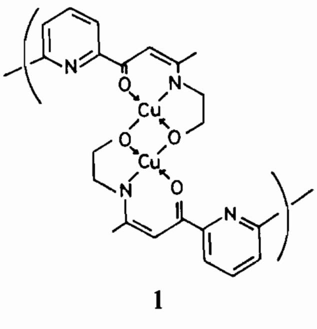
There has been recent interest in the metal complexation properties of various tetraketones and their Schiff bases [1–5] stimulated in part by their potential to form oligometallic arrays which could be utilised in electron transport processes. We report here the synthesis, crystal and molecular structure of a mononuclear copper(II) complex derived from 1,1′-(2,6-pyridyl)-bis-1,3-butanedione and 3-amino-1-propanol; this compound, which may be viewed as a precursor for oligometallic species, is found to be dimeric with well-separated copper(II) atoms.

Results and Discussion

The tetraketone, 1,1′-(2,6-pyridyl)-bis-1,3-butanedione reacts with amino-alcohols to yield the Schiff bases, (H_4L) [2]. These bases have been found to give metal complexes of the types M_2L, $M_2(H_2L)X_2$ and $M(H_4L)X_2$ depending on the nature of the metal salt used [2].



The reaction of $Cu(ClO_4)_2\cdot6H_2O$ with H_4L^1 in ethanol gave a green product, $Cu_2(H_2L^1)(ClO_4)_2\cdot EtOH$. The IR spectrum shows a band at 1620 cm^{-1}, assigned to C–O vibrations, bands at 1580 and 1550 cm^{-1} assigned to C–C + C–N vibrations and three bands centred on 1100 cm^{-1} indicative of the presence of coordinated perchlorate anions [6]. The structure of this complex is not established but it is proposed that the copper cations sit in the outer $N(O)_2$ donor sets. The magnetic moment, measured by the Gouy technique at ambient temperature, was found to be 1.18 BM per Cu atom and so it is likely that dimerisation, or oligomerisation, has occurred to give a μ-alkoxy bridged species in which there is an orbital pathway for spin exchange (**1**). This type of behaviour would parallel the known behaviour of related Schiff base complexes in which the ligands are derived from aminoalcohols and simple β-diketones [7].



1

The reaction of H_4L^2 with $Cu(ClO_4)_2\cdot6H_2O$ in ethanol gave a green product, $Cu(H_4L^2)(ClO_4)_2$. The IR spectrum was similar to that for the previous compound and the product had a normal magnetic moment. It was therefore possible to consider that the structure was monomeric and related to that proposed for the copper(II) complex of 2,6-diformylpyridine, (**2**) [8]. The copper(II) would then be coor-

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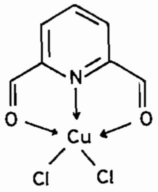
dinated by the central $N(O)_2$ donor set. Crystals of $Cu(H_4L^2)(ClO_4)_2$ were grown from ethanol and a structural determination showed that a dimeric species had been formed.



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The aquated molecular di-cation dimerises across an approximate inversion centre and the structure of the resulting binuclear tetra-cation is illustrated in Fig. 1 which also shows the positions of the four perchlorate anions and the atom labelling used in the corresponding Tables. Selected bond lengths and angles (together with estimated standard deviations) are compared in Table I; full Tables of bond lengths and angles and of details of planar fragments are deposited with the Editor-in-Chief.

The distances between pairs of copper atoms are long and show a closer intermolecular distance (5.46 Å) than intramolecular distance (8.93 Å). Each copper atom has a coordination polyhedron which is best described as distorted square-based pyramidal, in which the basal sites are occupied by the pyridyl nitrogen, two mutually *trans* ketonic oxygen atoms of the (H_4L^2) ligand and by a coordinated water molecule. The axial site is occupied, at a somewhat greater distance, by a terminal –OH group of the second molecular fragment. Each of the four outer keto-imino compartments of the binuclear dimer show bond conjugation, a hydrogen having been transferred from the γ-carbon atom to the imino-nitrogen atom which takes no part in the bonding to the copper atom, but forms an internal hydrogen bond to the ketonic oxygen atom. The four perchlorate anions are all hydrogen bonded, to varying degrees, to the binuclear dimeric cations and lead to polymerisation parallel to a C-face diagonal of the unit cell*. Two perchlorates involving atoms Cl(2) and Cl(3) are merely terminally hydrogen bonded to atoms O(6) and O(9), respectively: that associated with atom Cl(4) and its inversion symmetry related counterpart bridge between inversion related coordinated water molecules O(10) across the crystallographic centre of symmetry at (0, 0, 0.5). The final perchlorate involving atom Cl(1) internally bridges the hydroxyl and water oxygen atoms O(4) and O(5) and, in addition, along with its symmetry related equivalent, forms a bifurcated hydrogen bond to the inversion symmetry related water oxygen O(5) across the crystallographic centre of symmetry at (0.5, 0.5, 0.5). The molecular association across this latter inversion centre is reinforced by a further symmetry related pair of hydrogen bonded interactions involving the terminal hydroxyl group O(4) and the coordinated hydroxyl group O(1). The deviation of the space group from $C\bar{1}$ is most clearly demonstrated by the absence of these last hydrogen bonding interactions across the approximate inversion centre at (0.25, 0.25, 0.5), by the different conformations adopted by terminal hydroxyl groups O(4) and O(9) at the ends of their respective chains and by the very different torsion angles in the two pairs of 3-imino-1-propanol chains, and by the different positions of perchlorates Cl(2) and Cl(3) with respect to the coordinated hydroxyl groups O(1) and O(6).

Bond lengths and angles within the molecular skeleton are unexceptionable and are very similar for the two fragments. The atoms of each of the two pyridine-diketone fragments of the molecular back-

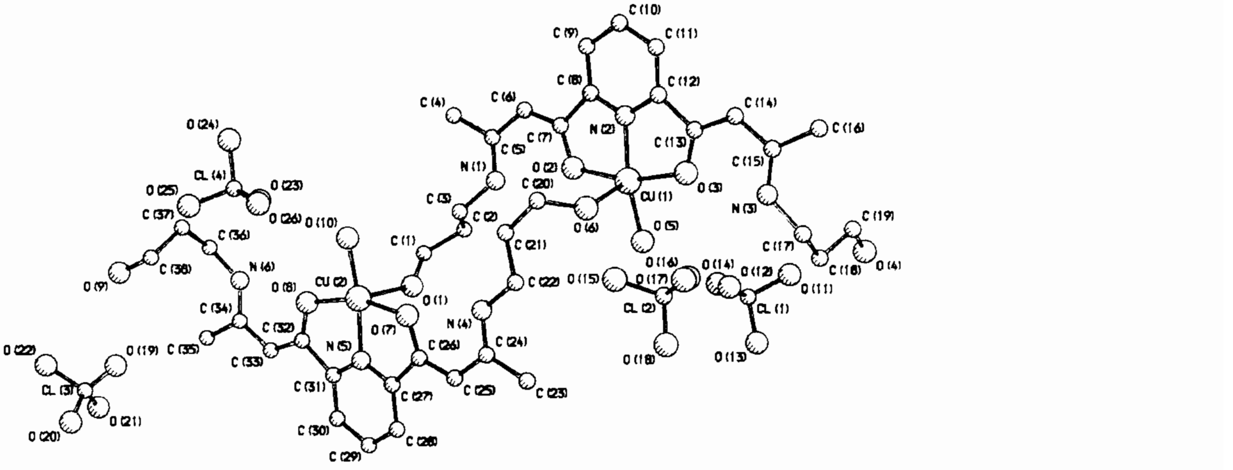

Fig. 1. The molecular structure of $[(H_4L^2)_2Cu_2(H_2O)_2](ClO_4)_4$ with atom labelling.

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*It should be noted that although the IR spectrum can be interpreted as indicating the presence of coordinated perchlorate – either as bidentate (C_{2v}), or as a mixture of monodentate (C_{3v}) and free (T_d), ClO_4^- – the structure shows no such interaction and the perchlorates are hydrogen bonded to the dimeric cations and lie in different environments.

TABLE I. Selected Bond Lengths (Å) and Bond Angles (°) with e.s.d.s for $[(H_4L^2)_2Cu_2(H_2O)_2](ClO_4)_4$

Cu(1)–O(2)	1.989(4)	Cu(2)–O(7)	2.017(5)
Cu(1)–O(3)	1.967(4)	Cu(2)–O(8)	1.983(4)
Cu(1)–O(5)	1.923(5)	Cu(2)–O(10)	1.911(5)
Cu(1)–O(6)	2.208(5)	Cu(2)–O(1)	2.254(6)
Cu(1)–N(2)	1.891(5)	Cu(2)–N(5)	1.901(5)
O(2)•••N(1)	2.672(7)	O(2)•••H(N1)	1.99
O(3)•••N(3)	2.647(7)	O(3)•••H(N3)	1.93
O(7)•••N(4)	2.700(8)	O(7)•••H(N4)	1.99
O(8)•••N(6)	2.711(7)	O(8)•••H(N6)	2.01
O(1)•••O(4)[a]	2.735(10)	O(4)•••H(O1)[a]	1.88
O(4)•••O(11)	2.811(12)	O(11)•••H(O4)	1.92
O(5)•••O(12)	2.802(9)	O(12)•••H(O5A)	1.86
O(5)•••O(13)[a]	2.959(9)	O(13)•••H(O5B)[a]	2.04
O(5)•••O(14)[a]	2.992(10)	O(14)•••H(O5B)[a]	2.15
O(6)•••O(15)	2.801(12)	O(15)•••H(O6)	1.82
O(9)•••O(19)	2.938(14)	O(19)•••H(O9)	2.00
O(10)•••O(23)	2.781(8)	O(23)•••H(O10A)	1.82
O(10)•••O(24)[b]	2.704(8)	O(24)•••H(O10B)[b]	1.71
O(2)–Cu(1)–O(3)	162.26(18)	O(7)–Cu(2)–O(8)	160.66(18)
O(2)–Cu(1)–O(5)	98.97(20)	O(7)–Cu(2)–O(10)	100.63(20)
O(2)–Cu(1)–O(6)	95.17(19)	O(7)–Cu(2)–O(1)	90.54(20)
O(2)–Cu(1)–N(2)	81.33(19)	O(7)–Cu(2)–N(5)	80.80(20)
O(3)–Cu(1)–O(5)	96.64(20)	O(8)–Cu(2)–O(10)	95.85(20)
O(3)–Cu(1)–O(6)	92.96(19)	O(8)–Cu(2)–O(1)	98.01(20)
O(3)–Cu(1)–N(2)	81.32(19)	O(8)–Cu(2)–N(5)	81.36(20)
O(5)–Cu(1)–O(6)	90.91(21)	O(10)–Cu(2)–O(1)	95.29(22)
O(5)–Cu(1)–N(2)	163.60(22)	O(10)–Cu(2)–N(5)	170.89(22)
O(6)–Cu(1)–N(2)	105.42(20)	O(1)–Cu(2)–N(5)	93.70(21)
Cu(2)–O(1)–C(1)	136.8(6)	Cu(1)–O(6)–C(20)	130.0(5)
Cu(1)–O(2)–C(7)	114.2(4)	Cu(2)–O(7)–C(26)	113.4(4)
Cu(1)–N(2)–C(8)	118.7(4)	Cu(2)–N(5)–C(27)	118.2(4)
Cu(1)–N(2)–C(12)	118.2(4)	Cu(2)–N(5)–C(31)	117.2(4)
Cu(1)–O(3)–C(13)	115.0(4)	Cu(2)–O(8)–C(32)	114.0(4)

[a] is $[1-x, 1-y, 1-z]$; [b] is $[-x, -y, 1-z]$.

bone are approximately coplanar; the adjacent keto-imine compartments are less perfectly planar and are not exactly coplanar with their adjacent chelate planes.

Experimental

Details of physical measurements have been given previously, as have the preparations of the tetraketone and the Schiff bases [2].

$Cu_2(H_2L^1)(ClO_4)_2 \cdot C_2H_5OH$

Copper(II) perchlorate (0.002 mol) in hot absolute ethanol (50 cm^3) was added to H_4L^1 (0.001 mol) in hot absolute ethanol (50 cm^3). The resulting solution was allowed to cool and the product precipitated out as a microcrystalline solid which was washed with cold ethanol and dried *in vacuo* over silica. *Anal.* Found: C, 32.4; H, 3.7; N, 6.1. Calc. for $C_{17}H_{21}N_3O_{12}Cu_3Cl_2$, C_2H_5OH: C, 32.4; H, 3.9; N, 6.0%. IR (KBr disc): 3400(bd), 1620(m), 1600(w), 1580(s), 1550(s), 1145(s), 1110(s), 1090(s), 800(m) cm^{-1}.

$Cu(H_4L^2)(ClO_4)_2$

This complex was prepared by following the above procedure using H_4L^2. The product was isolated as a green microcrystalline material and was dried *in vacuo* over silica. *Anal.* Found: C, 36.3; H, 4.9; N, 6.5. Calc. for $C_{19}H_{27}N_3O_{12}CuCl_2$: C, 36.6; H, 4.4; N, 6.7%. IR 3450(sh), 3380(bd), 1600(s), 1580(s), 1555(s), 1147(s), 1110(s), 1085(s), 785(m) cm^{-1}.

Crystal Data

$[(H_4L^2)Cu(H_2O)](ClO_4)_2$, $C_{19}H_{29}Cl_2CuN_3O_{13}$, $M = 641.89$, crystallises from ethanol as pale green plates; crystal dimensions 0.57 × 0.44 × 0.06 mm. Triclinic, $a = 15.536(8)$, $b = 19.587(9)$, $c = 9.841(6)$ Å, $\alpha = 105.97(4)$, $\beta = 106.32(5)$, $\gamma = 104.60(4)°$, $U = 2580.9(23)$ Å^3, $Z = 4$, $D_c = 1.577$ g cm^{-3}, space group $P\bar{1}$ (C_i, no. 2; assumed and confirmed by the analysis), Mo Kα radiation ($\bar{\lambda} = 0.71069$ Å), μ(Mo Kα) = 10.73 cm^{-1}, $F(000) = 1324$.

Three-dimensional X-ray diffraction data from a crystal mounted in an A-face-centred setting were collected in the range $6.5 < 2\theta < 50°$ on Stoe Stadi-2

TABLE II. Atomic Positional Parameters with e.s.d.s for $[(H_4L^2)_2Cu_2(H_2O)_2]^{4+}(ClO_4^-)_4$

	x/a	*y/b*	*z/c*
Cu(1)	0.20735(5)	0.37040(4)	0.16635(8)
Cu(2)	0.29810(5)	0.14402(4)	0.84082(8)
Cl(1)	0.53482(13)	0.59657(10)	0.36502(19)
Cl(2)	0.18222(15)	0.58785(10)	0.52644(21)
Cl(3)	0.30821(15)	−0.10616(12)	1.47955(21)
Cl(4)	−0.00511(12)	−0.07743(9)	0.65060(19)
O(1)	0.4025(4)	0.1586(3)	0.7224(6)
O(2)	0.2171(3)	0.2718(2)	0.1717(4)
O(3)	0.1739(3)	0.4481(2)	0.0945(4)
O(4)	0.4481(5)	0.7060(4)	0.1097(9)
O(5)	0.3271(4)	0.4379(3)	0.3293(5)
O(6)	0.1306(4)	0.3831(3)	0.3243(5)
O(7)	0.2857(3)	0.2446(2)	0.8451(5)
O(8)	0.3281(3)	0.0642(2)	0.9117(4)
O(9)	0.1947(6)	−0.2048(3)	1.0453(7)
O(10)	0.1900(3)	0.0758(2)	0.6602(5)
O(11)	0.5356(6)	0.6184(5)	0.2419(8)
O(12)	0.4428(4)	0.5833(3)	0.3720(8)
O(13)	0.6037(5)	0.6535(4)	0.5012(7)
O(14)	0.5577(6)	0.5299(4)	0.3453(9)
O(15)	0.1387(8)	0.5176(4)	0.5313(11)
O(16)	0.2347(6)	0.5779(4)	0.4303(8)
O(17)	0.1081(7)	0.6130(6)	0.4716(11)
O(18)	0.2397(6)	0.6373(6)	0.6698(8)
O(19)	0.2759(8)	−0.0907(7)	1.3571(9)
O(20)	0.2889(7)	−0.0639(4)	1.5976(8)
O(21)	0.4023(6)	−0.1003(7)	1.5206(11)
O(22)	0.2570(7)	−0.1840(4)	1.4443(13)
O(23)	0.0880(4)	−0.0662(3)	0.6474(7)
O(24)	−0.0734(4)	−0.1302(3)	0.5046(6)
O(25)	−0.0145(5)	−0.1088(4)	0.7607(7)
O(26)	−0.0228(4)	−0.0081(3)	0.6794(7)
N(1)	0.2522(4)	0.1682(3)	0.2859(6)
N(2)	0.1118(3)	0.3055(2)	−0.0272(5)
N(3)	0.1719(4)	0.5828(3)	0.0946(6)
N(4)	0.2439(4)	0.3536(3)	0.7511(6)
N(5)	0.3929(3)	0.2078(3)	1.0374(5)
N(6)	0.3294(4)	−0.0735(3)	0.9146(6)
C(1)	0.4083(7)	0.1195(5)	0.5900(9)
C(2)	0.3843(6)	0.1486(5)	0.4627(9)
C(3)	0.2865(6)	0.1529(5)	0.4264(8)
C(4)	0.1732(5)	0.0349(4)	0.1157(9)
C(5)	0.1954(5)	0.1184(3)	0.1495(7)
C(6)	0.1499(5)	0.1400(3)	0.0332(7)
C(7)	0.1570(4)	0.2132(3)	0.0519(6)
C(8)	0.0925(4)	0.2306(3)	−0.0699(6)
C(9)	0.0209(5)	0.1819(3)	−0.2082(7)
C(10)	−0.0286(4)	0.2126(3)	−0.2990(7)
C(11)	−0.0078(5)	0.2906(3)	−0.2531(7)
C(12)	0.0649(4)	0.3368(3)	−0.1138(6)
C(13)	0.1049(4)	0.4217(3)	−0.0381(6)
C(14)	0.0716(4)	0.4660(3)	−0.1092(7)
C(15)	0.1084(4)	0.5468(3)	−0.0434(7)
C(16)	0.0723(5)	0.5886(4)	−0.1395(8)
C(17)	0.2182(5)	0.6659(3)	0.1793(8)
C(18)	0.3252(5)	0.6910(4)	0.2131(9)
C(19)	0.3483(5)	0.6861(4)	0.0741(10)
C(20)	0.0748(5)	0.3273(4)	0.3621(8)
C(21)	0.1373(6)	0.3088(4)	0.4852(8)
C(22)	0.1913(5)	0.3758(4)	0.6319(8)
C(23)	0.3321(5)	0.4852(4)	0.9197(9)
C(24)	0.3092(5)	0.4015(4)	0.8831(8)
C(25)	0.3587(5)	0.3766(3)	0.9898(7)
C(26)	0.3486(4)	0.3019(3)	0.9657(7)
C(27)	0.4131(4)	0.2824(3)	1.0804(7)
C(28)	0.4880(5)	0.3298(3)	1.2169(7)
C(29)	0.5393(5)	0.2977(4)	1.3029(7)
C(30)	0.5160(4)	0.2199(4)	1.2557(7)
C(31)	0.4390(4)	0.1750(3)	1.1178(6)
C(32)	0.3974(4)	0.0903(3)	1.0415(6)
C(33)	0.4329(5)	0.0455(3)	1.1105(7)
C(34)	0.3965(5)	−0.0346(4)	1.0508(7)
C(35)	0.4374(5)	−0.0735(4)	1.1480(9)
C(36)	0.2840(6)	−0.1567(4)	0.8386(8)
C(37)	0.1783(5)	−0.1829(4)	0.8138(8)
C(38)	0.1589(6)	−0.1656(4)	0.9573(9)

diffractometer by the omega-scan method; the data showed a pronounced weakness for $(k, l = 2n + 1)$. The 5602 independent reflections for which $I/\sigma(I) > 3.0$ were reindexed to the primitive cell above and were corrected for Lorentz and polarisation effects and for absorption. The data with $(h + k = 2n + 1)$ now showed the pronounced systematic weakness which leads to the presence in the lattice of additional approximate symmetry elements of a C-face-centre and a set of inversion centres at (0.25, 0,25, 0) etc. Considerable care was exercised in order to consistently break the approximate symmetry and to determine the correct, slightly different, conformations of each independent molecular fragment. The structure was eventually solved by Patterson and Fourier techniques and refined by block-diagonal least-squares methods. Hydrogen atoms were placed in calculated positions (C–H 0.96, O–H 1.02, N–H 0.93 Å, C–C–H(methyl) 111°); their contributions were included in structure factor calculations (B = 6.0 Å^2) but no refinement of positional parameters was permitted. Refinement converged at $R = 0.0521$ with allowance for anisotropic thermal motion of all non-hydrogen atoms and for the anomalous scattering of copper and chlorine. Table II lists the atomic positional parameters with estimated standard deviations. Tables of anisotropic thermal vibrational parameters with estimated standard deviations and of predicted hydrogen atom positional parameters and tables of observed structure amplitudes and calculated structure factors are available from the authors. Scattering factors were taken from reference 9; unit weights were used throughout the refinement; computer programs formed part of the Sheffield X-ray system.

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