Crystallographic Identification of a 'Stepped-cubane' Structure for the Cu_4O_4 Core in $[Cu_4L_2(bipy)_4(\mu_3\text{-}OH)_2][ClO_4]_4$ (HL = 5-hydroxy-6-methylpyridine-3,4-dimethanol, bipy = 2,2'-bipyridine)[†]

Irimpan I. Mathews and Hattikudur Manohar *
Department of Inorganic and Physical Chemistry, Indian Institute of Science, Bangalore-560 012, India

The structure of $[Cu_4L_2(bipy)_4(\mu_3\text{-}OH)_2][ClO_4]_4$ containing a Vitamin B_6 ligand, pyridoxine (5-hydroxy-6-methylpyridine-3,4-dimethanol, HL), and 2,2'-bipyridine (bipy) has been determined by single-crystal X-ray analysis. This is the first report on a copper(II) complex having a 'stepped-cubane' structure. The compound crystallizes in the triclinic space group $P\bar{1}$ ($Z = 1$) with $a = 11.015(3)$, $b = 11.902(1)$, $c = 13.142(2)$ Å, $\alpha = 105.07(1)$, $\beta = 102.22(1)$ and $\gamma = 99.12(1)°$; $R = 0.050$ ($R' = 0.054$). The co-ordination geometry around each copper is trigonally distorted square pyramidal. Two of the basal sites are occupied by bipyridyl nitrogens in a bidentate fashion. The remaining basal positions for Cu(1) are filled by a phenolic oxygen and a 4-hydroxymethyl oxygen of the L moiety, whereas for Cu(2) they are occupied by two μ_3-OH oxygens. The axial sites are occupied by a μ_3-OH oxygen and the 4-hydroxymethyl oxygen of the same pyridoxine for Cu(1) and Cu(2), respectively. Both the bridging nature of the 4-hydroxymethyl oxygen of the L moiety and the unsymmetrical bridging nature of the μ_3-OH groups with axial–equatorial bridging are novel features. The structure is discussed in relation to stepped-cubane structures reported in the literature. A comparative study is also made with μ_3-hydroxo-bridged copper(II) complexes. Both the plasticity effect of Cu^{II} and the stacking interactions between the various rings appear to be important in stabilizing this unusual structure.

The structures of copper(II) complexes display a richness in shapes.[1] This is due to the great number of co-ordination geometries observed, related to the possibility of distortion of the co-ordination polyhedra around Cu^{II}.[2] The distortion isomers occur as a consequence of the 'plasticity' of the co-ordination sphere combined with the stabilization properties of the crystal lattice.[2] The plasticity effects have been shown to be due to Jahn–Teller or pseudo-Jahn–Teller effects.[2,3]

The structures of copper(II) compounds have been studied extensively, several hundreds having been solved by single-crystal X-ray analysis.[1] A literature survey shows that even though the variety in shapes of copper(II) complexes is large compared to those of Cu^{I}, this trend shows a decrease with increase in nuclearity.[1] For example, for tetranuclear complexes there are seven types for Cu^{I}, whereas only four types have been structurally identified for Cu^{II}.[4] There are two types of pentanuclear complexes of Cu^{I}, none of Cu^{II}. In the tetranuclear copper(II) complexes with cubane-type stereochemistry both closed [5] and open [6] structures have been characterized by single-crystal X-ray studies.

In this paper we report, for the first time, the crystal structure of a novel tetranuclear copper(II) complex $[Cu_4L_2(bipy)_4(\mu_3\text{-}OH)_2][ClO_4]_4$ having a stepped-cubane structure. The 2,2'-bipyridine (bipy) ligands used in this study are well known for their stabilization properties in copper(II) complexes,[7] which is attributed to π backbonding from the metal ion to the aromatic amine.[8] Furthermore, the relatively rigid nature of this ligand imparts severe steric effects, resulting in unusual geometries for the metal ions,[9] as evidenced in the present study. The biologically important Vitamin B_6 moiety, pyridoxine (5-hydroxy-6-methylpyridine-3,4-dimethanol, HL), acts as the ternary ligand.

Experimental

Preparation of the Complex.—The complex was prepared by mixing $Cu(NO_3)_2{\cdot}3H_2O$, H_2L and bipy in 2:1:2 molar ratio in aqueous ethanolic solution. The pH was adjusted to 5.4 using 0.1 mol dm^{-3} NaOH. Very slow evaporation yielded dark green crystals suitable for X-ray diffraction in ≈6 weeks. Yield: ≈ 0.018 g, 11%.

Physical Measurements.—The electronic spectrum of the compound was recorded with a Hitachi model U-3400 spectrophotometer in aqueous ethanolic solution, the ESR spectrum on a Varian E109 spectrometer and the infrared spectrum on a Perkin-Elmer spectrometer.

X-Ray Intensity Data Collection, Solution and Refinement.—Details regarding the data collection and processing are presented in Table 1. The data were corrected for Lorentz and polarization effects but not for absorption. The structure was solved by conventional heavy-atom and Fourier techniques and refined by full-matrix least-squares treatment. All hydrogen atoms were located from difference electron-density maps and their positions and isotropic thermal parameters refined in the last few cycles. The perchlorate groups showed disorder about one of the Cl–O bonds. The disordered oxygens were refined with partial occupancy. The shifts in parameters in the last cycle were less than 0.1σ. The final difference electron-density map revealed no significant electron density, except for 0.55 e Å^{-3} near the disordered perchlorate.

Major calculations were performed on a DEC 1090 computer using the SHELX 76 system of programs [10] for Fourier and least-squares calculations and ORTEP II [11] and PLUTO 78 [12] programs for diagrams. The scattering factors for H, C, N, O

[†] Di-μ_3-hydroxo-1:2:3κ^3O;2:3:4κ^3O'-bis[μ-5-hydroxy-6-methylpyridine 3,4-dimethanolato(1−)]-1κO^5,1:2κ^2O^4;3:4$\kappa^2O^{4'}$,4$\kappa O^{5'}$-tetrakis-[(2,2'*bipyridine*-κ^2N,N')copper(II)] tetraperchlorate.

Supplementary data available: see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1991, Issue 1, pp. xviii–xxii.

and Cl atoms were used as available in the SHELX programs, and for Cu they were taken from ref. 13 (anomalous dispersion corrections applied). The final atomic coordinates are given in Table 2.

Table 1 Summary of crystallographic data for $[Cu_4L_2(bipy)_4(\mu_3\text{-}OH)_2][ClO_4]_4$

Formula	$C_{56}H_{52}Cl_4Cu_4N_{10}O_{24}$
M	1643.96
Crystal colour	Dark green
Crystal size (mm)	0.28 × 0.20 × 0.10
Crystal system	Triclinic
Space group	$P\bar{1}$
a/Å	11.015(3)
b/Å	11.902(1)
c/Å	13.142(2)
α/°	105.07(1)
β/°	102.22(1)
γ/°	99.12(1)
U/Å^3	1584
Z	1
F(000)	834
D_c/g cm^{-3}	1.723
D_m/g cm$^{-3\,a}$	1.73
μ/cm^{-1}	15.83
Diffractometer	CAD4
Radiation	Graphite-monochromated Mo-Kα (λ 0.7107 Å)
T/°C	21
Reflections measured	$0 < h < 14, -15 < k < 15, -17 < l < 17$
Scan type	ω–2θ
θ range/°	1.0–28.0
No. of reflections measured	5529
No. of observed unique reflections	4772 [$I > 2\sigma(I)$]
Weighting scheme (w)	$[\sigma^2(F_o) + 0.000\,000F_o^2]^{-1}$
Number of variables	543
R^b	0.050
R'^c	0.054

^{a} By flotation in $CHCl_3 + CHBr_3$. ^{b} $\Sigma|F_o - |F_c||/\Sigma F_o$. ^{c} $[\Sigma w(F_o - |F_c|)^2/\Sigma F_o^2]^{\frac{1}{2}}$.

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

Results and Discussion

The molecular structure with atom-labelling scheme is shown in Fig. 1. Selected bond distances and angles are presented in Table 3.

The crystal consists of discrete molecular units of $[Cu_4L_2(bipy)_4(\mu_3\text{-}OH)_2]^{4+}$ with a centre of symmetry and ClO_4^- ions. The co-ordination geometry around the coppers is distorted square pyramidal. The co-ordination sites of Cu(1) are occupied by two bipy nitrogens, a phenolic oxygen and a 4-hydroxymethyl oxygen of pyridoxine in the basal plane and a hydroxide ion in the axial position. On the other hand, for Cu(2) the basal sites are filled by two bipy nitrogens and two hydroxide ions and the axial position is occupied by the 4-hydroxymethyl oxygen of the same L moiety co-ordinated to Cu(1).

Pyridoxine normally acts as a bidentate ligand in the zwitterionic form with the phenolic oxygen and 4-hydroxymethyl oxygen as co-ordinating sites.[14–16] In the complex $[Cu(HL)L]NO_3{\cdot}2.5H_2O$[15] the monoanionic L is tridentate, the third site being pyridine nitrogen which is co-ordinated to a metal of a neighbouring molecule. A new anionic form of pyridoxine has been structurally characterized in the cobalt(II) complex $[CoL(bipy)]ClO_4$,[16] where the 4-hydroxymethyl group is deprotonated. These studies show that various forms of pyridoxine can be stabilized by varying the experimental conditions and in favourable cases it can even change its denticity. The present study, where L functions as a monoanion akin to that reported in the cobalt complex, reveals that it can use its deprotonated 4-hydroxymethyl group to bridge two metal centres.

The monoatomic bridging nature observed here is unusual in the Vitamin B_6 family of compounds. There are only three complexes reported in the literature[14,17] where phenolic

Table 2 Fractional atomic coordinates (× 10^5 for Cu, × 10^4 for the rest) with estimated standard deviations (e.s.d.s) in parentheses

Atom	x	y	z	Atom	x	y	z
Cu(1)	21 120(5)	41 491(5)	92 977(4)	N(4)	5 607(4)	2 339(3)	9 365(3)
N(1)	1 389(3)	5 597(3)	9 482(3)	C(19)	5 953(6)	2 036(4)	10 278(4)
C(1)	966(5)	6 042(4)	8 664(4)	C(20)	6 405(6)	1 020(5)	10 301(6)
C(2)	516(5)	7 088(5)	8 840(5)	C(21)	6 473(6)	265(5)	9 339(6)
C(3)	490(5)	7 652(4)	9 890(5)	C(22)	6 122(6)	553(5)	8 386(6)
C(4)	926(5)	7 185(5)	10 718(5)	C(23)	5 701(4)	1 617(4)	8 416(4)
C(5)	1 383(4)	6 169(4)	10 506(4)	C(24)	5 311(5)	2 034(4)	7 461(4)
C(6)	1 895(4)	5 604(4)	11 321(4)	C(25)	5 396(7)	1 435(5)	6 429(5)
C(7)	1 894(5)	5 983(5)	12 421(4)	C(26)	4 986(8)	1 880(6)	5 582(5)
C(8)	2 384(6)	5 360(6)	13 099(4)	C(27)	4 476(7)	2 879(6)	5 778(4)
C(9)	2 854(6)	4 372(6)	12 685(4)	C(28)	4 430(5)	3 444(4)	6 832(4)
C(10)	2 826(5)	4 031(5)	11 592(4)	N(5)	4 844(3)	3 019(3)	7 659(3)
N(2)	2 351(4)	4 633(3)	10 920(3)	Cl(1)	6 404(2)	3 503(1)	13 455(1)
N(3)	1 122(4)	1 653(3)	5 217(3)	Cl(2)	8 676(2)	−846(1)	7 530(1)
C(11)	1 003(5)	2 602(4)	5 975(3)	O(6)^a	6 693(6)	4 102(5)	12 699(5)
C(12)	1 371(4)	2 643(4)	7 075(3)	O(6′)^b	5 631(7)	3 652(6)	12 458(5)
C(13)	1 874(4)	1 699(4)	7 339(3)	O(7)^c	7 531(6)	3 403(5)	14 195(20)
C(14)	1 940(5)	732(4)	6 503(4)	O(7′)^d	7 526(21)	3 190(18)	13 128(18)
C(15)	1 573(5)	743(5)	5 438(4)	O(8)^a	5 816(8)	4 214(7)	14 189(6)
C(16)	496(6)	3 562(5)	5 617(4)	O(8′)^b	6 612(20)	4 638(17)	14 356(15)
C(17)	2 248(5)	1 746(4)	8 542(3)	O(9)	5 613(7)	2 398(6)	13 031(6)
C(18)	2 406(6)	−321(4)	6 712(4)	O(10)	9 429(5)	−1 539(5)	6 994(3)
O(1)	1 216(3)	3 564(3)	7 792(2)	O(11)^c	8 846(8)	282(6)	7 344(6)
O(2)	2 964(3)	2 879(2)	9 248(2)	O(11′)^b	8 150(22)	−31(19)	7 002(17)
O(3)	2 456(7)	−1 105(4)	5 712(4)	O(12)^e	9 238(18)	−451(9)	8 643(9)
Cu(2)	48 657(5)	37 391(4)	92 602(4)	O(12′)^f	8 526(20)	−1 079(14)	8 456(13)
O(4)	4 231(3)	5 171(2)	9 247(2)	O(13)	7 432(7)	−1 435(6)	7 020(8)

Fractional occupancies for the disordered perchlorate oxygens: ^{a} 0.7, ^{b} 0.3, ^{c} 0.8, ^{d} 0.2, ^{e} 0.6, ^{f} 0.4.

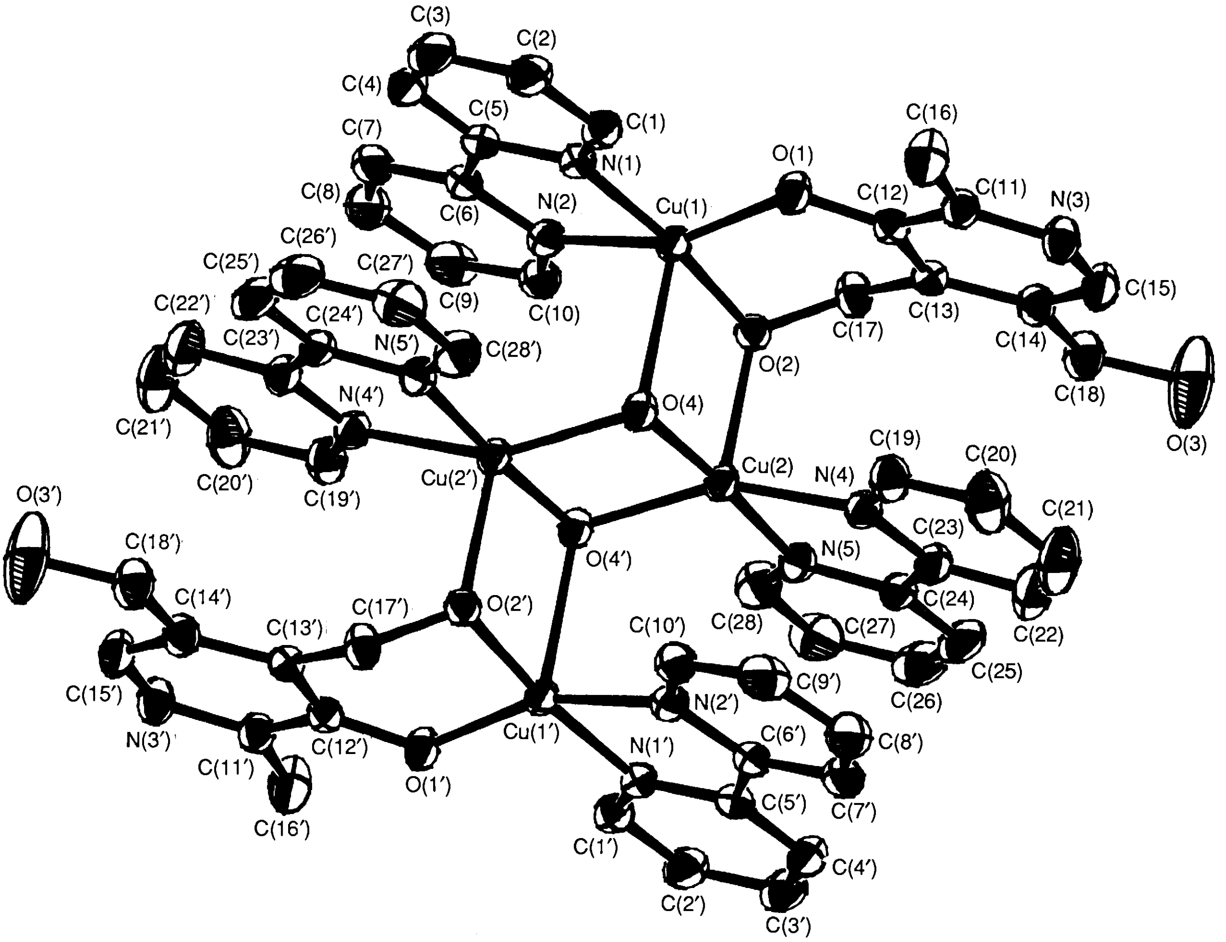

Fig. 1 Molecular structure of the complex with atom labelling scheme, showing 30% probability ellipsoids. Atoms with primed labels are related to the unprimed ones by the crystallographic centre of symmetry

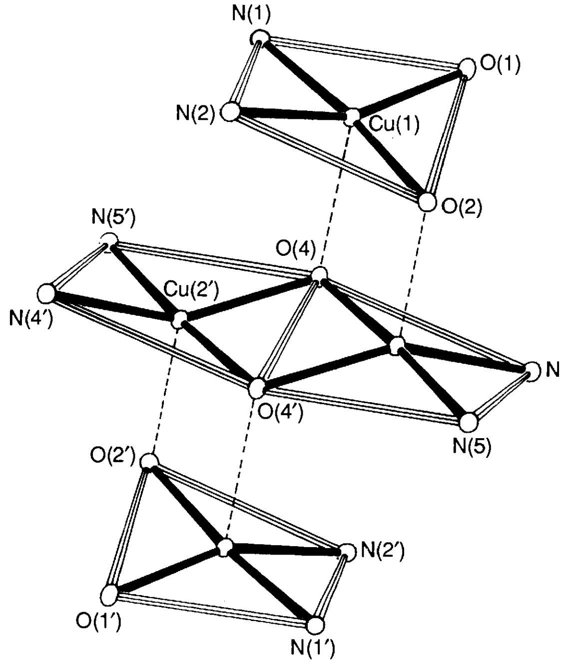

Fig. 2 Co-ordination of copper in the structure showing the strain

oxygen is used in bridging two metals. In all other complexes where a Vitamin B_6 moiety acts as a bridge it always binds in the bidentate form to the first metal through phenolic oxygen and the group at the 4 position, while different groups, namely 5-hydroxymethyl,[18] phosphate in the 5 position,[19] and pyridine nitrogen,[20] are used in binding to the second metal.

In the present compound the Cu_4O_4 core has a 'step' structure (Fig. 2). The coppers are bridged by two bidentate 4-hydroxymethyl oxygens, O(2) amd O(2′) of L and two tridentate μ_3-hydroxide groups, O(4) and O(4′). The 'step structure' is defined by three four-membered rings: the strictly planar Cu(2)–O(4)–Cu(2′)–O(4′) and the non-planar Cu(1)–O(2)–Cu(2)–O(4) and Cu(1′)–O(2′)–Cu(2′)–O(4′). The last two are related by the crystallographic centre of symmetry located at the centroid of the former Cu_2O_2 ring. The dihedral angle between the central ring and the outer ring is 70.6°. This angle shows a systematic decrease with decrease in size of the bridging atom. In the case of the copper(I) complexes $[\{CuX(PPh_3)\}_4]$ its value is 115.06 and 107.8° for the iodo[21] and bromo[22] derivatives, respectively. This decrease has been attributed to steric factors.[21] The trend is seen to be maintained even with a change in metal oxidation state and co-ordinating groups.

Since this is the first structural report on a copper(II) complex with a stepped cubane-like (chair-like) structure a comparison with similar structures is worthwhile. A striking difference between this structure and those reported earlier[21,22] is the similarity in co-ordination number exhibited by all the four copper centres in the present case. Variable co-ordination numbers of the core atoms in stepped cubane-like structures have been considered as the most important feature of these types of structures.[23] A careful examination of the copper polyhedra in the present complex shows that, while all four are five-co-ordinated, the Cu(2) and Cu(2′) centres show more trigonal distortion. The trigonal distortion of the square-pyramidal stereochemistry, τ,[24] for Cu(1) and Cu(2) is 26.7 and 44.0%, respectively. The deviations of the copper atoms from the basal plane are 0.1212(6) Å for Cu(1) and 0.2854(6) Å for Cu(2). These types of distortions are well explained by the plasticity effect of

Table 3 Selected bond distances (Å) and angles (°) with e.s.d.s in parentheses

Cu(1)–*N(1)*	1.990(4)	Cu(2)–N(4)	1.992(4)
Cu(1)–N(2)	2.006(4)	Cu(2)–N(5)	2.049(4)
Cu(1)–O(1)	1.901(3)	Cu(2)–O(2)	2.176(3)
Cu(1)–O(2)	1.896(3)	Cu(2)–O(4)	1.945(3)
Cu(1)–O(4)	2.478(3)	Cu(2)–O(4′)	1.991(3)
C(12)–O(1)	1.307(5)	C(17)–O(2)	1.416(5)
O(4)–H(O4)	0.66(3)	C(18)–O(3)	1.418(7)
N(1)–Cu(1)–N(2)	80.6(2)	O(2)–Cu(2)–N(4)	94.4(1)
N(1)–Cu(1)–O(1)	91.0(1)	O(2)–Cu(2)–N(5)	100.7(1)
N(1)–Cu(1)–O(2)	173.5(1)	O(4)–Cu(2)–N(4)	176.1(1)
N(1)–Cu(1)–O(4)	95.1(1)	O(4)–Cu(2)–N(5)	102.7(1)
N(2)–Cu(1)–O(1)	157.5(2)	N(4)–Cu(2)–N(5)	80.0(2)
N(2)–Cu(1)–O(2)	95.4(1)	O(4)–Cu(2)–O(4′)	78.5(1)
N(2)–Cu(1)–O(4)	99.3(1)	O(2)–Cu(2)–O(4)	87.8(1)
O(1)–Cu(1)–O(2)	94.6(1)	O(2)–Cu(2)–O(4′)	109.5(1)
O(1)–Cu(1)–O(4)	102.2(1)	Cu(1)–O(1)–C(12)	125.6(3)
O(2)–Cu(1)–O(4)	80.5(1)	Cu(1)–O(2)–C(17)	115.5(3)
Cu(1)–N(1)–C(1)	124.2(3)	Cu(1)–O(2)–Cu(2)	101.4(1)
Cu(1)–N(1)–C(5)	116.1(3)	Cu(1)–O(4)–Cu(2′)	108.2(1)
Cu(1)–O(4)–Cu(2)	90.2(1)	Cu(2)–O(4)–Cu(2′)	101.7(1)
Cu(2)–N(4)–C(19)	125.2(4)	Cu(2)–O(2)–C(17)	125.8(3)
Cu(2)–N(4)–C(23)	116.1(3)	Cu(2)–N(5)–C(24)	114.4(3)
C(19)–N(4)–C(23)	118.5(4)	Cu(2)–N(5)–C(28)	126.5(3)
Cu(1)–N(2)–C(6)	114.5(3)	C(24)–N(5)–C(28)	119.2(4)
Cu(1)–N(2)–C(10)	125.5(3)	C(11)–N(3)–C(15)	124.4(4)
C(6)–N(2)–C(10)	119.8(4)	C(11)–C(12)–O(1)	116.7(4)
C(12)–C(13)–C(17)	118.2(4)	C(13)–C(12)–O(1)	124.4(4)
C(14)–C(18)–O(3)	109.3(5)	C(13)–C(17)–O(2)	113.5(4)
H(O4)–O(4)–Cu(1)	109(3)	H(O4)–O(4)–Cu(2)	122(3)
H(O4)–O(4)–Cu(2′)	120(3)		

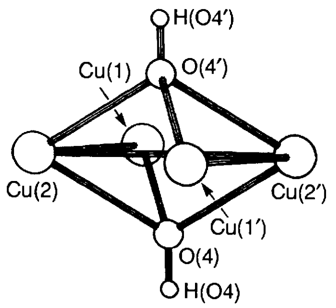

Fig. 3 The stereochemistry of the $Cu_4(OH)_2$ group

the copper(II) ion. The strain in the copper polyhedra is clearly seen in Fig. 2 which shows the stereochemistry of the coppers with all co-ordinating atoms. Thus the present study shows that a stepped cubane-like structure can very well be formed by metals with the same co-ordination numbers, provided that the co-ordination polyhedra of the metal ions are amenable to distortion.

The ten edges of the Cu_4O_4 'step' are each defined by a Cu–O bond. The bond lengths, 1.945(3)–2.478(3) Å, show considerable variation, the axial ones being longer as expected. The 'through-space' contacts involving coppers Cu(1) ··· Cu(2′) and Cu(1′) ··· Cu(2) are 3.632(1) Å, whereas the contacts involving oxygen atoms O(2) ··· O(4′) and O(2′) ··· O(4) are 3.405(3) Å. This shows that there is no close interaction between these atoms. Therefore, the reason for this compound adopting a stepped cubane structure could be the effect of other ligands in the system. A cubane-like structure would bring the copper atoms closer together, resulting in steric crowding in the molecule.

Within each of the three Cu–O–Cu–O rings individual bond angles at copper and the bridging atoms vary significantly from 90°, the value expected for an ideal cubane-like structure. The angles at copper in these rings vary from 78.5(1) to 87.8(1)° (<90), whereas those at the bridging oxygen atoms are in the range 90.1(1)–101.5(1)° (>90) (Table 3). On the other hand, in other stepped-cubane structures reported earlier[11,24] the angles at the metal atom, namely Cu^I and Ag^I, are greater than 90° ($\approx 100°$), whereas angles at bridging halide atoms are less than 90° ($\approx 80°$). The non-stereospecific nature of the rather large spherical halide ion seems to be an important factor for this difference at the bridging atom. However, the plasticity effect of the copper(II) ion assumes significance in the present structure. The external angles between the various four-membered rings are not so dependent upon the nature of the central atom (Table 3).

Another interesting feature of this structure is the function of the hydroxide ion as a novel unsymmetrically bridging tridentate anion, where all three of its lone pairs are used for co-ordination. It is interesting that of the three Cu–OH bonds two occupy equatorial positions for Cu(2) while the third is axial for Cu(1). The structure of the $Cu_4(OH)_2$ fragment is shown in Fig. 3. The two hydroxide ions appear to play a crucial role in bringing the four coppers together. Some relevant geometrical parameters of the μ_3-OH bridged copper complexes reported in the literature are given in Table 4. Such complexes usually show almost equal Cu–O distances, all of them being in the equatorial position. There are no reports on axially co-ordinated μ_3-OH groups. The axial–equatorial bridging shown in the present structure by the hydroxide ion is novel, and is unusual even for hydroxo-bridged copper(II) dimers.[32] The Cu–O(4) distance of 2.478(3) Å observed here appears to be the longest in hydroxo-bridged copper(II) complexes. No doubly μ_3-hydroxo-bridged tetranuclear copper complex is known. With the exception of $[Cu_6(OH)_2(etsal)_6(O_2CCF_3)_4]$, the Cu_3 clusters (Table 4) achieve extra stability by incorporating additional bridges in the equatorial position between the coppers. In the present structure, while Cu(1) and Cu(2) and Cu(2) and Cu(2′) are additionally bridged by O(2) and O(4′) atoms, respectively, the absence of such a bridge between Cu(1) and Cu(2′) is compensated by the stacking interactions (see below) between the co-ordinated bipy rings.

The structure is stabilized by stacking interactions between the various rings. The L ring co-ordinated to Cu(1) is involved in stacking interactions with one of the pyridine rings of the bipy co-ordinated to Cu(2), the distance between the centres of the rings being 3.64 Å with a dihedral angle of 5.51°. The bipy on Cu(1) is involved in similar interactions with the bipy on Cu(2′). The distance between the centres of the rings is 3.61 Å with a dihedral angle of 2.45°.

Magnetic and Spectral Studies.—The relatively short metal–metal distances [Cu(1) ··· Cu(2) 3.156(1) and Cu(2) ··· Cu(2′) 3.052(1) Å] in this complex makes it a very good candidate for magnetic studies. A number of such studies have been reported for binuclear copper(II) complexes.[33] The ESR spectra of the present complex were recorded at room (296 K) and liquid-nitrogen temperatures and showed broadening (0.0120 T) at low temperature. This implies antiferromagnetic interaction between the coppers for which the three Cu_2O_2 rings with relatively short Cu ··· Cu separations are the major contributors.

The electronic spectrum in aqueous ethanolic solution showed a broad absorption around 680 nm, comparable to those reported for most square-pyramidal copper(II) complexes, *e.g.* 670 nm for [Cu(HL)(bipy)Cl]. The UV region of the electronic spectrum is characterized by the usual intraligand bands around 311, 301 and 243 nm.

In the infrared spectra the peaks characteristic of co-ordinated bipy are observed at 1608, 1496 and 642 cm^{-1}. A weak band around 1570 cm^{-1} probably corresponds to protonated pyridinium nitrogen.[34] A band of medium intensity at ≈ 1504 cm^{-1} is characteristic of co-ordinated C–O$^-$ for Vitamin B_6 complexes.[35] The broad band around 1080 cm^{-1} is characteristic of the perchlorate group.

Table 4 Comparison of structural parameters for Cu_3OH groups in copper(II) complexes[a]

Compound	Cu···Cu/Å	Cu–O/Å	Cu–O–Cu/°	O···Cu_3 plane/Å	Ref.
$[Cu_3(OH)(pao)_3(SO_4)]$	3.220(3)	1.99(1)	108.2(4)	0.697	25
$[Cu_3(OH)_{0.5}O_{0.5}L^1{}_3(H_2O)_3][ClO_4]_{1.5}$	3.246(3)	1.97(1)	110.9(4)	0.70	26
$[Cu_3(OH)L^2{}_3(ClO_4)][ClO_4]$	3.177(1)	1.946(6)	107.1(3)	0.695	27
	3.183(1)	1.969(4)	109.3(3)		
	3.172(1)	1.978(6)	110.0(3)		
$[Cu_3(OH)(pz)_3(Hpz)_2(NO_3)_2]$	3.325(1)	1.969(3)	112.0(1)	0.478	28
	3.364(1)	1.990(3)	115.0(1)		
	3.365(1)	2.022(3)	116.4(1)		
$[Cu_3(OH)_2L^3][ClO_4]_4$	2.808(3)	1.99(1)			29
		2.05(2)			
$[Cu_6(OH)_2(deae)_4(O_2CMe)_6]$	2.926(4)	1.93(1)	94.5(4)	0.63(1)	30
	3.102(3)	2.00(1)	104.1(6)		
	3.675(4)	2.05(1)	130.4(5)		
$[Cu_6(OH)_2(etsal)_6(O_2CCF_3)_4]$	3.111(1)	*b*	*b*	*b*	31
	3.229(1)				
	3.398(1)				
	3.130(1)	*b*	*b*	*b*	31
	3.194(1)				
	3.471(1)				
$[Cu_4L_2(bipy)_4(OH)_2][ClO_4]_4$	3.052(1)	1.945(3)	90.2(1)	0.978(3)	Present work
	3.156(1)	1.991(3)	101.7(1)		
	3.632(1)	2.478(3)	108.2(1)		

[a] pao = Pyridine-2-carbaldehyde oximate, L^1 = 3-methyl-3-propylaminobutan-2-one oximate, L^2 = 3-phenyliminobutan-2-one oximate, Hpz = pyrazole, L^3 = 1,10,19-trioxa-4,7,13,16,22,25-hexaazacycloheptacosane, deae = 2-diethylaminoethanolate and etsal = *N*-ethylsalicylideneiminate. [b] Value not available in the original communication or in the Cambridge Structural Database.

Acknowledgements

We thank Professor D. N. Sathyanarayana for helpful discussions.

References

1 B. J. Hathaway, in *Comprehensive Coordination Chemistry*, ed. G. Wilkinson, Pergamon, Oxford, 1987, vol. 5, pp. 533–774; R. Mergehenn and W. Haase, *Acta Crystallogr., Sect. B*, 1977, **33**, 1877.
2 L. Gazo, I. B. Bersuker, J. Garaj, M. Kabesova, J. Kohout, H. Langfeldorova, M. Melnik, M. Serator and F. Valach, *Coord. Chem. Rev.*, 1976, **19**, 253.
3 N. J. Ray, L. Hulett, R. Sheahan and B. J. Hathaway, *J. Chem. Soc., Dalton Trans.*, 1981, 1463.
4 B. J. Hathaway, in *Comprehensive Coordination Chemistry*, ed. G. Wilkinson, Pergamon, Oxford, 1987, vol. 5, p. 636.
5 R. Mergehenn, L. Merz and W. Haase, *J. Chem. Soc., Dalton Trans.*, 1980, 1703.
6 R. Belford, D. E. Fenton and M. R. Truter, *J. Chem. Soc., Dalton Trans.*, 1972, 2345.
7 H. Sigel, *Chimia*, 1967, **21**, 489.
8 H. Sigel, in *Metal Ions in Biological Systems*, ed. H. Sigel, Marcel Dekker, New York, 1973, vol. 2, p. 63; *Angew. Chem., Int. Ed. Engl.*, 1975, **14**, 394.
9 E. D. McKenzie, *Coord. Chem. Rev.*, 1971, **6**, 187.
10 G. M. Sheldrick, SHELX 76, A Program for Crystal Structure Determination, University of Cambridge, Cambridge, 1976.
11 C. K. Johnson, ORTEP II, A Program for Thermal Ellipsoid Plotting, Oak Ridge National Laboratory, Oak Ridge, Tennessee, 1976.
12 S. Motherwell and W. Clegg, PLUTO 78, A Program for Drawing Crystal and Molecular Structures, University of Cambridge, Cambridge, 1978.
13 *International Tables for X-Ray Crystallography*, Kynoch Press, Birmingham, 1974, vol. 4.
14 A. Mosset, F. N. Juras, R. Havan and J. J. Bonnet, *J. Inorg. Nucl. Chem.*, 1978, **40**, 1259.
15 V. Kh. Sabirov, As. Batsanov, Vu. T. Struchkov and M. A. Azizov, *Koord. Khim.*, 1983, **9**, 1701.
16 S. P. S. Rao, K. I. Varughese and H. Manohar, *Inorg. Chem.*, 1985, **25**, 734 and refs. therein.
17 P. M. Darriet, A. Cassaigne, J. Darriet and E. N. Neuzil, *Acta Crystallogr., Sect. B*, 1978, **34**, 2105; S. P. S. Rao, H. Manohar, K. Aoki and H. Yamazaki, *J. Chem. Soc., Dalton Trans.*, 1987, 1009.
18 H. M. Dawes, J. M. Waters and T. N. Waters, *Inorg. Chim. Acta*, 1982, **66**, 29; K. Aoki and H. Yamazaki, *J. Chem. Soc., Chem. Commun.*, 1987, 1241.
19 S. P. S. Rao, H. Manohar and R. Bau, *J. Chem. Soc., Dalton Trans.*, 1985, 2051 and refs. therein.
20 J. F. Cutfield, D. Hall and T. N. Waters, *Chem. Commun.*, 1967, 785.
21 M. R. Churchill, B. G. DeBoer and D. J. Donovan, *Inorg. Chem.*, 1975, **14**, 617.
22 M. R. Churchill and K. L. Khan, *Inorg. Chem.*, 1974, **13**, 1427.
23 B. K. Teo and J. C. Calabrese, *Inorg. Chem.*, 1976, **15**, 2474.
24 B. J. Hathaway, in *Comprehensive Coordination Chemistry*, ed. G. Wilkinson, Pergamon, Oxford, 1987, vol. 5, pp. 607–609.
25 R. Beckett and B. F. Hoskins, *J. Chem. Soc., Dalton Trans.*, 1972, 291.
26 P. F. Ross, R. K. Murmann and E. O. Schlemper, *Acta Crystallogr., Sect. B*, 1974, **30**, 1120.
27 R. J. Butcher, E. J. O'Connor and E. Sinn, *Inorg. Chem.*, 1981, **20**, 537.
28 F. B. Hulsberger, R. W. M. ten Hoedt, G. C. Verschoor and J. Reedijk, *J Chem. Soc., Dalton Trans.*, 1983, 539.
29 J. Comarmond, B. Dietrich, J. M. Lehn and R. Louis, *J. Chem. Soc., Chem. Commun.*, 1985, 74.
30 M. Ahlgren, U. Turpeinen and K. Smolander, *Acta Crystallogr., Sect. B*, 1980, **36**, 1091.
31 R. J. Butcher, J. W. Overman and E. Sinn, *J. Am. Chem. Soc.*, 1980, **102**, 3276.
32 K. D. Karlin, Y. Gultneh, J. C. Hayes and J. Zubieta, *Inorg. Chem.*, 1984, **23**, 519.
33 M. F. Charlot, S. Jeannin, Y. Jeannin, O. Kahn, L. L. Abaul and J. M. Frere, *Inorg. Chem.*, 1979, **18**, 1675 and refs. therein; M. F. Charlot, O. Kahn, S. Jeannin and Y. Jeannin, *Inorg. Chem.*, 1980, **19**, 1410; V. H. Crawford, H. W. Richardson, J. R. Wasson, D. J. Hodgson and W. E. Hatfield, *Inorg. Chem.*, 1976, **15**, 2107.
34 T. A. Franklin and M. F. Richardson, *Inorg. Chim. Acta*, 1980, **46**, 191.
35 F. Nepveu, J. J. Bonnet and J. P. Laurent, *J. Coord. Chem.*, 1981, **11**, 185.

Received 21*st January* 1991; *Paper* 1/00290B