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A Dimeric, Tetranuclear Copper(II) Complex of 2,6-Bis{*N*-[2-(4-imidazolyl)ethyl]iminomethyl}-4-methylphenol

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Abstract. $[Cu_2(C_{19}H_{21}N_6O)(H_2O)(OH)]^{2+}.BF_4^-.\frac{1}{2}SiF_6^{2-}.0{\cdot}42H_2O$, $M_r = 676{\cdot}95$, monoclinic, $C2/c$, $a = 14{\cdot}67\,(1)$, $b = 22{\cdot}23\,(1)$, $c = 19{\cdot}18\,(1)$ Å, $\beta = 125{\cdot}13\,(2)°$ from diffractometer measurements (Cu $K\alpha$ radiation), $Z = 8$, $D_x = 1{\cdot}758\,(2)$ Mg m^{-3}, $\mu = 3{\cdot}14$ mm^{-1}; $R = 0{\cdot}070$ for 2371 reflections with positive net intensity. The two Cu^{II} atoms in the binuclear species are five-coordinate, and are bridged by the O atom of the multidentate ligand and by an OH group. The axial position at one Cu^{II} atom is occupied by a water molecule and at the second Cu^{II} atom by an OH group of a neighboring cation, resulting in a dimeric, tetranuclear complex with crystallographic symmetry 2.

Introduction. The multidentate ligand 2,6-bis{*N*-[2-(4-imidazolyl)ethyl]iminomethyl}-4-methylphenol forms as the condensation product between histamine and 2-hydroxy-5-methylisophthalaldehyde at a mole ratio of 2:1 in ethanol solution. It has been studied (Gagné, Kreh & Dodge, 1979) as a ligand able to form binuclear copper complexes which might show interesting oxygen-binding properties. The present Cu^{II} compound was prepared by treating the ligand, formed *in situ*, with $Cu(BF_4)_2$.

A few small crystals were obtained by slow evaporation of an ethanol solution. Preliminary oscillation and Weissenberg photographs showed monoclinic symmetry and systematic absences (hkl with $h + k$ odd, $h0l$ with l odd) characteristic of space groups Cc and $C2/c$; the structure analysis was carried out in $C2/c$. Unit-cell dimensions and intensity data were obtained from an approximately rectangular prism with dimensions $0{\cdot}1 \times 0{\cdot}3 \times 0{\cdot}1$ mm, which was sealed in a Lindemann capillary and mounted on a Datex-automated General Electric quarter-circle diffractometer with its **c** direction nearly parallel to the φ axis.

Intensity data were measured using Ni-filtered Cu $K\alpha$ radiation and θ–2θ scans at a rate of 2° min^{-1}; backgrounds were collected for 20 s at each end of the scan. Continual monitoring of a check reflection indicated no crystal decay or instrument instability. Of the 2416 reflections in the quadrant that was surveyed out to $2\theta = 100°$, 2371 had positive net intensity. Observational variances $\sigma^2(F_o^2)$ included counting statistics plus a term $(0{\cdot}02S)^2$, where S is the scan count.

Initial attempts to locate the Cu atoms from a three-dimensional Patterson map were unsuccessful, perhaps due to the presence of the SiF_6^{2-} group which was not suspected at the time. The structure was successfully solved by *MULTAN* 74 (Main, Woolfson, Lessinger, Germain & Declercq, 1974), which yielded the positions of the two Cu atoms and parts of each inner-coordination sphere. The remaining atoms were recovered from difference maps; they included a BF_4^- group and an octahedral group which we first believed to be PF_6^- (even though the charge balance was confusing). During the course of the refinement, when the 'P'—F distances were surprisingly long at 1·68 Å and difference maps showed suspicious features in this region, we included among the parameters a population factor for the central atom; it converged to the value 0·931 (0·014), essentially identical to the ratio 0·933 between the atomic numbers of Si and P. Accordingly, this group is identified as SiF_6^{2-} rather than PF_6^-. Since almost all of the available crystals had already been expended, no further chemical analysis was attempted.

The H atoms of the methyl group C(11), the bridging OH group O(2), and the coordinated water molecule O(3) were located on difference maps; the remaining H atoms were positioned from geometrical considerations. Near the end of the refinement a difference map showed, as its largest features, two small peaks (heights: 1·5 and 0·8 e Å^{-3}) in otherwise empty regions on a twofold axis at $x = 0$, $z = \frac{1}{4}$. They were presumed to represent water molecules in partially occupied sites, which were included in subsequent calculations.

In the final least-squares cycles, two separate matrices were collected: coordinates of all non-hydrogen atoms in one (117 parameters), isotropic B's for the boron and partially-occupied water sites,

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anisotropic *B*'s for the remaining heavy atoms, population factors for the water sites, a scale factor and an extinction parameter in the second (233 parameters). The H parameters were not adjusted. The quantity minimized was $\sum w(F_o^2 - F_c^2)^2$, with $w = \sigma^{-2}(F_o^2)$. Convergence was presumed when parameter shifts were less than $0{\cdot}1\sigma$ for all atoms except for the highly anisotropic, and probably disordered, BF_4^- group, where shifts reached $0{\cdot}9\sigma$ for F(6) and $0{\cdot}5\sigma$ for F(7). The final *R* was 0·070 for the 2371 reflections with positive net intensity and the goodness-of-fit was 4·6 for all 2416 measured reflections and 350 parameters. While this latter value is rather high, it is not atypical of structures with low observational variances and regions of disorder. The weighted residuals $\sqrt{w}(F_o^2 - F_c^2)$ seem to be distributed quite uniformly through the data set. Final parameters are given in Table 1.* Calculations were carried out on an IBM 370 computer using the *CRYM* system of programs.

Table 1. *Atomic coordinates* [$\times 10^5$ *for* Cu(*A*) *and* Cu(*B*); $\times 10^4$ *for others*] *and equivalent B values* (*Hamilton*, 1959)

	x	*y*	*z*	B_{eq} (Å^2)
Cu(*A*)	50335 (9)	57717 (5)	33961 (7)	2·79 (4)
Cu(*B*)	33340 (9)	48377 (4)	21766 (7)	2·78 (4)
O(1)	4725 (4)	4904 (2)	3329 (3)	2·9 (2)
O(2)	3834 (4)	5666 (2)	2203 (3)	2·4 (1)
O(3)	2204 (6)	5204 (3)	2574 (4)	5·1 (2)
N(1*A*)	4910 (6)	6650 (3)	3431 (4)	3·1 (2)
N(1*B*)	2126 (5)	4827 (3)	961 (4)	2·8 (2)
N(2*A*)	4428 (6)	7582 (3)	3049 (5)	3·6 (2)
N(2*B*)	864 (6)	5111 (3)	−348 (4)	3·7 (2)
N(3*A*)	6282 (6)	5715 (3)	4584 (4)	3·4 (2)
N(3*B*)	3221 (5)	3974 (3)	2317 (4)	2·8 (2)
C(1*A*)	4230 (7)	7019 (4)	2797 (5)	3·2 (3)
C(1*B*)	1598 (7)	5288 (4)	460 (5)	3·4 (3)
C(2*A*)	5277 (8)	7592 (4)	3876 (6)	4·2 (3)
C(2*B*)	940 (8)	4506 (4)	−365 (6)	4·1 (3)
C(3*A*)	5574 (8)	7014 (4)	4133 (6)	3·9 (3)
C(3*B*)	1716 (7)	4327 (4)	440 (5)	3·3 (3)
C(4*A*)	6416 (10)	6761 (5)	4983 (6)	6·0 (4)
C(4*B*)	2125 (8)	3714 (4)	806 (6)	3·9 (3)
C(5*A*)	6996 (8)	6266 (4)	4989 (6)	5·3 (3)
C(5*B*)	2251 (8)	3630 (4)	1620 (6)	3·8 (3)
C(6*A*)	6575 (8)	5244 (4)	5026 (5)	3·8 (3)
C(6*B*)	3922 (7)	3669 (4)	2982 (6)	3·4 (3)
C(7*A*)	6139 (7)	4642 (4)	4769 (5)	3·2 (3)
C(7*B*)	4896 (7)	3887 (4)	3765 (5)	3·3 (3)
C(8*A*)	6710 (7)	4192 (4)	5396 (5)	3·9 (3)
C(8*B*)	5525 (8)	3454 (4)	4429 (6)	3·9 (3)
C(9)	5256 (7)	4490 (4)	3941 (5)	3·1 (3)
C(10)	6403 (8)	3586 (4)	5222 (6)	3·9 (3)
C(11)	7049 (9)	3114 (4)	5894 (6)	5·3 (3)
Si	0	4097 (1)	2500	2·9 (1)
F(1)	999 (4)	4632 (2)	2998 (3)	4·4 (2)
F(2)	−123 (4)	4097 (2)	3316 (3)	4·8 (2)
F(3)	996 (4)	3567 (2)	2978 (3)	4·2 (1)
B	1197 (11)	6844 (6)	1381 (8)	6·4 (3)
F(4)	1642 (8)	6354 (3)	1844 (5)	10·6 (3)
F(5)	1719 (5)	7340 (2)	1799 (5)	8·4 (3)
F(6)	1458 (16)	6716 (4)	855 (10)	19·3 (8)
F(7)	204 (6)	6892 (4)	950 (8)	13·8 (4)
O(4)	0	7535 (14)	2500	14 (2)
O(5)	0	5894 (31)	2500	19 (4)

Discussion. The binuclear species, with the numbering scheme used here, is shown in Fig. 1; bond lengths and some angles are given in Tables 2 and 3. The two Cu^{II} atoms are bridged by the OH group, O(2), and by the oxygen atom O(1) of the multidentate ligand; the four N atoms of the ligand complete a roughly square-planar coordination about the two Cu atoms. Each Cu atom has an additional, weakly bound axial ligand: a water molecule, O(3), in the case of Cu(*B*) and, in the case of Cu(*A*), the hydroxyl oxygen atom O(2) from a neighboring binuclear species related by a diad. Thus, the entire molecule can be described as dimeric and tetranuclear, with crystallographic symmetry 2. A stereoscopic view is shown in Fig. 2.

The four equatorial atoms about Cu(*B*) are coplanar within experimental error (see Table 4), and the Cu atom is displaced from this plane by 0·15 Å in the direction of the axial water molecule O(3). On the other hand, the equatorial atoms about Cu(*A*) are appreciably non-planar. While the individual aromatic rings are satisfactorily planar, the multidentate ligand itself is forced to be non-planar by the ethylene groups C(4)–C(5). The details of its puckering are complicated and, like the difference in geometries about

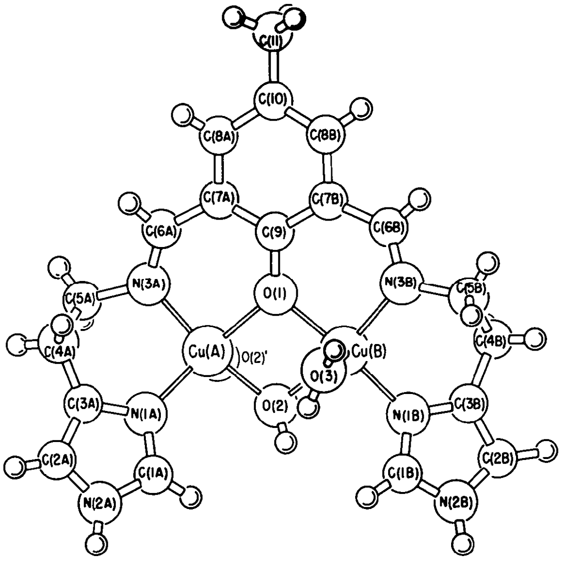

Fig. 1. The binuclear cation, with the numbering system used.

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* Coordinates of the hydrogen atoms, isotropic *B*'s or anisotropic *U*'s for all the atoms, and the structure factors have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 35265 (19 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

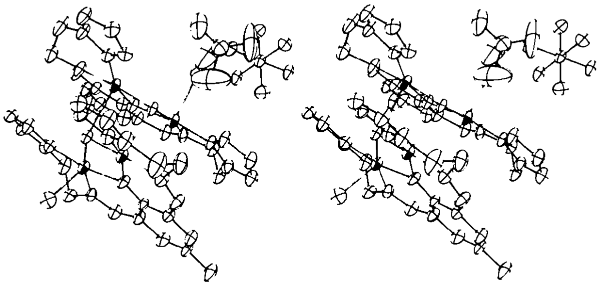

Fig. 2. A stereoscopic view of two binuclear cations linked through axial Cu(*A*)–O(2) bonds to form a tetranuclear dimer. One set of neighboring $\mathrm{BF_4^-}$ and $\mathrm{SiF_6^{2-}}$ ions is also shown. The view direction is approximately parallel to **b**.

Table 2. *Bond distances* (Å)

Cu(*A*)–O(1)	1·969 (6)	Cu(*B*)–O(1)	1·970 (6)
–O(2)	1·937 (5)	–O(2)	1·971 (5)
–N(1*A*)	1·965 (8)	–N(1*B*)	1·955 (7)
–N(3*A*)	1·939 (8)	–N(3*B*)	1·958 (7)
–O(2)′	2·516 (5)	–O(3)	2·334 (8)
N(1*A*)–C(1*A*)	1·323 (12)	N(1*B*)–C(1*B*)	1·310 (12)
–C(3*A*)	1·382 (13)	–C(3*B*)	1·379 (12)
C(1*A*)–N(2*A*)	1·313 (12)	C(1*B*)–N(2*B*)	1·340 (12)
N(2*A*)–C(2*A*)	1·340 (13)	N(2*B*)–C(2*B*)	1·353 (13)
C(2*A*)–C(3*A*)	1·355 (15)	C(2*B*)–C(3*B*)	1·347 (14)
C(3*A*)–C(4*A*)	1·478 (16)	C(3*B*)–C(4*B*)	1·492 (14)
C(4*A*)–C(5*A*)	1·387 (17)	C(4*B*)–C(5*B*)	1·475 (14)
C(5*A*)–N(3*A*)	1·506 (14)	C(5*B*)–N(3*B*)	1·486 (12)
N(3*A*)–C(6*A*)	1·255 (13)	N(3*B*)–C(6*B*)	1·279 (12)
C(6*A*)–C(7*A*)	1·443 (14)	C(6*B*)–C(7*B*)	1·435 (13)
C(7*A*)–C(8*A*)	1·410 (14)	C(7*B*)–C(8*B*)	1·432 (14)
–C(9)	1·396 (13)	–C(9)	1·408 (13)
C(8*A*)–C(10)	1·400 (14)	C(8*B*)–C(10)	1·342 (14)
C(9)–O(1)	1·333 (11)	C(10)–C(11)	1·501 (16)
Si–F(1)	1·691 (6)	B–F(4)	1·318 (18)
–F(2)	1·675 (6)	–F(5)	1·318 (17)
–F(3)	1·680 (6)	–F(6)	1·300 (23)
		–F(7)	1·196 (19)

Table 3. *Angles* (°) *at the copper atoms*

E.s.d.'s are about 0·2°.

N(1*A*)–Cu(*A*)–N(3*A*)	93·9	N(1*B*)–Cu(*B*)–N(3*B*)	93·5
–O(1)	162·5	–O(1)	169·1
–O(2)	97·0	–O(2)	96·3
–O(2)′	101·9	–O(3)	93·8
N(3*A*)–Cu(*A*)–O(1)	92·2	N(3*B*)–Cu(*B*)–O(1)	91·9
–O(2)	169·0	–O(2)	166·2
–O(2)′	96·0	–O(3)	99·5
O(1)–Cu(*A*)–O(2)	77·6	O(1)–Cu(*B*)–O(2)	76·8
–O(2)′	93·7	–O(3)	94·6
O(2)–Cu(*A*)–O(2)′	80·7	O(2)–Cu(*B*)–O(3)	89·4
Cu(*A*)–O(1)–Cu(*B*)	101·4	Cu(*A*)–O(2)′–Cu(*A*)′	97·9
Cu(*A*)–O(2)–Cu(*B*)	102·5	–Cu(*B*)′	114·2

Table 4. *Deviations* (Å) *from the planes through the equatorial sites about the copper atoms* [(*a*) Cu(*A*); (*b*) Cu(*B*)]

E.s.d.'s are about 0·01 Å.

(*a*)		(*b*)	
O(1)*	0·16 Å	O(1)*	0·00 Å
O(2)*	−0·16	O(2)*	0·00
N(1*A*)*	0·16	N(1*B*)*	0·00
N(3*A*)*	−0·16	N(2*B*)*	0·00
Cu(*A*)	−0·12	Cu(*B*)	0·15
O(2)′	−2·61	O(3)	2·48

* Included in calculation of least-squares planes.

the Cu atoms, difficult to understand; they are probably due to the exigencies of the interactions between the two halves of the dimer (see Fig. 2). Distances and angles within the ligand are normal except for the bonds C(4)–C(5) which – especially for fragment *A* – seem to be shortened because of out-of-plane librations or, possibly, partial disorder.

The $\mathrm{BF_4^-}$ ion undergoes very large apparent librations and is probably disordered; accordingly, the B–F bond lengths (Table 2) are of little significance. Only one atom, F(4), accepts a reasonable hydrogen bond – from O(3), at 2·83 Å. On the other hand, the atoms of the $\mathrm{SiF_6^{2-}}$ ion have reasonable *B*'s and show no evidence of disorder. All three independent F atoms accept relatively strong hydrogen bonds: F(1) from O(3) at 2·65 Å, F(2) from N(2*B*) at 2·73 Å, and F(3) from N(2*A*) at 2·76 Å. The Si–F distances are typical (Ray, Zalkin & Templeton, 1973, and references therein), and all the *cis* F–Si–F angles are between 89 and 91°. As noted earlier, the presence of the $\mathrm{SiF_6^{2-}}$ ion was unexpected, as it was not one of the formal reagents used in preparing the compound (Gagné *et al.*, 1979). It is likely that the silicon was leached from glassware during the synthesis.

The partially occupied water sites O(4) and O(5) have occupancy factors of 0·53 (4) and 0·31 (4). They are in the region of the $\mathrm{BF_4^-}$ and $\mathrm{SiF_6^{2-}}$ ions and the water molecule O(3), but have no neighbors within 3·0 Å.

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