Table 3. *Comparison of mean bond lengths* (Å) *and angles* (°) *in some tetrazole-containing compounds*

| | HTz | NaTz | $[Fe(1PrTz)_6](BF_4)_2$ | $[Zn(1MeTz)_2Cl_2]$ | $[Ni(2MeTz)_6](BF_4)_2$ |
|---|---|---|---|---|---|
| *M*—N(4) | — | — | 2·153 | 2·05 | 2·095 |
| N(4)—N(3) | 1·33 | 1·348 | 1·369 | 1·34 | 1·322 |
| N(4)—C(5) | 1·33 | 1·329 | 1·328 | 1·30 | 1·333 |
| N(3)—N(2) | 1·30 | 1·310 | 1·297 | 1·29 | 1·300 |
| N(2)—N(1) | 1·33 | 1·348 | 1·337 | 1·34 | 1·324 |
| N(1)—C(5) | 1·30 | 1·329 | 1·326 | 1·30 | 1·311 |
| N(3)—N(4)—C(5) | 108·5 | 104·3 | 105·7 | 106 | 106·1 |
| *M*—N(4)—C(5) | — | — | 130·2 | 133 | 134·9 |
| *M*—N(4)—N(3) | — | — | 124·1 | 121 | 118·6 |
| N(4)—N(3)—N(2) | 107·6 | 109·5 | 109·8 | 111 | 105·7 |
| N(3)—N(2)—N(1) | 107·8 | 109·5 | 107·0 | 106 | 114·1 |
| C(5)—N(1)—N(2) | 109·4 | 104·3 | 109·1 | 108 | 101·7 |
| N(1)—C(5)—N(4) | 106·7 | 112·5 | 108·4 | 109 | 112·5 |

be 0·57 and 0·43. The very large temperature parameters of the fluoroborate anions are not unusual in hexacoordinated compounds in which the anions are very weakly bonded to the cations.

There is a reasonable agreement between the geometries of the tetrazole rings as established in the literature {Table 3, data taken from van der Putten, Heijderijk & Schenk (1974) for HTz; Palenik (1963) for NaTz; Franke (1982) for $[Fe(1\text{-propyltetrazole})_6](BF_4)_2$ and from Baenziger & Schultz (1971) for $[Zn(1MeTz)_2Cl_2]$} and the bond distances and angles as given in Table 2.

The structure of $[Ni(2MeTz)_6](BF_4)_2$ with its octahedral $[NiN_6]$ chromphore and the space group with threefold symmetry is not unusual for transition-metal(II) complexes of azoles, *e.g.* for pyrazole and imidazole the same types of structures were reported (Santoro, Mighell, Zocchi & Reimann, 1969; Reimann, Santoro & Mighell, 1970; ten Hoedt, Driessen & Verschoor, 1983).

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# Structure of Bis[5-hydroxymethyl-2-methyl-4-(phenylethyliminomethyl)-3-pyridinolato-*N*,*O*]copper(II), $Cu(C_{16}H_{17}N_2O_2)_2$

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**Abstract.** $M_r = 602·2$, monoclinic, $P2_1/c$, $a = 11·3403$ (6), $b = 8·916$ (2), $c = 14·283$ (1) Å, $\beta = 90·600$ (6)°, $Z = 2$, $V = 1444·2$ (5) Å$^3$, $D_m = 1·37$ (1), $D_x = 1·38$ Mg m$^{-3}$, Mo $K\alpha$, $\lambda = 0·71069$ Å, $\mu = 7·98$ mm$^{-1}$, $F(000) = 630$, $T = 293$ K, $R = 0·036$ for 2860 independent reflections. The copper-atom environment is exactly square planar.

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**Introduction.** The structural determination of the Schiff base copper(II) complex with pyridoxal and phenylethylamine forms part of a stereochemical investigation concerning copper(II) complexes with pyridoxal and biogenic amines (Nepveu, Laurent & Massol, 1980).

**Experimental.** Prepared according to Purdy (1976), final purification by column chromatography on 70–230 mesh Silicagel with a methanol/acetone mixture (80:20, v/v) as eluant, green-brown parallelepipeds, by slow evaporation, m.p. 462–463 K, $D_m$ by flotation in aqueous $ZnCl_2$ at 293 K, 0·42 × 0·22 × 0·88 mm; cell constants and e.s.d.'s at 293 K from least-squares refinement of 25 reflections automatically collected on an Enraf–Nonius CAD-4 diffractometer, 3967 intensities measured, $2\theta_{\max}(\mathrm{Mo}) = 50°$, $-13 < h < 13$, $0 < k < 11$, $0 < l < 16$, 4 standard reflections, intensity variation <3%, 2860 unique reflections with $F_o^2 > 3\sigma(F_o^2)$, 584 unobserved; absorption corrections, minimum and maximum transmission factors 0·719 and 0·845; direct methods (*F* refined) (*MULTAN*; Main, Hull, Lessinger, Germain, Declercq & Woolfson, 1978) for non-hydrogen atoms (21 atoms), atomic scattering factors for non-hydrogen atoms from Cromer & Waber (1974), for hydrogen from Stewart, Davidson & Simpson (1965), anomalous dispersion for Cu included in $F_c$; anisotropic refinement, no contribution from H atoms, $R = 0·062$, $R_w = 0·092$, $w = 4F_o^2/\sigma(F_o)^2$; ten hydrogen atoms [H(5), H*A*(7), H*A*(8), H*A*(9), H*B*(9), H*A*(10), H*B*(10), H(12), H(13), H(14)] from difference Fourier synthesis, their positions idealized (C—H = 0·95 Å) and their contributions to $F_c$ fixed, isotropic secondary extinction correction; anisotropic thermal parameters for non-hydrogen atoms, isotropic for hydrogen atoms with a value 1·0 $Å^2$ greater than that of the atom to which it is attached, ratio of LS shift to error DEL/SIG <0·25; final difference Fourier map with peaks <0·4 e $Å^{-3}$ was essentially featureless; final full-matrix least-squares refinement, 187 variables, 2860 observations, gave $R = 0·036$, $R_w = 0·047$.*

All calculations were performed on the CII IRIS 80 computer of the Centre Interuniversitaire de Calcul de Toulouse. In addition to various local programs, modified versions of the following were employed: *FORDAP* Fourier summation program (A. Zalkin, unpublished); *NUCLS* full-matrix least-squares program (R. J. Doedens & J. A. Ibers, unpublished) which in its non-group form resembles *ORFLS* (Busing, Martin, & Levy, 1962); *ORTEP* thermal ellipsoid plotting program (Johnson, 1965); *ORFFE* error function program (Busing, Martin & Levy, 1964); *MULTAN* direct method program (Main, Hull, Lessinger, Germain, Declercq & Woolfson, 1978).

**Discussion.** The atomic coordinates are listed in Table 1. A perspective view of the molecule with the atom-numbering scheme is shown in Fig. 1. The bond distances and angles involving non-H atoms are given in Table 2. The bidentate ligand is coordinated to the copper atom *via* its phenolic oxygen atom O(1) and its imino nitrogen atom N(1). The molecule is centrosymmetric, the copper is at the centre of symmetry and the coordination (2N, 2O) around the copper(II) ion is therefore exactly planar. Thus, the geometry around the copper atom is different from that which we have observed in the similar complex with benzylamine (Nepveu, Bonnet, Laurent & Massol, 1981): in that non-centrosymmetric complex, the square plane around the metal is distorted with a dihedral angle of 35·31°. While the Cu—O(1) distance of 1·909 (1) Å compares well with the corresponding one in the benzylamine complex [1·900 (3) Å], the Cu—N(1) distance of 2·017 (2) Å is significantly longer [1·967 (3) Å]. This may be connected, in part, to the different electronic effect of benzylamine, compared to phenylethylamine, as regards the nitrogen atom and also to steric effects. The values of the other interatomic distances and angles are similar to those found earlier in the bis[5-hydroxymethyl-2-methyl-4-(benzyliminomethyl)-3-pyridinolato]copper(II) complex. To date, we have considered the X-ray structural determinations of these two model systems, for the enzymatic reaction of oxidative deamination (Hamilton, 1968), involving

Table 1. *Fractional coordinates* (×10⁴) *and equivalent isotropic temperature factors with e.s.d.'s in parentheses*

$$B_{\rm eq} = \tfrac{4}{3}\textstyle\sum_i\sum_j B_{ij}(a_i a_j).$$

| | *x* | *y* | *z* | $B_{\rm eq}$(Å²) |
|---|---|---|---|---|
| Cu | 0 | 0 | 0 | 2·57 (2) |
| O(1) | 0·0637 (1) | 0·1897 (2) | −0·0352 (1) | 3·04 (3) |
| O(2) | −0·1466 (2) | 0·3311 (2) | −0·3745 (1) | 4·42 (3) |
| N(1) | −0·1252 (1) | 0·0183 (2) | −0·1007 (1) | 2·31 (3) |
| N(2) | 0·0422 (2) | 0·5476 (2) | −0·1454 (1) | 2·82 (3) |
| C(1) | 0·0212 (2) | 0·2922 (2) | −0·0911 (1) | 2·30 (3) |
| C(2) | −0·0756 (2) | 0·2722 (2) | −0·1516 (1) | 2·26 (3) |
| C(3) | −0·1398 (2) | 0·1320 (2) | −0·1551 (1) | 2·35 (3) |
| C(4) | −0·1111 (2) | 0·3927 (2) | −0·2115 (1) | 2·53 (3) |
| C(5) | −0·0518 (2) | 0·5261 (2) | −0·2021 (2) | 2·86 (1) |
| C(6) | 0·0802 (2) | 0·4343 (2) | −0·0928 (1) | 2·54 (3) |
| C(7) | 0·1880 (2) | 0·4583 (3) | −0·0341 (2) | 3·34 (1) |
| C(8) | −0·2005 (2) | 0·3793 (3) | −0·2897 (2) | 3·49 (1) |
| C(9) | −0·2106 (2) | −0·1034 (2) | −0·1170 (2) | 2·96 (1) |
| C(10) | −0·3191 (2) | −0·0830 (3) | −0·0546 (2) | 3·63 (1) |
| C(11) | −0·3911 (2) | 0·0527 (3) | −0·0807 (2) | 3·27 (1) |
| C(12) | −0·4760 (2) | 0·0469 (3) | −0·1515 (2) | 4·33 (1) |
| C(13) | −0·5384 (2) | 0·1745 (4) | −0·1788 (2) | 5·05 (2) |
| C(14) | −0·5170 (2) | 0·3085 (4) | −0·1347 (2) | 5·05 (2) |
| C(15) | −0·4338 (2) | 0·3160 (3) | −0·0639 (2) | 4·79 (1) |
| C(16) | −0·3714 (2) | 0·1898 (3) | −0·0371 (2) | 3·96 (1) |

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* Lists of structure factors, anisotropic thermal parameters, hydrogen-atom coordinates and least-squares planes have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 38244 (18 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

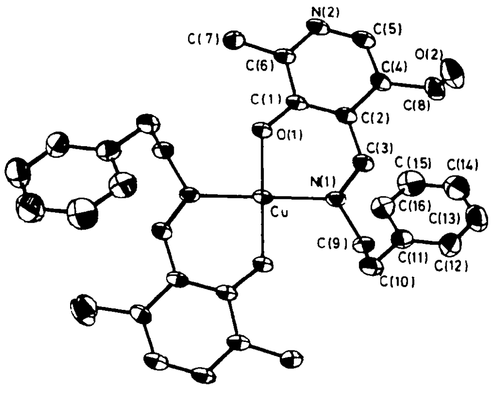

Fig. 1. A perspective representation of the molecule. Hydrogen atoms have been omitted for clarity. The vibrational ellipsoids are drawn at the 50% probability level.

Table 2. *Bond lengths* (Å) *and angles* (°)

| | | | |
|---|---|---|---|
| Cu–O(1) | 1·909 (1) | C(8)–O(2) | 1·428 (3) |
| Cu–N(1) | 2·017 (2) | C(6)–C(7) | 1·490 (3) |
| O(1)–C(1) | 1·303 (2) | N(1)–C(9) | 1·472 (3) |
| N(1)–C(3) | 1·287 (2) | C(9)–C(10) | 1·537 (3) |
| C(3)–C(2) | 1·448 (3) | C(10)–C(11) | 1·505 (4) |
| C(2)–C(4) | 1·428 (3) | C(11)–C(12) | 1·390 (3) |
| C(4)–C(5) | 1·372 (3) | C(12)–C(13) | 1·393 (4) |
| C(5)–N(2) | 1·347 (3) | C(13)–C(14) | 1·372 (4) |
| N(2)–C(6) | 1·328 (3) | C(14)–C(15) | 1·376 (4) |
| C(6)–C(1) | 1·434 (3) | C(15)–C(16) | 1·381 (4) |
| C(1)–C(2) | 1·402 (3) | C(16)–C(11) | 1·389 (3) |
| C(4)–C(8) | 1·506 (3) | | |

| | | | |
|---|---|---|---|
| O(1)–Cu–N(1) | 90·4 (1) | C(2)–C(1)–C(6) | 117·7 (2) |
| O(1)–Cu–N(1$^{i}$) | 89·6 (1) | C(6)–C(1)–O(1) | 117·4 (2) |
| C(1)–O(1)–Cu | 130·1 (1) | O(1)–C(1)–C(2) | 124·8 (2) |
| C(3)–N(1)–C(9) | 113·9 (2) | O(2)–C(8)–C(4) | 111·2 (2) |
| C(3)–N(1)–Cu | 125·4 (1) | N(1)–C(9)–C(10) | 110·5 (2) |
| C(6)–N(2)–C(5) | 118·9 (2) | C(9)–C(10)–C(11) | 112·8 (2) |
| N(1)–C(3)–C(2) | 126·7 (2) | C(10)–C(11)–C(12) | 121·3 (2) |
| C(1)–C(2)–C(4) | 119·2 (2) | C(16)–C(11)–C(12) | 117·8 (2) |
| C(1)–C(2)–C(3) | 121·4 (2) | C(10)–C(11)–C(16) | 120·8 (2) |
| C(2)–C(4)–C(5) | 117·4 (2) | C(11)–C(12)–C(13) | 121·2 (3) |
| C(5)–C(4)–C(8) | 117·8 (2) | C(12)–C(13)–C(14) | 119·8 (3) |
| N(2)–C(5)–C(4) | 124·5 (2) | C(13)–C(14)–C(15) | 119·7 (3) |
| C(1)–C(6)–N(2) | 122·2 (2) | C(14)–C(15)–C(16) | 120·6 (3) |
| N(2)–C(6)–C(7) | 118·0 (2) | C(15)–C(16)–C(11) | 120·8 (2) |

Symmetry code: (i) $-x,-y,-z$.

copper(II), pyridoxal and either benzylamine or phenylethylamine. No reaction but complex formation was observed under a variety of experimental conditions which have been found convenient for inducing oxidative deamination of amino acids (Hamilton, 1971). According to the proposed mechanism (Martell, 1973) the behaviour of the model system is expected to depend largely on stereochemical conditions. It is noteworthy that the C(9) atom, which bears the hydrogen atoms possibly involved in the deamination process, lies exactly in the mean plane of the chelate ring and roughly in the plane through the pyridoxal–aldimine group in the phenylethylamine complex, while in the benzylamine complex it significantly deviates from these planes. Thus, the plausible rôle of the metal ion in maintaining a conjugated system appropriate to the requirements of proposed mechanisms in the effective oxidative deamination reaction of amino acids is not sufficient for obtaining the same transformation with amines.

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