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## Structure of (2-Acetylpyrrolato){*N*-[1-(2-pyrrolyl)ethylidene]ethylaminato}copper(II)

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**Abstract.** [Cu(C<sub>8</sub>H<sub>11</sub>N<sub>2</sub>)(C<sub>6</sub>H<sub>6</sub>NO)],  $M_r = 306.86$ , orthorhombic, *Pbca*,  $a = 7.146$  (1),  $b = 19.762$  (3),  $c = 19.443$  (4) Å,  $V = 2753$  (1) Å<sup>3</sup>,  $Z = 8$ ,  $D_x = 1.481$  Mg m<sup>-3</sup>, Mo K $\alpha$  radiation,  $\lambda = 0.71073$  Å,  $\mu = 1.58$  mm<sup>-1</sup>,  $F(000) = 1272$ ,  $T = 293$  (1) K,  $R = 0.032$  for 1015 observed reflections with  $I > 3\sigma(I)$ . The Cu atom is coordinated to two different bidentate ligands and has distorted square-planar geometry with a Cu–O distance of 2.022 (2) and Cu–N distances of 1.942 (3) (*trans* to O), 1.980 (3) and 1.935 (3) Å, and angles O–Cu–N(2) 91.5 (1), O–Cu–N(3) 82.2 (1), N(1)–Cu–N(2) 82.6 (1) and N(1)–Cu–N(3) 103.8 (1)°.

**Introduction.** Crystal structures of several bis(2-pyrrolylmethylenamine)–metal complexes, prepared by the interaction of tertiary butylamine Schiff-base derivatives of 2-pyrrolicarbaldehyde with Zn<sup>II</sup> (Kanters, Spek, Postma, van Stein & van Koten, 1983), Cu<sup>II</sup> (Wei, 1972*a*), Ni<sup>II</sup> (Wei & Einstein, 1972) and Co<sup>II</sup> (Wei, 1972*b*) ions, have been reported in recent years. Syntheses and solution studies have been performed on metal complexes of other Schiff-base derivatives of 2-pyrrolicarbaldehyde (Holm, Chakravorty & Theriot, 1966; Yeh & Barker, 1967), as well as on the products of the direct substitution of 2-pyrrolicarbaldehyde and 2-acetylpyrrole on Cr<sup>III</sup>, Cu<sup>II</sup> and Co<sup>III</sup> metal centers (Davies & Gogan, 1972; Habeeb, Tuck & Walters, 1978; Perry & Weber, 1971).

In the present study, bis{*N*-[1-(2-pyrrolyl)ethylidene]ethylaminato}copper(II) was synthesized by published methods (Holm *et al.*, 1966; Yeh & Barker, 1967) and allowed to hydrolyze slowly in air to produce

a mixed-ligand product containing one ethylamine Schiff base and one 2-acetylpyrrole chelate per metal center. The title compound is the result of a novel synthetic pathway to the formation of 2-acetylpyrrole chelate complexes of Cu<sup>II</sup>, as well as an interesting example of a mixed-ligand copper adduct.

**Experimental.** Bis{*N*-[1-(2-pyrrolyl)ethylidene]ethylaminato}copper(II) was synthesized by the 1:1 interaction of 2-acetylpyrrole with CuSO<sub>4</sub>·5H<sub>2</sub>O in 35% ethylamine/H<sub>2</sub>O. The blue product slowly turned light brown in air (3–5 d), and was subsequently recrystallized from petroleum ether to yield black crystals of [Cu(C<sub>8</sub>H<sub>11</sub>N<sub>2</sub>)(C<sub>6</sub>H<sub>6</sub>NO)]. Analysis: calculated for C<sub>14</sub>H<sub>17</sub>CuN<sub>3</sub>O, C: 54.81, H: 5.55, N: 13.70, Cu: 20.71%. Found, C: 54.49, H: 5.50, N: 13.21, Cu: 20.93%.

A very thin plate of hexagonal shape with dimensions 0.45 × 0.45 × 0.08 mm was mounted on a glass fiber with epoxy resin. Accurate cell dimensions and a crystal orientation matrix were determined on an Enraf–Nonius CAD-4 diffractometer by a least-squares refinement of the setting angles of 25 reflections with  $\theta$  in the range 10–15°. Intensity data were collected by the  $\omega/2\theta$  scan method using monochromatized radiation in the range  $2 < \theta < 20^\circ$ ; as the crystal was very thin it did not diffract at all beyond 20° in  $\theta$ . The intensities of two reflections, chosen as standards, were monitored at 2 h intervals of exposure time and decreased in a linear fashion by 0.5% over the course of the data collection; this decay was corrected for by appropriate scaling. Intensities of 1280 independent reflections ( $h$  0–7,  $k$  0–19,  $l$  0–19) were measured using

Table 1. Final fractional coordinates and equivalent isotropic thermal parameters ( $\text{\AA}^2$ ) with e.s.d.'s in parentheses

	x	y	z	$B_{eq}^*$
Cu	0.40347 (8)	0.35701 (2)	0.36242 (2)	3.05 (1)
O	0.4857 (5)	0.4549 (1)	0.3637 (1)	3.6 (1)
N(1)	0.3615 (5)	0.2605 (2)	0.3730 (2)	3.3 (1)
N(2)	0.3728 (5)	0.3564 (1)	0.4636 (2)	2.7 (1)
N(3)	0.4400 (5)	0.3683 (2)	0.2645 (2)	3.2 (1)
C(1)	0.3554 (7)	0.2022 (2)	0.3370 (2)	4.3 (1)
C(2)	0.3224 (8)	0.1483 (2)	0.3803 (2)	4.4 (1)
C(3)	0.3096 (6)	0.1738 (2)	0.4448 (2)	3.4 (1)
C(4)	0.3324 (5)	0.2433 (2)	0.4401 (2)	2.7 (1)
C(5)	0.3399 (5)	0.2973 (2)	0.4891 (2)	2.4 (1)
C(6)	0.3146 (6)	0.2827 (2)	0.5630 (2)	3.6 (1)
C(7)	0.3889 (6)	0.4155 (2)	0.5080 (2)	3.2 (1)
C(8)	0.2128 (7)	0.4556 (2)	0.5109 (2)	4.3 (1)
C(9)	0.4207 (7)	0.3350 (2)	0.2048 (2)	4.0 (1)
C(10)	0.4709 (7)	0.3777 (3)	0.1507 (2)	4.1 (1)
C(11)	0.5200 (7)	0.4380 (2)	0.1776 (2)	3.7 (1)
C(12)	0.4993 (6)	0.4319 (2)	0.2487 (2)	2.9 (1)
C(13)	0.5244 (6)	0.4762 (2)	0.3045 (2)	3.0 (1)
C(14)	0.5915 (7)	0.5459 (2)	0.2952 (2)	4.4 (1)

$$* B_{eq} = \frac{1}{3}[a^2B(1,1) + b^2B(2,2) + c^2B(3,3) + ab(\cos\gamma)B(1,2) + ac(\cos\beta)B(1,3) + bc(\cos\alpha)B(2,3)].$$

Table 2. Molecular dimensions ( $\text{\AA},^\circ$ ) with e.s.d.'s in parentheses

Cu—O	2.022 (2)	C(1)—C(2)	1.378 (5)
Cu—N(1)	1.942 (3)	C(2)—C(3)	1.356 (5)
Cu—N(2)	1.980 (3)	C(3)—C(4)	1.385 (4)
Cu—N(3)	1.935 (3)	C(4)—C(5)	1.432 (4)
O—C(13)	1.257 (4)	C(5)—C(6)	1.477 (5)
N(1)—C(1)	1.349 (4)	C(7)—C(8)	1.490 (5)
N(1)—C(4)	1.364 (4)	C(9)—C(10)	1.394 (5)
N(2)—C(5)	1.291 (4)	C(10)—C(11)	1.348 (5)
N(2)—C(7)	1.456 (4)	C(11)—C(12)	1.396 (5)
N(3)—C(9)	1.342 (4)	C(12)—C(13)	1.404 (5)
N(3)—C(12)	1.362 (4)	C(13)—C(14)	1.470 (5)
O—Cu—N(1)	169.5 (1)	Cu—O—C(13)	111.9 (2)
O—Cu—N(2)	91.5 (1)	Cu—N(1)—C(1)	142.1 (3)
O—Cu—N(3)	82.1 (1)	Cu—N(1)—C(4)	111.7 (2)
N(1)—Cu—N(2)	82.6 (1)	C(1)—N(1)—C(4)	106.2 (3)
N(1)—Cu—N(3)	103.8 (1)	Cu—N(2)—C(5)	114.0 (2)
N(2)—Cu—N(3)	173.5 (1)	Cu—N(2)—C(7)	125.1 (2)
C(5)—N(2)—C(7)	120.9 (3)	C(4)—C(5)—C(6)	119.8 (3)
Cu—N(3)—C(9)	141.4 (3)	N(2)—C(7)—C(8)	112.5 (3)
Cu—N(3)—C(12)	111.7 (2)	N(3)—C(9)—C(10)	109.2 (3)
C(9)—N(3)—C(12)	106.9 (3)	C(9)—C(10)—C(11)	108.1 (3)
N(1)—C(1)—C(2)	110.4 (4)	C(10)—C(11)—C(12)	106.3 (3)
C(1)—C(2)—C(3)	106.8 (3)	N(3)—C(12)—C(11)	109.6 (3)
C(2)—C(3)—C(4)	107.4 (3)	N(3)—C(12)—C(13)	116.2 (3)
N(1)—C(4)—C(3)	109.2 (3)	C(11)—C(12)—C(13)	134.2 (4)
N(1)—C(4)—C(5)	116.4 (3)	O—C(13)—C(12)	118.1 (3)
C(3)—C(4)—C(5)	134.3 (3)	O—C(13)—C(14)	119.9 (3)
N(2)—C(5)—C(4)	115.2 (3)	C(12)—C(13)—C(14)	122.1 (3)
N(2)—C(5)—C(6)	124.9 (3)		

variable scan speed of  $0.60\text{--}3.5^\circ \text{min}^{-1}$ . 1015 reflections had  $I > 3\sigma(I)$  and were used in the structure solution and refinement. Data were corrected for Lorentz-polarization effects but not for absorption.

The structure was solved by the heavy-atom method and refined by full-matrix least-squares calculations on  $F^2$ , initially with isotropic and finally with anisotropic temperature factors for the non-H atoms. At an intermediate stage in the refinement, a difference map

revealed all H atoms which were included in the subsequent cycles at their geometrically idealized positions with an overall isotropic thermal parameter. Refinement converged with  $R = 0.032$  and  $wR = 0.039$ ;  $\Delta/\sigma$  in the last cycle  $< 0.05$  and  $S = 1.656$ . In the refinement, weights were derived from  $w = 1/(\sigma^2F + 0.040F^2)$  where  $\sigma F$  is from counting statistics. A difference map calculated at the conclusion of the refinement had no chemically significant features with  $\Delta\rho$  within  $\pm 0.23 \text{ e \AA}^{-3}$ . Scattering factors were those of Cromer & Mann (1968) and Stewart, Davidson & Simpson (1965) and allowance was made for anomalous dispersion (Cromer & Liberman, 1970). Computer programs used were from the Enraf-Nonius *Structure Determination Package* (B. A. Frenz & Associates Inc., 1985).

Final fractional coordinates are in Table 1 and details of molecular dimensions are in Table 2.\* Fig. 1 is an ORTEP (Johnson, 1976) drawing of the molecule with the numbering scheme, and Fig. 2 is a stereoview of the unit cell.

\* Lists of structure factors, anisotropic temperature factors, H-atom parameters and mean planes have been deposited with the British Library Document Supply Center as Supplementary Publication No. SUP 44981 (17 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

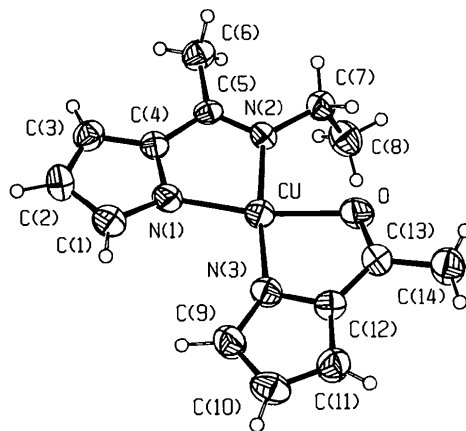


Fig. 1. ORTEP view of a single molecule with the numbering scheme.

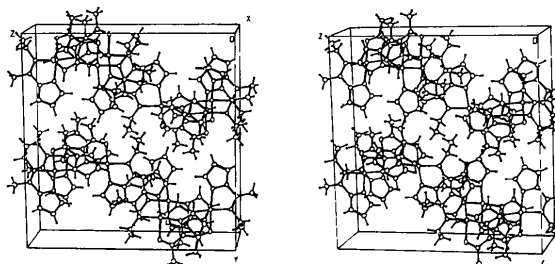


Fig. 2. Stereoview of a unit cell showing molecular packing.

**Discussion.** The structure of the title compound consists of discrete molecules separated by normal van der Waals distances. The Cu atom is coordinated to two bidentate ligands and has a distorted square-planar geometry with one Cu—O bond, two chemically equivalent Cu—N bonds which are not significantly different from each other in length and a Cu—N distance which is 0.04 Å longer than the other two Cu—N distances. The Cu—N distances observed in the title compound fall within the range observed for the corresponding distances reported in [Cu(C<sub>8</sub>H<sub>11</sub>N<sub>2</sub>)<sub>2</sub>] (Wei, 1972a) and the other related complexes referred to in Wei's (1972a) paper. The angles around Cu also deviate from the values for square-planar angles, e.g. *trans* O—Cu—N and N—Cu—N angles are 169.5 (1) and 173.5 (1)°, respectively, and the *cis* angles are: O—Cu—N 91.5 (1), 82.2 (1), N—Cu—N 82.6 (1) and 103.8 (1)°. It is interesting to note that the shorter Cu—N bond distances which involve N(1) and N(3) are associated with the largest *cis* angle around Cu.

All the five-membered rings are individually planar to within 0.012 (4) Å. The short N(2)—C(5) bond length of 1.29 (4) Å is comparable with the values reported in the Schiff-base-metal complexes with Co<sup>II</sup> [1.27 (1) Å (Wei, 1972a)], Ni<sup>II</sup> [1.287 (4) Å (Braun & Lingafelter, 1966)] and Cu<sup>II</sup> [1.25 (1) Å (Cheeseman, Hall & Waters, 1966)].

The bond distances and angles in the ligand agree well with those reported for similar complexes, e.g.

[Zn(C<sub>9</sub>H<sub>15</sub>N<sub>2</sub>)<sub>2</sub>] (Kanters *et al.*, 1983), [Co(C<sub>9</sub>H<sub>15</sub>N<sub>2</sub>)<sub>2</sub>] (Wei, 1972a), [Ni(C<sub>9</sub>H<sub>15</sub>N<sub>2</sub>)<sub>2</sub>] (Wei & Einstein, 1972) and [Cu(C<sub>9</sub>H<sub>15</sub>N<sub>2</sub>)<sub>2</sub>] (Wei, 1972b).

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## Structure of Bis(2,2',2''-triaminotriethylamine)lead(II) Dichloride

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**Abstract.** [Pb{N(CH<sub>2</sub>CH<sub>2</sub>NH<sub>2</sub>)<sub>3</sub>}<sub>2</sub>]Cl<sub>2</sub>, *M*<sub>r</sub> = 570.6, trigonal, *R* $\bar{3}$ , *a* = 8.1556 (8), *c* = 26.198 (4) Å, hexagonal setting, *U* = 1509.1 (3) Å<sup>3</sup>, *Z* = 3, 1.808(1,4-dibromobutane) < *D*<sub>m</sub> < 1.95(iodoethane), *D*<sub>x</sub> = 1.883 Mg m<sup>-3</sup>, λ(Mo *K*α) = 0.71069 Å, μ = 8.73 mm<sup>-1</sup>, *F*(000) = 840, *T* = 298 K, *R* = 0.036 and *wR* = 0.042 for 1093 unique reflections. The compound is crystallized from a commercial grade of triethylenetetramine solution. The Pb atom at a symmetry center is surrounded by six terminal N atoms

of the ligand with Pb—N bond distance of 2.742 (6) Å, and two tertiary N atoms on the crystallographic threefold axis at 2.829 (6) Å. The coordination polyhedron around the Pb atom is a distorted cube contracted around the threefold axis.

**Introduction.** Commercially available triethylenetetramine (tren) has been found to contain more than 10% of 2,2',2''-triaminotriethylamine (tren) (Utsuno, Yoshikawa & Tahata, 1985). It is a nuisance for the coordination chemist to separate tren from trien before using trien.

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