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Structure of Dichloro[*N*-(2-pyridylmethylene)histamine-*N*,*N*′,*N*″]copper(II) Hemihydrate,* $[CuCl_2(C_{11}H_{12}N_4)]{\cdot}0{\cdot}5H_2O$

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Abstract. $M_r = 343{\cdot}7$, monoclinic, $C2/c$, $a = 15{\cdot}698\,(3)$, $b = 9{\cdot}135\,(2)$, $c = 19{\cdot}378\,(4)$ Å, $\beta = 90{\cdot}91\,(1)^\circ$, $V = 2778{\cdot}5$ Å^3, $Z = 8$, $D_x = 1{\cdot}64$, $D_m = 1{\cdot}65\,(1)$ Mg m^{-3}, λ(Mo $K\alpha$) = 0·71069 Å, $\mu = 1{\cdot}86$ mm^{-1}, $F(000) = 1392$, $T = 296$ K. Final $R = 0{\cdot}042$ for 1697 independent observed reflections. The ligand is tridentate. The coordination sphere of Cu is square-pyramidal, with basal distances Cu—N(imino) = 2·032 (4), Cu—N(pyridine) = 2·022 (4), Cu—N(imidazole) = 1·971 (4) Å and Cu—Cl = 2·280 (1) Å. Cu—Cl(ax) = 2·587 (1) Å.

Introduction. Tetrameric structures were proposed for the Schiff-base copper(II) complexes derived from histamine and salicylaldehyde or 2-pyridinecarbaldehyde (Nakao, Mori, Okuda & Nakahara, 1979). The previously reported preparation using the copper(II) perchlorate hexahydrate salt did not yield crystals, but we obtained monomeric species with the chloride salt. As an extension of our work (Walz, Paulus, Haase, Langhof & Nepveu, 1983, and references therein), it was of interest to determine the crystal structure of these derivatives. We now report the structure of the Schiff-base copper(II) complex derived from histamine and 2-pyridinecarbaldehyde. This complex provides new structural information about the bonding positions of histamine when this biologically interesting molecule is involved in ternary systems.

Experimental. Prepared according to Nepveu (1982). Slow evaporation of a methanolic solution in air gives dark-green parallelepiped crystals, 0·25 × 0·25 × 0·50 mm. D_m by flotation in $CHBr_3/CCl_4$. Stoe STADI-4 diffractometer, Mo $K\alpha$, graphite monochromator. 50 reflections used to measure lattice parameters. 2379 reflections scanned in range $3 < 2\theta < 45^\circ$, 1761 unique, $R_{\rm int} = 0{\cdot}018$, 1697 observed $[I > 2\sigma(I)]$, index range $h \pm 16$, k 0/9, l 0/20. Three standard reflections measured every 50 reflections, intensity variation < 3%. Numerical absorption corrections, transmission factors 0·62–0·66. Structure solved by direct and Fourier methods; *SHELX76* (Sheldrick, 1976). After refining all non-H atoms by least squares (F magnitudes) with anisotropic temperature factors ($R = 0{\cdot}0525$) the positions of all H atoms were calculated geometrically (C—H = 1·08 Å), refinement continued until convergence (max. $\Delta/\sigma < 1$). Final R, wR 0·042, 0·050; $w = 1/\sigma^2(F)$. Final difference map showed one peak of 1·1 e Å^{-3} which is positioned between C(7) and C(8), max. negative electron density −0·7 e Å^{-3}. Scattering factors for Cu from Cromer & Mann (1968), others as supplied by *SHELX76* (Sheldrick, 1976). Diagrams drawn with *PLUTO* (Motherwell & Clegg, 1978).

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* Systematic ligand name: 2-(4-imidazolyl)-*N*-(2-pyridylmethylene)ethylamine.

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Table 1. *Atomic parameters*

$U_{eq} = \frac{1}{3}(U_{11} + U_{22} + U_{33})$.

	x	y	z	U_{eq}(Å^2)
Cu	0·1945 (1)	0·1306 (1)	0·4195 (1)	0·041
Cl(1)	0·1148 (1)	−0·0759 (2)	0·3539 (1)	0·060
Cl(2)	0·3324 (1)	0·0618 (2)	0·4036 (1)	0·054
O(*W*)	0·5000	0·2146 (7)	0·2500	0·105
N(1)	0·0871 (2)	0·2222 (4)	0·4576 (2)	0·046
N(2)	0·1879 (2)	0·0259 (4)	0·5112 (2)	0·041
N(3)	0·1947 (2)	0·2714 (5)	0·3424 (2)	0·051
N(4)	0·2292 (3)	0·3937 (5)	0·2509 (2)	0·060
C(1)	0·0656 (3)	0·1730 (6)	0·5151 (2)	0·047
C(2)	0·1194 (3)	0·0616 (5)	0·5480 (2)	0·042
C(3)	0·1013 (3)	−0·0017 (6)	0·6111 (2)	0·054
C(4)	0·1578 (3)	−0·1052 (6)	0·6376 (3)	0·060
C(5)	0·2271 (3)	−0·1417 (6)	0·6006 (3)	0·057
C(6)	0·2413 (3)	−0·0744 (6)	0·5374 (2)	0·052
C(7)	0·0391 (4)	0·3431 (7)	0·4244 (3)	0·078
C(8)	0·0420 (4)	0·3410 (10)	0·3518 (4)	0·116
C(9)	0·1279 (3)	0·3555 (7)	0·3213 (3)	0·076
C(10)	0·1498 (4)	0·4336 (7)	0·2646 (3)	0·072
C(11)	0·2552 (3)	0·2961 (6)	0·2976 (2)	0·053

Table 2. *Bond distances* (Å) *and angles* (°) *with e.s.d.'s in parentheses*

Cu–Cl(1)	2·587 (1)	C(6)–N(2)	1·336 (6)
Cu–Cl(2)	2·280 (1)	N(2)–C(2)	1·341 (5)
Cu–N(1)	2·032 (4)	N(1)–C(7)	1·478 (6)
Cu–N(2)	2·022 (4)	C(7)–C(8)	1·407 (8)
Cu–N(3)	1·971 (4)	C(8)–C(9)	1·487 (8)
N(1)–C(1)	1·252 (5)	C(9)–C(10)	1·359 (7)
C(1)–C(2)	1·462 (6)	C(10)–N(4)	1·329 (7)
C(2)–C(3)	1·386 (6)	N(4)–C(11)	1·331 (6)
C(3)–C(4)	1·389 (7)	C(11)–N(3)	1·316 (6)
C(4)–C(5)	1·354 (7)	N(3)–C(9)	1·359 (6)
C(5)–C(6)	1·392 (7)		
Cl(1)–Cu–Cl(2)	100·7 (1)	C(4)–C(5)–C(6)	119·9 (5)
Cl(1)–Cu–N(1)	94·6 (1)	C(5)–C(6)–N(2)	122·0 (5)
Cl(1)–Cu–N(2)	93·2 (1)	C(6)–N(2)–C(2)	117·9 (4)
Cl(1)–Cu–N(3)	96·3 (1)	Cu–N(2)–C(6)	128·2 (3)
Cl(2)–Cu–N(1)	163·4 (1)	Cu–N(2)–C(2)	113·9 (3)
Cl(2)–Cu–N(2)	92·9 (1)	Cu–N(1)–C(7)	124·7 (3)
Cl(2)–Cu–N(3)	93·7 (1)	N(1)–C(7)–C(8)	113·6 (5)
N(1)–Cu–N(2)	79·7 (1)	C(7)–C(8)–C(9)	116·1 (6)
N(1)–Cu–N(3)	91·0 (2)	C(8)–C(9)–C(10)	127·7 (6)
N(3)–Cu–N(2)	167·2 (2)	C(8)–C(9)–N(3)	122·0 (5)
C(7)–N(1)–C(1)	120·9 (4)	C(9)–C(10)–N(4)	105·5 (5)
Cu–N(1)–C(1)	114·3 (3)	C(10)–N(4)–C(11)	109·1 (4)
N(1)–C(1)–C(2)	118·4 (4)	N(4)–C(11)–N(3)	110·3 (5)
C(1)–C(2)–N(2)	113·6 (4)	C(11)–N(3)–C(9)	105·4 (4)
C(1)–C(2)–C(3)	123·4 (4)	Cu–N(3)–C(9)	125·9 (3)
N(2)–C(2)–C(3)	123·0 (4)	Cu–N(3)–C(11)	128·4 (4)
C(2)–C(3)–C(4)	118·2 (5)	N(3)–C(9)–C(10)	109·6 (5)
C(3)–C(4)–C(5)	119·0 (5)		

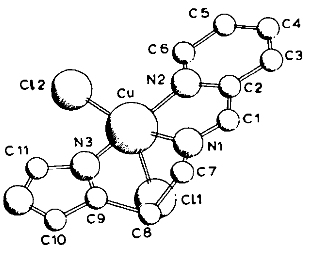

Fig. 1. Molecular structure of the complex. H atoms have been omitted.

Discussion. Final atomic parameters are given in Table 1* and bond lengths and angles in Table 2. Fig. 1 shows the molecular structure of the complex. The copper atom is coordinated through the imino N(1), the imidazole N(3), and the pyridine N(2). The square-pyramidal coordination is completed by Cl(2) in the plane and the axial Cl(1). The copper atom lies 0·232 (7) Å above the mean plane including N(1), N(2), N(3) and Cl(2) in the direction of the axial Cl(1). The oxygen atom of the water molecule lies on the twofold axis ($\frac{1}{2},y,\frac{1}{4}$). The molecular packing is shown in Fig. 2.

The present structure can be compared directly with the recently published structure of the copper(II) complex of the pyridoxylidenehistamine Schiff base (Aoki & Yamazaki, 1984). The coordination and the geometry around Cu are identical but in the present complex the pyridine N(2) of 2-pyridinecarbaldehyde replaces the phenolate O(3′) of the pyridoxal. Corresponding distances and angles around Cu are similar; only the Cu–Cl equatorial bond is shorter [2·280 (1) Å] than in the pyridoxal histamine derivate [2·369 (2) Å]. In both complexes the imidazole nitrogen occupies a strong bonding position. Such coordination has also been observed in a Schiff-base copper(II) complex of pyridoxal and L-histidine (Dawes & Waters, 1982). The presence of the imidazole nitrogen modifies the coordination around the copper atom compared to that observed in the corresponding complexes derived from monoamines (Nepveu, Bonnet & Laurent, 1981; Nepveu, Laurent & Bonnet, 1983). These studies confirm the biological importance of this donor atom.

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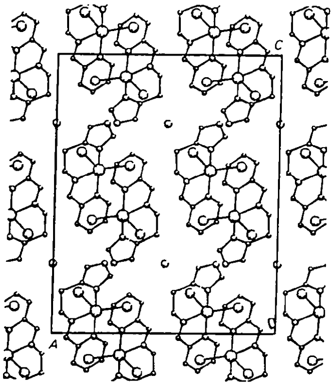

Fig. 2. View of the unit cell along the *b* axis.

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* Lists of structure factors, anisotropic thermal parameters and H-atom parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 39854 (11 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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Structure of (η^5-Indenyl)uranium Tribromide–Bis(tetrahydrofuran), $[U(C_9H_7)]Br_3.2C_4H_8O$

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Abstract. $M_r = 737{\cdot}1$, monoclinic, $P2_1/c$, $a = 9{\cdot}260\,(3)$, $b = 15{\cdot}997\,(4)$, $c = 14{\cdot}756\,(3)$ Å, $\beta = 108{\cdot}22\,(2)°$, $V = 2076\,(2)$ Å^3, $Z = 4$, $D_x = 2{\cdot}358$ g cm^{-3}, $\lambda(\text{Mo } K\bar{\alpha}) = 0{\cdot}71073$ Å, $\mu = 130{\cdot}960$ cm^{-1}, $F(000) = 1352$, $T = 295\,(1)$ K, $R = 0{\cdot}033$ for 1969 observed reflections. The title compound is isostructural with its chlorine analogue. Coordination about the U atom is pseudo-octahedral with one η^5-C_9H_7 ligand and one coordinated C_4H_8O molecule occupying *trans* axial positions. A second C_4H_8O molecule and three Br atoms occupy equatorial positions. The results and conclusions reported for $[U(C_9H_7)]Cl_3.2C_4H_8O$ are entirely corroborated by the present structure analysis.

Introduction. As part of our investigation on the bonding and coordination geometry in organoactinide complexes, we recently reported the structure of indenyluranium trichloride–bis(tetrahydrofuran), $[U(C_9H_7)]Cl_3.2C_4H_8O$ (Rebizant, Spirlet & Goffart, 1983).

The synthesis and characterization of the title compound were undertaken with the aim of establishing whether the halide-ion size could modify the crowding and therefore the geometry of the coordination polyhedron about uranium.

Experimental. Brown, prismatic single crystal ($0{\cdot}30 \times 0{\cdot}25 \times 0{\cdot}24$ mm), suitable for X-ray analysis, obtained at room temperature by recrystallization from tetrahydrofuran solution and sealed in a thin-walled glass capillary under an inert atmosphere. Enraf–Nonius CAD-4 X-ray diffractometer, graphite-monochromated Mo $K\bar{\alpha}$ radiation. Cell parameters refined by least squares from angle data of 25 reflections. Space group unequivocally established from systematic absences. 7755 reflections collected (θ–2θ scan mode) in range $4 \leq 2\theta \leq 50°$, 5475 considered observed $[I \geq 1\sigma(I)$, $\pm h$, $+k$, $\pm l]$, averaged to 3633 unique reflections ($R_{\text{int}} = 0{\cdot}025$). Intensities of three standard reflections measured at 30 min intervals showed no significant deviations from mean. Intensities corrected for Lorentz–polarization effects; empirical absorption corrections (transmission factors range from 38·57 to 99·88%). Structure solved by direct methods and

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