

An Anhydrous Theophylline–Copper(II) Chloride Compound,* $[\text{Cu}(\text{C}_7\text{H}_8\text{N}_4\text{O}_2)_2\text{Cl}_2]$

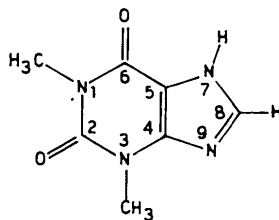
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Abstract. $M_r = 494.78$, monoclinic, $C2/c$, $a = 20.328$ (10), $b = 6.871$ (5), $c = 14.374$ (12) Å, $\beta = 107.83$ (7)°, $V = 1911$ (2) Å³, $Z = 4$, $D_x = 1.719$ g cm⁻³, $\lambda = 0.71069$ Å, $\mu(\text{Mo } K\alpha) = 14.66$ cm⁻¹, $F(000) = 1004$, room temperature. The structure was solved by Patterson and Fourier methods and refined to $R = 0.083$ for 880 independent observed reflections. The coordination geometry of the copper is flattened tetrahedral and involves two imidazole N atoms from the organic ligands and two Cl atoms. Intermolecular hydrogen bonds between N(9) hydrogen donor atoms and O(6) exocyclic oxygen atoms join the complexes in chains running along c .

Introduction. Several X-ray crystal structure determinations (Kistenmacher, Szalda & Marzilli, 1975; Sorrel, Marzilli & Kistenmacher, 1976; Szalda, Kistenmacher & Marzilli, 1976*a,b*; Kistenmacher, Szalda, Chiang & Rossi, 1978) have shown that the theophyllinate anion is normally bonded to metal ions through the N(7) imidazole N atom (protonated in the free neutral theophylline), usually with the exocyclic O atom involved in a strong intramolecular interligand hydrogen bond rather than in a long axial coordinative interaction. A similar feature is present also in the few reported complexes (Kindberg, Griffith, Amma & Jones, 1976; Biagini Cingi, Manotti Lanfredi, Tiripicchio & Tiripicchio Camellini, 1979) with neutral theophylline



whose coordination to metal ions through N(7) involves the shift of an H atom on the N(9). Only in the theophyllinium trichlorotheophyllineplatinatate(II) (Griffith & Amma, 1979), does the metal bond to the N(9) atom, an unusual coordination site of the

* Theophylline is 3,7-dihydro-1,3-dimethyl-1H-purine-2,6-dione.

theophylline, probably as a consequence of the effects of a previous protonation of the ligand. The structure of a new copper(II) complex of neutral theophylline containing no other potential hydrogen-bond donor ligands is now reported in this paper.

Experimental. Red-brown flattened prisms [from ethanolic green solution of copper(II) chloride and theophylline], $0.14 \times 0.07 \times 0.24$ mm, Siemens AED diffractometer, Nb-filtered Mo $K\alpha$, 25 reflections for lattice-parameter measurements, 1679 independent reflections with $2\theta < 48^\circ$ ($-24 \leq h \leq 19$, $0 \leq k \leq 8$, $0 \leq l \leq 16$), 880 reflections with $I > 2\sigma(I)$, no significant intensity deterioration of standard reflection (512), Lp correction, absorption ignored; Patterson and Fourier methods; full-matrix least-squares refinement, anisotropic for Cu and Cl only (SHELX, Sheldrick, 1976); the introduction of anisotropic thermal parameters also for the other non-hydrogen atoms gave no improvement in the refinement; H (from ΔF synthesis) isotropically refined; $\sum w|\Delta F|^2$ minimized with final $R = 0.083$, $wR = 0.094$, unit weight used in each stage of the refinement; $(\Delta/\sigma)_{\text{max}} = 0.08$, final $\Delta\rho$ excursions $\leq |0.7| \text{ e \AA}^{-3}$; atomic scattering factors from *International Tables for X-ray Crystallography* (1974); calculations performed on the CYBER76 computer of the Centro di Calcolo Interuniversitario dell'Italia Nord Orientale, Casalecchio (Bologna) with financial support from the University of Parma.†

Discussion. Table 1 shows the atomic parameters, Table 2 the bond distances and angles. The molecular structure of the title complex, having crystallographically imposed C_2 symmetry, is depicted in Fig. 1. The coordination polyhedron around the Cu atom can be described as a flattened tetrahedron involving two N(7) imidazole N atoms from theophylline ligands and two Cl atoms. The extent of this flattening is given

† Lists of calculated and observed structure factors, H-atom coordinates and thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 38742 (9 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

by the angle of 53° between the planes containing ClCuCl^{I} and $\text{N}(7)\text{CuN}(7^{\text{I}})$, so the coordination is intermediate between tetrahedral and *cis*-square-planar. The $\text{Cu}-\text{N}(7)$ bond distances [$2.004(13) \text{ \AA}$] are slightly longer than the mean distance [$1.985(3) \text{ \AA}$] found in diaquanitratobis(theophylline)copper(II) nitrate (Kindberg *et al.*, 1976), in which the square-pyramidal arrangement around the metal involves two $\text{N}(7)$ atoms from theophylline ligands in the equatorial plane in *cis* positions. The $\text{Cu}-\text{Cl}$ distances [$2.234(5) \text{ \AA}$] are in good agreement with those found [$2.230(2)$ – $2.271(2) \text{ \AA}$] in *N*-phenylpiperazinium tetrachlorocuprate(II) (Battaglia, Bonamartini Corradi,

Table 1. Fractional atomic coordinates ($\times 10^4$) with equivalent (for Cu and Cl) or isotropic thermal parameters for the non-hydrogen atoms, with *e.s.d.*'s in parentheses

$$B_{\text{eq}} = \frac{3}{2}\pi^2 \text{trace } \bar{U}$$

	<i>x</i>	<i>y</i>	<i>z</i>	B_{eq} or $B(\text{\AA}^2)$
Cu	0	1139 (5)	$\frac{1}{2}$	2.08 (9)
Cl	157 (2)	−997 (7)	1415 (3)	2.92 (15)
O(2)	2051 (10)	9498 (30)	3766 (15)	3.8 (5)
O(6)	1075 (6)	4357 (17)	1836 (9)	2.7 (2)
N(1)	1610 (7)	6812 (22)	2848 (11)	2.3 (3)
N(3)	1508 (7)	7298 (21)	4438 (11)	2.4 (3)
N(7)	523 (7)	3072 (20)	3498 (10)	2.1 (2)
N(9)	834 (7)	4752 (21)	4896 (11)	2.2 (3)
C(2)	1706 (10)	7970 (29)	3623 (14)	2.5 (4)
C(4)	1093 (9)	5672 (23)	4226 (12)	2.0 (3)
C(5)	922 (9)	4659 (24)	3401 (12)	1.9 (3)
C(6)	1175 (8)	5189 (24)	2604 (12)	1.9 (3)
C(8)	467 (9)	3202 (24)	4365 (13)	1.8 (3)
C(10)	1906 (12)	7488 (32)	2109 (17)	3.0 (4)
C(11)	1559 (12)	8519 (30)	5265 (16)	3.3 (4)

Table 2. Bond distances (\AA) and angles ($^\circ$) with *e.s.d.*'s in parentheses

In the coordination polyhedron			
$\text{Cu}-\text{N}(7)$	2.004 (13)	$\text{Cu}-\text{Cl}$	2.234 (5)
$\text{N}(7)-\text{Cu}-\text{Cl}$	141.0 (5)	$\text{N}(7)-\text{Cu}-\text{N}(7^{\text{I}})$	97.0 (6)
$\text{N}(7)-\text{Cu}-\text{Cl}^{\text{I}}$	95.4 (4)	$\text{Cl}-\text{Cu}-\text{Cl}^{\text{I}}$	97.9 (2)
In the theophylline ligand			
$\text{N}(1)-\text{C}(2)$	1.33 (2)	$\text{C}(5)-\text{N}(7)$	1.39 (2)
$\text{C}(2)-\text{N}(3)$	1.43 (3)	$\text{N}(7)-\text{C}(8)$	1.29 (2)
$\text{N}(3)-\text{C}(4)$	1.38 (2)	$\text{C}(8)-\text{N}(9)$	1.39 (2)
$\text{C}(4)-\text{C}(5)$	1.33 (2)	$\text{C}(4)-\text{N}(9)$	1.38 (2)
$\text{C}(5)-\text{C}(6)$	1.44 (3)	$\text{C}(6)-\text{O}(6)$	1.20 (2)
$\text{N}(1)-\text{C}(6)$	1.40 (2)	$\text{N}(1)-\text{C}(10)$	1.45 (3)
$\text{C}(2)-\text{O}(2)$	1.24 (3)	$\text{N}(3)-\text{C}(11)$	1.43 (3)
$\text{C}(2)-\text{N}(1)-\text{C}(6)$	127 (2)	$\text{C}(4)-\text{C}(5)-\text{C}(6)$	121 (2)
$\text{C}(6)-\text{N}(1)-\text{C}(10)$	116 (2)	$\text{C}(4)-\text{C}(5)-\text{N}(7)$	109 (1)
$\text{C}(2)-\text{N}(1)-\text{C}(10)$	116 (2)	$\text{C}(6)-\text{C}(5)-\text{N}(7)$	130 (1)
$\text{N}(1)-\text{C}(2)-\text{N}(3)$	119 (2)	$\text{N}(1)-\text{C}(6)-\text{C}(5)$	111 (1)
$\text{N}(1)-\text{C}(2)-\text{O}(2)$	125 (2)	$\text{N}(1)-\text{C}(6)-\text{O}(6)$	122 (2)
$\text{N}(3)-\text{C}(2)-\text{O}(2)$	115 (2)	$\text{C}(5)-\text{C}(6)-\text{O}(6)$	127 (2)
$\text{C}(2)-\text{N}(3)-\text{C}(4)$	113 (1)	$\text{C}(5)-\text{N}(7)-\text{C}(8)$	106 (1)
$\text{C}(2)-\text{N}(3)-\text{C}(11)$	122 (2)	$\text{C}(5)-\text{N}(7)-\text{Cu}$	130 (1)
$\text{C}(4)-\text{N}(3)-\text{C}(11)$	123 (2)	$\text{C}(8)-\text{N}(7)-\text{Cu}$	124 (1)
$\text{N}(3)-\text{C}(4)-\text{C}(5)$	127 (2)	$\text{N}(7)-\text{C}(8)-\text{N}(9)$	113 (2)
$\text{C}(5)-\text{C}(4)-\text{N}(9)$	109 (1)	$\text{C}(4)-\text{N}(9)-\text{C}(8)$	103 (1)
$\text{N}(9)-\text{C}(4)-\text{N}(3)$	124 (1)		

Symmetry code: (i) $-x, y, \frac{1}{2} + z$.

Marcotrigiano, Menabue & Pellacani, 1979) where flattened tetrahedral $[\text{CuCl}_4]^{2-}$ anions are present. The absence of intramolecular interligand hydrogen bonds and the presence of the O(6) exocyclic atoms close to the relatively open positions along the flattening direction of the primary coordination suggest the possibility of significant $\text{Cu}\cdots\text{O}(6)$ interactions. But in this case rather weak interactions [$\text{Cu}\cdots\text{O}(6) = 3.443(13) \text{ \AA}$] are present, probably associated only with crystal-packing forces. This system is also in agreement with the proposition that the chelate formation involving $\text{N}(7)$ and O(6) atoms is not a primary mode of metal–ligand bonding in copper(II) complexes of 6-oxopurines. The structural parameters of the theophylline ligand are in good agreement with other determinations for copper(II) complexes of neutral theophylline (Kindberg *et al.*, 1976; Biagini Cingi *et al.*, 1979). The purine skeleton of the organic ligand is reasonably planar with a dihedral angle between the imidazole and pyrimidine rings of 3.3° ; this value is a common feature of coordinated purine moieties.

The exocyclic bond angles at C(7) show the same dissymmetry found in theophylline and theophyllinato complexes, in which O(6) is involved in interligand (axial or equatorial) hydrogen bonds. The deviation of the $\text{Cu}-\text{N}(7)$ bond from the purine plane (6°) is intermediate between the values found for the copper(II) complexes, in which coordinated purines take

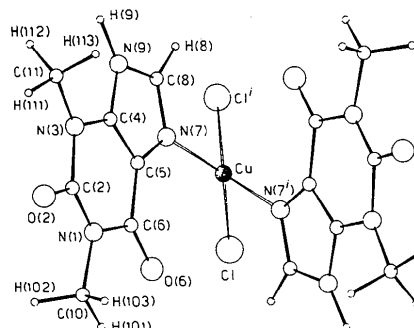


Fig. 1. Perspective view of the complex with the atomic numbering scheme.

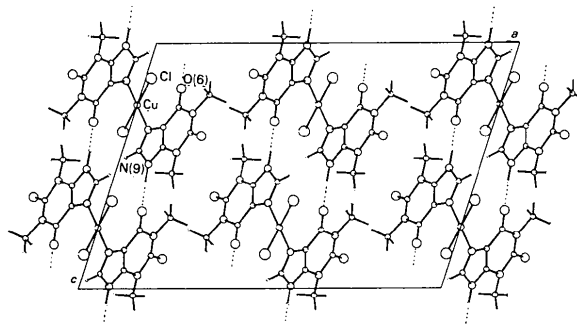


Fig. 2. Projection of the structure along *b*.

part in interligand hydrogen bonds with axial (10–15°) or equatorial (2.5°) sites in the coordination sphere (Szalda *et al.*, 1976a).

The crystal packing of the complexes is shown in Fig. 2. The principal feature is the connection in chains, running along *c*, of the translationally related complexes *via* hydrogen bonds involving the N(9) hydrogen donor atom from a complex and the O(6) exocyclic O atom from a complex at $x, 1-y, \frac{1}{2}+z$ [N(9)···O(6) = 2.75 (2) Å, H(9)···O(6) = 1.83 (16), N(9)–H(9)–O(6) = 150 (14)°]. Van der Waals contacts complete the packing.

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{N-[2-(2-Aminoethylamino)ethyl]salicylideneaminato-O,N,N',N''} nickel(II) Tetraphenylborate, [Ni(C₁₁H₁₆N₃O)] [B(C₆H₅)₄]

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Abstract. $M_r = 583.9$, monoclinic, $P2_1/n$, $a = 11.475$ (2), $b = 14.544$ (2), $c = 18.295$ (3) Å, $\beta = 102.7$ (1), $U = 2979$ (1) Å³, $Z = 4$, $D_x = 1.30$ g cm⁻³, $\mu = 6.84$ cm⁻¹, $\lambda(\text{Mo } K\alpha) = 0.71069$ Å, $F(000) = 1232$, $T = 298$ K. Final $R = 0.086$ and $R_w = 0.084$ for 2593 reflections. The coordination polyhedron around Ni is an irregular square, with the saldien ligand tetradentate to the metal through one O and three N atoms. A short intermolecular contact Ni···O of 3.377 (6) Å indicates partial dimerization of the cation.

Introduction. Metal complexes of Schiff bases have contributed widely to the inorganic chemistry of chelate systems. Particular attention has been paid to the salicylaldimino complexes owing to the electronic and structural similarity between salicylaldehyde and pyridoxal, a very active component of vitamin B₆, which plays an important part in some enzymatic reactions in the presence of metal ions (Snell, Fasella, Bramstein & Rossi Fanelli, 1963). Metal-coordination compounds of Schiff bases received a renewed pronounced impetus since Floriani & Calderazzo (1969) and Crumbliss & Basolo (1970) discovered that

salicylideneamino derivatives of cobalt(II), in the proper conditions, reversibly bind one molecule of O₂ per atom of cobalt, mimicking the naturally occurring system of haemoglobin.

A more recent application of Schiff bases derived from polyfunctional diprimary amines concerns the synthesis of compartmental ligands capable of forming homo- and heterobinuclear complexes (Costes, Cros, Darbien & Laurent, 1982). The synthesis of 'half-units', that is of non-symmetrical Schiff bases, seems to be of great potential usefulness in providing a facile extension to the available range of compartmental ligands (Bett, Fenton & Tate, 1981). We have recently described the copper(II)-template non-symmetrical synthesis of diethylenetriamine with salicylaldehyde within the coordination sphere of the metal (Rotondo & Cusmano Priolo, 1982). The crystal structure determination of the resulting copper(II) cationic derivative demonstrated the tetradentate behaviour of the 'half-unit' in a square-pyramidal complex whose apical position was occupied by a water molecule (Cusmano Priolo, Rotondo, Rizzardi, Bruno & Bombieri, 1983). We now report the result concerning the crystal structure of the same monoimine with nickel(II). In the present case the hydrophobic nature of the bulky tetraphenylborate

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