

Fig. 3. Packing of molecules in the unit cell. Large circles indicate  $I^-$ . Intermolecular stacking of quinoline heterocycles shields the  $Rb^+$  cation so that coordination with  $I^-$  is prevented.

Table 3. Some data describing the coordination of  $Rb^+$  by (I)

Atoms	Distance (Å)	Angle (°)	Distance (Å)
1-2-3	1-2	1-2-3	1-3
N(1)-Rb-O(4)	2.959 (8)	52.2 (2)	2.659 (9)
O(4)-Rb-O(7)	3.081 (7)	56.7 (2)	2.866 (10)
O(7)-Rb-O(10)	2.953 (7)	57.3 (2)	2.799 (10)
O(10)-Rb-O(13)	2.885 (7)	58.8 (2)	2.876 (10)
O(13)-Rb-O(16)	2.975 (7)	54.5 (2)	2.768 (8)
O(16)-Rb-N(19)	3.070 (7)	52.6 (2)	2.660 (9)
N(19)-Rb-N(1)	2.927 (7)	71.0 (2)	>3.2 Å

O(7), O(10), O(13), O(16), N(19) are coplanar; deviations (Å) from the least-squares plane are -0.154 (4), 0.197 (5), -0.077 (5), -0.088 (5), 0.122 (4).  $Rb^+$  is 0.745 (4) Å from this plane.

sequence of the lower electronegativity of the former (Table 3). Similar cation...O distances occur in other complexes of linear polyethers containing aromatic and aliphatic O atoms (Saenger & Reddy, 1979; Suh, Weber & Saenger, 1978).

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## Crystallographic Studies on Metal-Nucleotide Base Complexes. X. *catena*-Tetraqua- $\mu$ -(9-methylpurine)-copper(II) Sulphate Monohydrate

BY EINAR SLETTEN AND EINY VÅLAND

Department of Chemistry, University of Bergen, 5014 Bergen, Norway

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### Abstract

$[Cu(C_8H_6N_4)(H_2O)_4]^{2+} \cdot SO_4^{2-} \cdot H_2O$ , monoclinic, space group  $P2_1/n$ ,  $a = 7.310$  (1),  $b = 13.117$  (1),  $c = 14.628$  (2) Å,  $\beta = 100.98$  (1)°,  $Z = 4$ ; final  $R = 0.029$ . The Cu ion is octahedrally surrounded, the purine

The achiral, linear polyether wraps around the cation to form a chiral, helical complex. This could occur by adjustment of all the C-C and C-O torsion angles such that the fitting is achieved with the angles in the usually observed range, *gauche* for C-C and *trans* for C-O or O-C (Truter, 1973; Dunitz, Dobler, Seiler & Phizackerley, 1974). This is the case for the chain between O(7) and N(19), and the heteroatoms in this chain are nearly coplanar (Table 3). However, in order to avoid collision between the heterocycles, the torsion angle C(5)-C(6)-O(7)-C(8), 69°, is rotated from the usual *trans* into a *gauche* orientation.

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gen bonding is missing. Cu–N(1) at 2.068 (1) Å is significantly longer than Cu–N(7) [2.030 (1) Å]. The exocyclic coordination angles at N(7) are dissymmetric:  $\angle\text{Cu–N(7)–C(5)} = 133.6^\circ$ ,  $\angle\text{Cu–N(7)–C(8)} = 121.8^\circ$ .  $\text{SO}_4^{2-}$  is hydrogen bonded to the coordination sphere, the sulphate O atoms forming bridges between the water molecules.

### Introduction

Structural studies on a series of  $\text{Cu}^{\text{II}}$  complexes of nucleoside analogues have been carried out (Sletten, 1977). The bonding scheme that emerges includes Cu binding at N(7) and formation of an energetically favourable intracomplex hydrogen bond between the substituent on C(6) and the coordination sphere. For other metal ions a similar coordination geometry has been observed, although in a few cases simultaneous N(1) and N(7) binding has been encountered (De Meester, Goodgame, Skapski & Warnke, 1973; McCall & Taylor, 1976; Gagnon & Beauchamp, 1977). Hodgson (1977) concludes that 'N(1) is almost as likely a candidate for binding as is N(7)'. However, an analysis of the available data indicates that the substituent on C(6) to some degree induces stereoselectivity. In order to evaluate the influence of the C(6) substituent on the coordination geometry a  $\text{Cu}^{\text{II}}$  complex of a N(9)-methylated purine, where the C(6) substituent is absent, has been synthesized and investigated by X-ray crystallography.

### Experimental

The compound was synthesized by a modified version of a procedure described by Weiss & Venner (1963): 0.07 g 9-methylpurine was dissolved in 0.5 ml hot 1*N*  $\text{H}_2\text{SO}_4$ , 0.5 ml saturated  $\text{CuSO}_4$  solution was added and the pH adjusted to  $\sim 4$  by addition of 1*N* NaOH. After a couple of hours a crystalline precipitate was obtained. The compound was redissolved in hot water and blue crystalline plates appeared within a few days. The freshly prepared crystals contain  $5\text{H}_2\text{O}$  per formula unit compared with the  $3\text{H}_2\text{O}$  reported for the silica-gel-dried compound.

#### Crystal data

$[\text{Cu}(\text{C}_6\text{H}_6\text{N}_4)(\text{H}_2\text{O})_4]^{2+} \cdot \text{SO}_4^{2-} \cdot \text{H}_2\text{O}$ , FW 383.9, space group  $P2_1/n$ ,  $a = 7.310$  (1),  $b = 13.117$  (1),  $c = 14.628$  (2) Å,  $\beta = 100.98$  (1)°,  $T = 293$  K,  $V = 1376.9$  Å<sup>3</sup>,  $Z = 4$ ,  $\lambda(\text{Mo } K\alpha_1) = 0.70926$  Å,  $D_m = 1.85$ ,  $D_x = 1.86$  Mg m<sup>-3</sup>,  $\mu = 1.836$  mm<sup>-1</sup>.

The crystal used for data collection was prismatic (0.13 × 0.20 × 0.28 mm) and was mounted along **b**. Cell parameters and the orientation matrix were deter-

mined from 25 centred reflexions on an Enraf–Nonius CAD-4 diffractometer with the subroutines *SEARCH*, *SETANG* and *INDEX*. An analysis of the intensity peak profile indicated that the  $\omega$ -scan technique should be applied rather than the  $\theta$ - $2\theta$  method.

The scan rate was determined by a fast prescan (10° min<sup>-1</sup>). Reflexions having  $\sigma(I)/I \geq 0.5$  were considered unobserved and were not remeasured. The relative standard deviation,  $\sigma(I)/I$ , required for the final data was set equal to 0.03 provided that the maximum time spent on any one reflexion was <90 s. Backgrounds were measured by extending the scan range 25% on either side of the peak. Two reflexions,  $\bar{5}1\bar{3}$  and  $\bar{2}1\bar{7}$ , were recorded every second hour: no significant deterioration in intensity was noticed, the maximum fluctuation being 3%. 3306 unique reflexions were recorded in the range  $1 \leq \theta \leq 27^\circ$ . Of these, 2557 were above the threshold value of  $2\sigma_c$ , where  $\sigma_c$  is the estimated error due to counting statistics. The expression used for calculating the random error in any one reflexion is  $\sigma_r = [\sigma_c^2 + (0.01\sigma_c^2)^2]^{1/2}$ .

An absorption correction was applied, the maximum and minimum transmission factors being 0.81 and 0.61. Several reflexions were checked by a series of azimuth scans, showing variations in intensities in the range 0.82 to 0.96.

The structure was solved by the Patterson method and refined by full-matrix least squares on a PDP11/55 computer. All non-hydrogen atoms were refined anisotropically and the H atoms isotropically. At  $R = 0.029$  ( $R = \sum |F_o| - |F_c| / \sum |F_o|$ ) the average shift in parameters was  $0.13\sigma$  and the maximum shift  $0.21\sigma$ . The standard deviation of an observation of unit weight was 2.20. A final difference map showed peaks in the vicinity of the Cu atom of approximately  $0.4 \text{ e } \text{Å}^{-3}$ .

Table 1 contains the final positional parameters.\* The Enraf–Nonius structure determination programs (*SDP*) were used for all calculations (Frenz, 1978). Scattering factors were from Cromer & Waber (1974). Corrections for the real and imaginary terms of the anomalous dispersion were included.

### Results and discussion

#### Coordination geometry

The dimensions of the complex are shown in Fig. 1 and Table 2. The coordination around the  $\text{Cu}^{\text{II}}$  centre is (4 + 2) with two of the equatorial positions occupied by N(1) and N(7) of two symmetry-related purine ligands,

\* Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 34167 (13 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 1. *Final positional parameters, and, for H, isotropic temperature factors* [ $\exp(-B \sin^2 \theta/\lambda^2)$ ]

E.s.d.'s are in parentheses.

	x	y	z	
Cu	0.31550 (4)	0.18232 (2)	0.25729 (2)	
S	0.76947 (9)	0.38045 (5)	0.15543 (4)	
O(1)	0.5741 (3)	0.3986 (2)	0.1103 (1)	
O(2)	0.7875 (3)	0.2754 (1)	0.1915 (1)	
O(3)	0.8914 (3)	0.3938 (2)	0.0875 (1)	
O(4)	0.8245 (3)	0.4503 (2)	0.2333 (2)	
O(5)	0.5346 (2)	0.1319 (1)	0.2108 (1)	
O(6)	0.1030 (3)	0.2321 (1)	0.3090 (1)	
O(7)	0.3951 (3)	0.0758 (2)	0.3909 (1)	
O(8)	0.2450 (3)	0.2944 (2)	0.1271 (1)	
O(9)	0.9624 (3)	0.1094 (1)	0.4198 (1)	
N(1)	0.3448 (3)	0.5687 (2)	0.3164 (2)	
N(3)	0.6354 (3)	0.5370 (2)	0.4196 (2)	
N(7)	0.4716 (3)	0.2942 (2)	0.3298 (2)	
N(9)	0.7217 (3)	0.3593 (2)	0.4242 (1)	
C(2)	0.4990 (4)	0.5966 (2)	0.3772 (2)	
C(4)	0.6062 (3)	0.4393 (2)	0.3959 (2)	
C(5)	0.4487 (4)	0.3991 (2)	0.3368 (2)	
C(6)	0.3163 (4)	0.4681 (2)	0.2967 (2)	
C(8)	0.6359 (4)	0.2753 (2)	0.3825 (2)	
C(9)	0.9117 (4)	0.3652 (2)	0.4795 (2)	
	x	y	z	B (Å <sup>2</sup> )
H(2)	0.517 (4)	0.666 (2)	0.395 (2)	1.9 (6)
H(6)	0.202 (4)	0.449 (2)	0.248 (2)	3.6 (8)
H(8)	0.695 (4)	0.207 (2)	0.395 (2)	1.7 (5)
H(51)	0.583 (4)	0.089 (2)	0.231 (2)	3.1 (7)
H(52)	0.616 (4)	0.172 (2)	0.199 (2)	1.9 (6)
H(61)	0.071 (5)	0.190 (2)	0.344 (2)	3.7 (8)
H(62)	0.025 (5)	0.248 (3)	0.276 (2)	5.4 (10)
H(71)	0.464 (5)	0.031 (2)	0.396 (2)	3.6 (7)
H(72)	0.369 (4)	0.088 (2)	0.436 (2)	2.9 (7)
H(81)	0.157 (5)	0.332 (3)	0.115 (2)	4.9 (9)
H(82)	0.313 (4)	0.328 (2)	0.116 (2)	3.1 (7)
H(91)	0.999 (5)	0.108 (3)	0.471 (2)	4.4 (8)
H(92)	0.947 (5)	0.052 (2)	0.402 (2)	3.8 (8)
H(93)	0.960 (6)	0.298 (3)	0.506 (3)	5.7 (10)
H(94)	1.008 (6)	0.394 (3)	0.442 (3)	6.1 (10)
H(95)	0.910 (6)	0.407 (3)	0.542 (3)	6.2 (11)

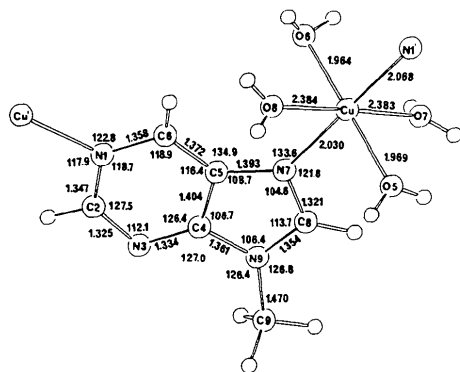


Fig. 1. Interatomic distances (Å) and angles (°) in the complex unit. The  $\sigma$ 's in bond lengths are: Cu-N(O) 0.001–0.002 Å, C–C(N) 0.002 Å, H–C(N)(O) 0.03 Å. The  $\sigma$ 's in angles at C(N)(O) not involving H atoms are 0.2°.

forming a polymeric chain of complexes. The other positions in the coordination sphere are occupied by water molecules.

In previous structure determinations of Cu<sup>II</sup> complexes of N(9)-substituted nucleobases only N(7)-coordination has been encountered. However, in complexes of other metal ions, e.g. Pt, Co, Zn, Ag, simultaneous N(1) and N(7) binding has been found (Table 3). An important feature observed in all these complexes, except in the linear Ag<sup>I</sup> complex, is the presence of a strong interligand hydrogen bond between the exocyclic atom attached to C(6) and the coordination sphere. The formation of this bond seems to be a decisive factor in determining the coordination geometry. N(9)-substituted guanine and hypoxanthine both appear predominantly as N(1)–H tautomers. In metal complexes of these ligands, N(7) is the exclusive binding site. The interligand hydrogen bond is established between the C(6) carbonyl and the coordination sphere. N(9)-substituted adenine has both N(1) and N(7) available for coordination. In tetrahedral and square-planar complexes both N(1) and N(7) have been found simultaneously as ligating atoms, while in octahedral complexes N(7) is the only binding site. This difference in binding pattern may be related to the interligand hydrogen bond mentioned above, which in the octahedral geometry is stereochemically feasible only when N(7) is the coordination site. The fact that no Cu–N(1) bonding has been observed in the normal nucleobases is thus in accordance with the preference of Cu for octahedral coordination.

In the present complex with no exocyclic atom attached at C(6) the coordination geometry adopted is independent of hydrogen-bond formation, leaving the N(1) and N(7) sites equally susceptible to octahedral coordination. The difference in basicity of the N atoms seems to play a secondary role in selection of binding sites. However, in the one known case where tetrahedral coordination is found at only one site, N(1) is preferred to N(7) in accordance with the order of basicity (McCall & Taylor, 1976).

Another interesting aspect of the metal–nucleobase geometry is the large dissymmetry of the exocyclic bond angles at N(7) observed in all the species investigated (Table 3). The angle M–N(7)–C(5) is appreciably larger than M–N(7)–C(8), the average difference

Table 2. *Bond angles (°) in the coordination sphere of copper* ( $\sigma = 0.06$ – $0.07^\circ$ )

N(1)–Cu–N(7)	179.70	O(7)–Cu–N(1)	91.73
O(5)–Cu–O(6)	179.59	O(7)–Cu–N(7)	88.30
O(7)–Cu–O(8)	177.48	O(7)–Cu–O(5)	89.93
N(1)–Cu–O(5)	89.76	O(7)–Cu–O(6)	88.08
N(1)–Cu–O(6)	91.66	O(8)–Cu–N(1)	90.78
N(7)–Cu–O(5)	90.54	O(8)–Cu–N(7)	89.19
N(7)–Cu–O(6)	88.04	O(8)–Cu–O(5)	89.86
		O(8)–Cu–O(6)	92.07

Table 3. *Metal complexes of N(9)-substituted purines*

Compound	Geometry at <i>M</i>	Coordination site ( <i>L</i> )	<i>M</i> — <i>L</i>	$\angle M-N(7)-C(5)$ $\angle M-N(1)-C(2)$	$\angle M-N(1)-C(8)$ $\angle M-N(1)-C(6)$	Reference
[Cu(9-MeHyp) <sub>2</sub> (OH) <sub>2</sub> Cl <sub>2</sub> ]	Octahedral (4 + 2)	N(7)	2.054 (2) Å	135.0°	120.2°	Sletten (1974)
[Cu(9-MeHyp) <sub>2</sub> (OH) <sub>2</sub> SO <sub>4</sub> ]	Octahedral (4 + 2)	N(7)	*2.026 (2)	135.2	120.2	Sletten & Kaale (1977)
[Cu(9-MeGua) <sub>2</sub> (OH) <sub>2</sub> SO <sub>4</sub> ]	Octahedral (4 + 2)	N(7)	*2.018 (5)	132.4	119.9	Sletten & Fløgstad (1976)
[Cu(9-MeGua) <sub>2</sub> (OH) <sub>2</sub> (NO <sub>3</sub> ) <sub>2</sub> ]	Octahedral (4 + 2)	N(7)	2.004 (3)	129.9	122.6	Sletten & Erevik (1977)
[Hg(guanosine)Cl <sub>2</sub> ]	Square-pyramidal	N(7)	2.16 (2)	118	134	Authier-Martin, Hubert, Rivest & Beauchamp (1978)
		O	3.08 (2)			
[Cu(9-MeAde)(OH) <sub>2</sub> SO <sub>4</sub> ]	Octahedral (4 + 2)	N(7)	1.995 (2)	133.6	120.5	Sletten & Thorstensen (1974)
[Cu(9-MeAde) <sub>2</sub> (OH) <sub>2</sub> Cl <sub>2</sub> ]	Octahedral (2 + 4)	N(7)	2.162 (2)	135.0	120.4	Sletten & Ruud (1975)
[Zn(9-MeAde) <sub>2</sub> Cl <sub>2</sub> ]	Tetrahedral	N(1)	2.068 (2)	117.2	123.1	McCall & Taylor (1976)
		N(7)	2.040 (2)	137.2	118.0	
[Zn(9-MeAde)Cl <sub>3</sub> ] <sup>-</sup>	Tetrahedral	N(1)	2.05			McCall & Taylor (1975)
[Co(9-MeAde) <sub>2</sub> Cl <sub>2</sub> ]	Tetrahedral	N(1)	2.030 (7)			De Meester <i>et al.</i> (1973)
		N(7)	2.047 (7)			
[Pt(9-MeAde)Cl <sub>2</sub> (iPrSO) <sub>2</sub> ]	Square-planar	N(1)	2.08 (3)			Lock, Speranzini, Turner & Powell (1976)
		N(7)	2.07 (3)			
[Ag(9-MeAde)NO <sub>3</sub> ]	Linear	N(1)	*2.17 (1)	118.5	122.9	Gagnon & Beauchamp (1977)
		N(7)	2.16 (1)	135.5	119.7	
[Cu(9-Me-6-thioPur)Cl <sub>2</sub> ] <sub>2</sub>	Square-pyramidal	N(7)	1.992 (4)	113.3	142.0	Sletten & Apeland (1975)
		S	2.424 (1)			
[Pd(9-Bzl-6-thioPur) <sub>2</sub> ]	Square-planar	N(7)	*2.07 (1)	109.6		Heitner & Lippard (1974)
		S	2.308 (3)			
[Cu(9-MePur)(OH) <sub>2</sub> SO <sub>4</sub> ]	Octahedral (4 + 2)	N(1)	2.068 (1)	117.9	122.8	This paper
		N(7)	2.030 (1)	133.6	121.8	

\* Average values.

being about 14°. The dissymmetry has been attributed to the steric requirements for the formation of the interligand hydrogen bond (Kistenmacher & Marzilli, 1977); however, in the present complex and in the linear Ag[9-MeAde]NO<sub>3</sub> complex (Gagnon & Beauchamp, 1977) the dissymmetry is approximately the same even though no interligand hydrogen bond is formed. Furthermore, there is no steric interaction between H(6) and the coordination sphere. In the present compound the H(6)···H(81) and H(6)···H(82) distances are both longer than the van der Waals distance. Coordination at N(9), on the other hand, is invariably found to be almost symmetric with respect to the exocyclic bond angles at N(9). Apparently, the coordination angles are determined to a large extent by the intrinsic bonding properties of the ligands with only minor adjustments brought about by steric requirements. In the imidazole ring N(9)—C(4) and N(9)—C(8) are of almost equal length while N(7)—C(5) is significantly longer than N(7)—C(8). Consequently the charge build-up at the N(7)—C(8) side may explain the observed dissymmetry. Theoretical calculations are in progress to determine the most favourable coordination angles.

The length of Cu—N(7) in complexes of the type

$$\begin{array}{c} | \\ >N(7)-Cu-N(7)< \\ | \end{array}$$

has been shown to be a function of the angle between the equatorial plane and the plane of the purine ring (Sletten & Erevik, 1977). According to the curve, a Cu—N(7) distance of 2.030 (1) Å would correspond to a dihedral angle of about 35° which is 16° larger than that observed. Apparently, in the

present compound where N(1) is *trans* to N(7) this simple relationship is not valid, the pyrimidine ring exerting a *trans* effect different from that of the imidazole ring. Cu—N(1), 2.068 (1) Å, is significantly longer than Cu—N(7), reflecting the greater amount of *s* character in the coordinating orbital of the imidazole N atom. This is consistent with corresponding observations in dimeric Cu—adenine and Cu—hypoxanthine complexes (Sletten, 1969, 1970).

In complexes with interligand bonding the coordination polyhedra are usually quite irregular. The Cu—O<sub>eq</sub> and Cu—O<sub>ax</sub> lengths have been found in the ranges 1.95–2.01 Å and 2.35–2.70 Å respectively. In the present compound the equatorial and axial pair of water molecules lie almost symmetrically around the metal centre. Cu—O<sub>eq</sub> of 1.964 (1) and 1.969 (1) Å and Cu—O<sub>ax</sub> of 2.383 (2) and 2.384 (2) Å are probably optimal values for Cu—O bonds in an unstrained (4 + 2) coordination. The ratio between the short (*R<sub>S</sub>*) and long (*R<sub>L</sub>*) Cu—O distances is 0.825 which is somewhat higher than the mean *R<sub>S</sub>*/*R<sub>L</sub>* value of 0.796 quoted for oxygen ligands in an elongated octahedral coordination (Hathaway, 1973).

#### The purine geometry

The purine ring is folded about C(4)—C(5) by 4.3° which is appreciably more than the typical folding angle of 1–2° found in most purines. The influence of the metal ion on the geometry of the purine ligand has not yet been established unambiguously owing to the lack of accurate structural data for the uncomplexed ligand. However, a comparison with the dimensions of

9-MeAde (Kistenmacher & Rossi, 1977) indicates a slight lengthening (0.010–0.015 Å) of the bonds adjacent to the coordination site. A similar effect has also been observed for the Cu(9-MeHyp) complex compared to an average inosine structure (Sletten, 1972).

#### Hydrogen bonding and crystal packing

The molecular packing in the unit cell in the *ab* plane is shown in Fig. 2. Hydrogen bonds are listed in Table 4. A polymeric chain of complexes linked through  $-N(1)-Cu-N(7)-$  bonds runs along **b**. The chains are linked together *via* a three-dimensional network of hydrogen bonds formed between sulphate ions and the coordination spheres. Pairs of coordinated water molecules are bridged by pairs of sulphate O atoms through strong dihydrogen bonds. Sulphate O(1) + O(2), O(2) + O(3), and O(3) + O(4) constitute the bridges between water molecules O(8) + O(5), O(6) + O(8), and O(7) + O(5), respectively, while the fourth bridge between O(6) and O(7) is formed by O(1), O(3) and the hydrate water O(9) (Fig. 2).

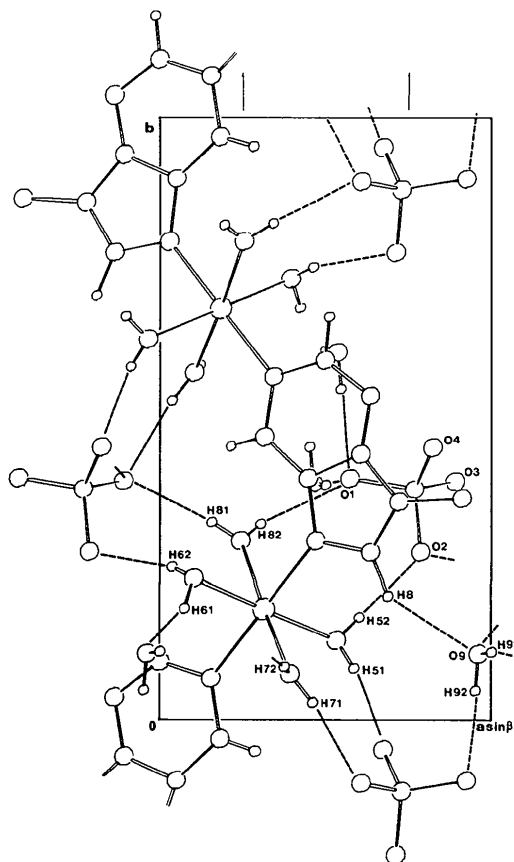


Fig. 2. The *c* projection of the unit cell.

Table 4. *Hydrogen-bond distances and angles*  
[ $\sigma(D \cdots A) = 0.002 \text{ \AA}$ ;  $\sigma(\text{angle}) = 3^\circ$ ]

<i>D-H</i> ... <i>A</i>	Position of acceptor atom	<i>D</i> ... <i>A</i>	<i>H</i> ... <i>A</i>	$\angle D-H$ ... <i>A</i>
C(8)-H(8)···O(9)	<i>x, y, z</i>	3.198 Å	2.30 Å	148°
O(5)-H(51)···O(4)	$\frac{1}{2} - x, -\frac{1}{2} + y, \frac{1}{2} - z$	2.662	1.97	166
O(5)-H(52)···O(2)	<i>x, y, z</i>	2.690	1.86	169
O(6)-H(61)···O(9)	$-1 + x, y, z$	2.629	1.82	170
O(6)-H(62)···O(2)	$-1 + x, y, z$	2.662	1.96	171
O(7)-H(71)···O(3)	$\frac{1}{2} - x, -\frac{1}{2} + y, \frac{1}{2} - z$	2.836	2.08	169
O(7)-H(72)···O(3)	$-\frac{1}{2} + x, \frac{1}{2} - y, \frac{1}{2} + z$	2.908	2.20	160
O(8)-H(81)···O(3)	$-1 + x, y, z$	2.854	2.07	165
O(8)-H(82)···O(1)	<i>x, y, z</i>	2.817	2.14	163
O(9)-H(91)···O(1)	$\frac{1}{2} + x, \frac{1}{2} - y, \frac{1}{2} + z$	2.753	2.01	174
O(9)-H(92)···O(1)	$\frac{1}{2} - x, -\frac{1}{2} + y, \frac{1}{2} - z$	2.805	2.02	166

Table 5. *Bond lengths (Å) and angles (°) in the sulphate ion* [ $\sigma(l) = 0.001 \text{ \AA}$ ;  $\sigma(\text{angle}) = 0.1^\circ$ ]

O(1)-S-O(2)	108.9	S-O(1)	1.474
O(1)-S-O(3)	109.9	S-O(2)	1.472
O(1)-S-O(4)	110.4	S-O(3)	1.467
O(2)-S-O(3)	109.3	S-O(4)	1.457
O(2)-S-O(4)	108.4		
O(3)-S-O(4)	110.0		

In previous structure investigations of Cu-nucleobase complexes the sulphate ion has been found to bind either to the metal or to the base. The different bonding modes may be rationalized in the following way: the direct metal-sulphate bond observed in Cu(9-MeAde) (Sletten & Thorstensen, 1974) is favoured by an interligand hydrogen bond between the sulphate and the C(6) amino group. In guanine and hypoxanthine, the sulphate interacts directly with the base since no interligand hydrogen bond can be formed involving  $SO_4^{2-}$  (Sletten & Fløgstad, 1976; Sletten & Kaale, 1977). In the present structure, where the 9-MePur ligand has no hydrogen donors, the sulphate ion is bonded to the coordination sphere. The geometry of the sulphate ion is quite regular (Table 5).

The interplanar distance between purines related by a centre of symmetry is 3.47 Å; however, the rings are almost non-overlapping when viewed perpendicular to the plane. The usual purine stacking interaction retained in most monodentate metal complexes is effectively prevented by the bidentate bonding.

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## The Crystal and Molecular Structure of *N*-*tert*-Butyldithiophthalimide

BY MAZHAR-UL-HAQUE\*

*Department of Chemistry, University of Petroleum and Minerals, Dhahran, Saudi Arabia*

AND MOHAMMAD BEHFOROZ

*Department of Chemistry, Pahlavi University, Shiraz, Iran*

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### Abstract

$C_{12}H_{13}NO_2S_2$  is triclinic,  $a = 8.627$  (3),  $b = 8.994$  (2),  $c = 9.606$  (3) Å,  $\alpha = 103.17$  (3),  $\beta = 114.28$  (3),  $\gamma = 95.77$  (3)°, space group  $P\bar{1}$ ,  $Z = 2$ . The structure was refined to  $R = 0.033$  for 2023 observed reflections. The angle between the planes C–S–S and S–S–N is 97.8°, and the S–S bond length is 2.007 (1) Å.

and an S–S length of 2.02 Å, indicating the presence of a considerable amount of  $\pi$  character. In this investigation, another dithioimide, having a phthalimide and an alkyl group in place of the two succinimide moieties on the S–S bond, was studied to compare the effect of these groups on the bond lengths and angles.

### Introduction

We have already reported the structure of *N,N'*-dithio-disuccinimide (Mazhar-ul-Haque & Behforouz, 1974); it has an angle of about 85° between the two S–S–N planes

\* To whom correspondence should be addressed.

### Experimental

*N*-*tert*-Butyldithiophthalimide is a white crystalline material (m.p. 378–379 K), which was prepared by the reaction of *tert*-butylthiosulphenyl chloride with phthalimide in the presence of triethylamine (Behforouz, Firouzabadi & Ardakani, 1971).