

Dinitratodiaquabis(9-methylguanine)copper(II)*

BY EINAR SLETTEN AND GAUTE EREVIK

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

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Abstract. $\text{Cu}(\text{NO}_3)_2(\text{H}_2\text{O})_2(\text{C}_6\text{H}_7\text{N}_5\text{O})_2$, monoclinic, $P2_1/c$, $a = 5.4087(8)$, $b = 16.696(15)$, $c = 11.8414(7)$ Å, $\beta = 109.874(15)^\circ$, $Z = 2$, $D_m = 1.84$, $D_x = 1.829$ g cm $^{-3}$, Mo $K\alpha$, $\lambda = 0.71069$ Å. Diffractometer data were refined by full-matrix least squares to an R of 0.072 including all reflexions. Cu^{2+} is situated at a centre of symmetry and is octahedrally surrounded by two water molecules and two guanine N(7) atoms in the basal plane, and NO_3^- ions axially. The nitrate also participates in two hydrogen bonds to a guanine involving N(1)–H and the amino group.

Introduction. The compound was synthesized by dissolving the corresponding chloro complex in a water/ethanol mixture and adding KNO_3 in excess. A wedge-shaped crystal, $0.10 \times 0.15 \times 0.40$ mm, was used for data collection and determination of cell dimensions. The experimental procedure is described elsewhere (Sletten, 1974). Within the sphere of reflexion limited at $\sin \theta/\lambda = 0.64$, 2178 reflexions were recorded; of these, 238 were negative and set equal to zero in the subsequent calculations. The least-squares refinement including all reflexions converged at an R of 0.072. The refinement was also carried out excluding 'less-thans' (2σ cutoff). In the latter case R was 0.052; however, the standard deviations were on average 5% higher. All calculations were performed with XRAY 72 (Stewart, Kruger, Ammon, Dickinson & Hall, 1972). Atomic parameters are listed in Tables 1 and 2.†

Discussion. The Cu ion is situated at a centre of symmetry and has regular (4 + 2) coordination (Fig. 1). The equatorial positions are occupied by two water molecules and two N(7) atoms. The length of Cu–N(7) may be related to the π interaction of the guanine ring with the Cu coordination polyhedron. An optimal π interaction between the p_z orbital of N(7) and the d_{xy} orbital of Cu^{II} is expected when the angle between the guanine ring and the basal plane is close to 90° . In Fig. 2 Cu–N(7) distances *vs* dihedral angles are plotted for

a number of Cu–purine complexes. The plot shows a correlation between the two variables, corroborating the above assumption. The variation in dihedral angle is probably determined by the accommodation of *inter*- and *intra*-complex hydrogen bonds. Cu–N(7) is less asymmetric than in analogous Cu–purine complexes, where Cu–N(7)–C(5) has been found to be close to 135° , *i.e.* approximately 5° greater than in the present compound (Sletten, 1976).

Table 1. The final positional parameters ($\times 10^5$) for the non-hydrogen atoms

Standard deviations are in parentheses.

	<i>x</i>	<i>y</i>	<i>z</i>
Cu	100000	0	0
C(2)	72501 (59)	7140 (17)	41744 (24)
C(4)	78647 (55)	–2898 (15)	30669 (23)
C(5)	90029 (55)	1722 (15)	24162 (22)
C(6)	95405 (61)	9849 (17)	27362 (24)
C(8)	87511 (60)	–10273 (18)	17306 (25)
C(9)	66928 (86)	–17520 (19)	30530 (25)
N(1)	84930 (54)	12109 (14)	36137 (21)
N(2)	64031 (66)	10441 (18)	50000 (26)
N(3)	69400 (44)	–648 (14)	39422 (18)
N(7)	95124 (47)	–3091 (13)	15457 (19)
N(9)	77556 (48)	–10530 (13)	26414 (19)
N(10)	70206 (52)	18403 (14)	–664 (21)
O(6)	107843 (45)	14817 (12)	23670 (18)
O(10)	68128 (42)	10925 (11)	–1015 (18)
O(11)	54688 (50)	22349 (13)	2762 (23)
O(12)	87125 (44)	21817 (12)	–3808 (19)
O(13)	128886 (50)	6931 (16)	9449 (22)

Table 2. Final positional ($\times 10^4$) and thermal ($\times 10^3$) parameters for the hydrogen atoms

The isotropic temperature factor = $\exp(-8\pi^2 U \sin^2 \theta/\lambda^2)$.

	<i>x</i>	<i>y</i>	<i>z</i>	$U(\text{Å}^2)$
H(1)	8762 (57)	1685 (16)	3832 (23)	27 (8)
H(8)	8842 (53)	–1529 (16)	1287 (23)	34 (8)
H(21)	5506 (70)	749 (20)	5312 (27)	55 (11)
H(22)	6437 (65)	1521 (20)	5087 (27)	45 (11)
H(31)	12430 (69)	1018 (21)	1401 (30)	59 (13)
H(32)	13823 (72)	809 (23)	700 (31)	57 (14)
H(91)	6986 (61)	–2163 (18)	2649 (26)	41 (10)
H(92)	7415 (68)	–1784 (19)	3925 (31)	58 (11)
H(93)	4842 (79)	–1695 (22)	2887 (32)	80 (14)

* Crystallographic Studies on Metal–Nucleotide Base Complexes. IX.

† Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 32441 (16 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

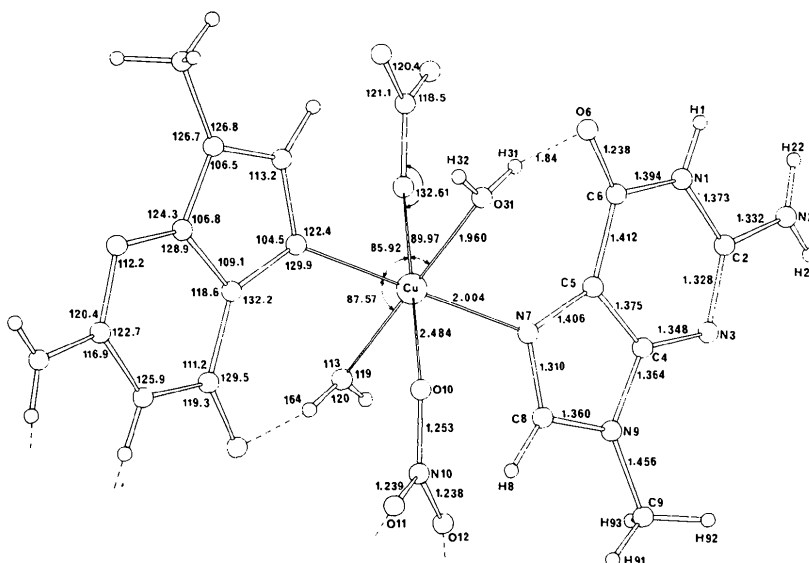


Fig. 1. Interatomic distances (Å) and angles ($^{\circ}$) in the complex unit. The σ 's in bond lengths are: Cu—O(N) 0.003 Å, C—C(N)(O) 0.004–0.005 Å. The σ 's for angles involving non-hydrogen atoms are in the range 0.02–0.03 $^{\circ}$.

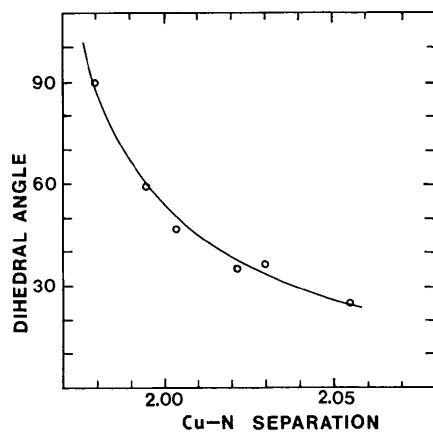


Fig. 2. The Cu—N bond lengths vs the dihedral angle between the purine plane and the basal plane in Cu^{II} -purine complexes.

In axial position, NO_3^- is unidentate at 2.484 Å. The Cu—O—N angle of 132.6° is appreciably above the range 110 – 120° generally observed at the coordinated O in corresponding nitrato complexes (Addison, Logan & Wallwork, 1971). Generally the metal ion lies in the

plane through NO_3^- ; however, in this compound Cu^{2+} deviates by 0.77 Å. The relatively weak metal coordination is probably adjusted to the geometrical requirement of the two hydrogen bonds involving the nitrate and guanine (Fig. 3, Table 3). However, the hydrogen-bond arrangement is also considerably strained with a dihedral angle of 25° between guanine and NO_3^- . There is also a close contact [C(8)—H...O(12)] between NO_3^- and guanine within the same complex unit, which may be considered a weak hydrogen bond.

The three O atoms in NO_3^- have fairly large thermal parameters with their main vibrational amplitudes directed approximately normal to the NO_3^- plane, exhibiting a riding motion relative to the N atom. O(11), which is involved in only one hydrogen bond, has the largest thermal motion. However, a riding-motion correction would not compensate for the differences in bond lengths between the coordinated and the uncoordinated N—O bonds. It has been shown that the length of the coordinated N—O bond is related to the M—O distance (Morosin, 1970). Considering only the more accurate determinations of Cu^{II} - NO_3^- complexes, a

Table 3. Hydrogen-bond distances and angles

	Position of acceptor atom	Distances (Å)		Angle ($^{\circ}$) D—H...A
		D...A	H...A	
N(2)—H(21)...N(3)	$1 - x, y, 1 - z$	3.008 (4)	2.15 (4)	176 (3)
N(2)—H(22)...O(11)	$x, \frac{1}{2} - y, \frac{1}{2} + z$	2.955 (4)	2.17 (3)	165 (4)
N(1)—H(1)...O(12)	$x, \frac{1}{2} - y, \frac{1}{2} + z$	2.922 (3)	2.11 (3)	164 (3)
O(13)—H(31)...O(6)	x, y, z	2.677 (4)	1.84 (4)	164 (4)
O(13)—H(32)...O(10)	$1 + x, y, z$	2.876 (4)	2.19 (4)	176 (4)
C(8)—H(8)...O(12)	$2 - x, y, z$	3.105 (4)	2.25 (3)	143 (2)

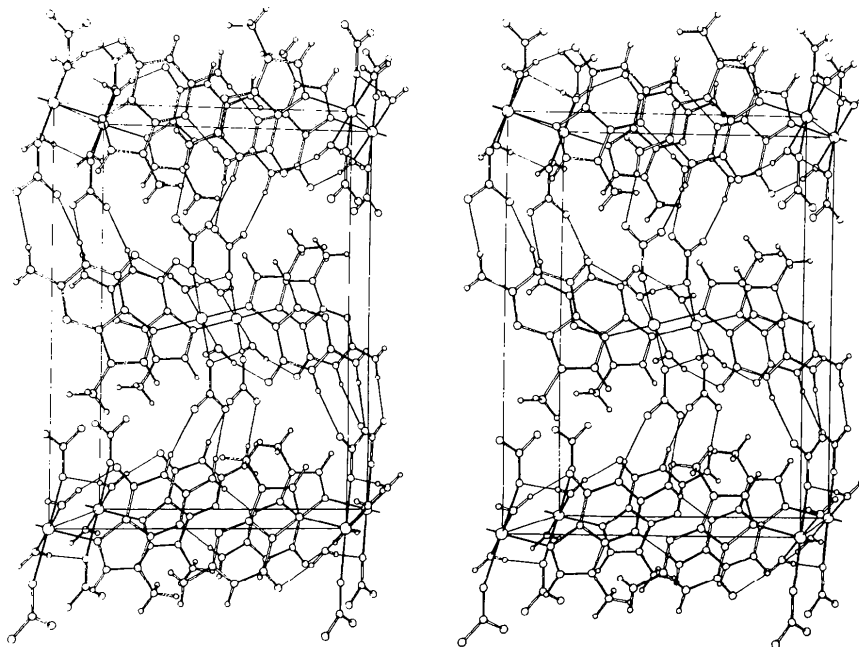


Fig. 3. Stereoscopic drawing of the crystal packing viewed along **a** with **c** parallel to the interocular line.

N—O range of 1.241–1.306 Å corresponds to a Cu—O range of 2.65–1.98 Å. The N(10)—O(10) bond of 1.253 Å *vs* Cu—O(10) of 2.484 Å is consistent with the observed trend.

The puckering of the guanine ligand is more pronounced in the present compound than in any similar complexes. The atoms in the C=O group are 0.06 and 0.19 Å out of plane, respectively, while the amino N atom deviates 0.10 Å on the opposite side of the plane. The relatively large deviation of C=O may be explained by the short contact to NO₃⁻, the O(6)···N(10) distance being 2.969 Å.

A stereoscopic drawing of the packing is shown in Fig. 3. Pairs of centrosymmetrically related guanine ligands are connected by hydrogen bonds involving N(3) and one of the amino H atoms. In the **b** direction the complex units are held together *via* the two hydrogen bonds between NO₃⁻ and guanine. Complexes separated by one unit of translation along **a** are connected through a water—NO₃⁻ hydrogen bond.

Generally the tendency of purine bases to associate in stacks is not prevented by the introduction of metal ions. However, in crystal structures where special crystallographic symmetry requirements are imposed, as in the present compound, the usual stacking interaction does not occur.

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