

Metal Complexes of Purine-N-Oxides.

II. The Crystal Structure of *Catena-μ-(4-aminoimidazole-5-carboxamidoxime) Diaquo Copper(II) Sulphate Trihydrate*, a Degradation Product of Adenine-N¹-Oxide

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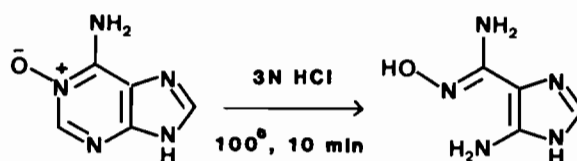
Abstract

[Cu(C₄H₇N₅O)(H₂O)₂SO₄]·3H₂O, monoclinic, space group *Cc*, *a* = 13.652(1) Å, *b* = 14.630(1) Å, *c* = 6.795(1) Å, β = 95.34(8)°, *Z* = 4. 1479 independent intensities above background were collected on a CAD-4 diffractometer using MoKα radiation. The structure was refined by full-matrix least-squares to *R* = 0.016. Adenine-N¹-oxide is degraded at a higher pH than expected when Cu ions are present. The degradation product is formed by scission of the C2-N1 and C2-N3 bonds. N1 is placed in a *cis* planar configuration to N7 by a rotation around the C5-C6 bond, thus enabling N1, N7 equatorial chelation to copper, which has a 4 + 2 octahedral coordination. Two water molecules occupy the remaining equatorial positions, while the axial positions are occupied by a sulphate group and N3 of an adjacent ligand. The coordination bond lengths are Cu-N1 = 1.960 Å, Cu-N7 = 1.972 Å, Cu-O2 = 1.949 Å, Cu-O4 = 1.987 Å, Cu-O9 = 2.500 Å, Cu-N3 = 2.793 Å.

Introduction

In a previous paper we described the crystal structure of a copper(II) complex of adenine-N¹-oxide, AdNO, obtained in basic solution [1]. UV data indicate that complexation also takes place at lower pH [2], but so far attempts to isolate these compounds have been unsuccessful. Sundaralingam and coworkers have tried to isolate such complexes both in strongly acidic perchloric solution and from less acidic sulphuric acid solution. In the first case a bis complex of the degraded adenine-N¹-oxide was isolated [3] and in the second case only the sulphate salt of the protonated ligand crystallized from solution [4].

The degradation of AdNO is reported to be quantitative after 10 minutes of refluxing at 100 °C in 3N HCl [5]:



By monitoring the UV spectrum for AdNO over the complete pH range at room temperature we detected an irreversible change at pH ≈ -0.3. The synthetic procedure reported for making the diaquo-AdNO-copper(II) sulphato complex involves dissolving the ligand in 1N H₂SO₄ prior to complexation [6]. At this pH, according to the UV data, the AdNO ring is still intact. However, the use of 1N perchloric acid prior to copper addition has proved to give ring opening [3]. This may be explained by invoking metal ion catalysis of the AdNO degradation reaction at this pH. In an attempt to circumvent this problem we modified the procedure for making the diaquo sulphato complex by using less acidic solution. However, the crystals obtained turned out to be those of a Cu complex of degraded AdNO.

Experimental

Preparation

100 mg adenine-N¹-oxide was dissolved in 0.5 N H₂SO₄, and 1 g CuSO₄·5H₂O in 1.5 ml H₂O was added [6]. Deep green needles crystallized from the refrigerated solution.

Crystal Data

[Cu(C₄H₇N₅O)(H₂O)₂SO₄]·3H₂O, F.W. 390.81, monoclinic, *Cc* (No. 9). Cell dimensions: *a* = 13.652(1) Å, *b* = 14.630(1) Å, *c* = 6.795(1) Å, β = 95.34(8)°, *V* = 1351.3(6) Å³. *Z* = 4, *D_x* = 1.921 g cm⁻³, μ(MoKα) = 18.26 cm⁻¹.

Crystallography

A crystal of dimensions 0.23 × 0.21 × 0.48 mm was mounted approximately along *c*. The cell parameters were determined at 20 °C from 25 centered

reflexions on an Enraf-Nonius CAD-4 diffractometer. The data were collected by the ω -scan technique. The scan rate was determined by a fast prescan. Reflexions having $\sigma(I)/I \geq 0.75$ 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 would not exceed 60 seconds. Backgrounds were measured by extending the scan by 25% on either side of the peak. A total of 1479 independent reflexions were recorded in the range $1^\circ \leq \theta \leq 27^\circ$. Of these 1469 had $I > 2\sigma_c$ where σ_c is the estimated error due to counting statistics. During data collection three standard reflexions were remeasured every two hours to check the stability of crystal and electronics. The intensities of the standards were plotted and showed fluctuations of less than 2%. The expression used for calculating the random error in any one reflexion is: $\sigma_1 = [\sigma_c^2 + (0.02\sigma_c^2)^2]^{1/2}$. Here both counting statistics errors and errors due to instrumental instability are taken into account. The data were corrected for absorption using Gaussian integration with grid $8 \times 8 \times 14$, giving transmission factors in the range 0.71–0.65. The usual corrections for Lorentz and polarization effects were carried out.

The structure was solved by direct methods and refined by full-matrix least-squares calculations. Isotropic refinement led to $R = \sum |F_o| - |F_c| / \sum |F_o| = 0.068$ and $R_w = [\sum w(|F_o| - |F_c|)^2 / \sum w |F_o|^2]^{1/2} = 0.093$. After anisotropic refinement the hydrogen atoms were located from a difference Fourier map, and were included in the refinement with isotropic temperature factors. In the final least-squares cycles the extinction parameter was included, and refined, $g = 5.34 \times 10^{-8}$. The agreement factors at convergence were $R = 0.016$ and $R_w = 0.022$. The goodness of fit ratio was 1.70. The refinement was based on 1469 reflexions with $F^2 > 2\sigma_F^2$.

The refined coordinates and isotropic equivalent thermal parameters are listed in Table I. Tables of anisotropic temperature factors and structure factors are available from the authors on request.

The scattering curves used were those of Cromer and Waber [7]. All calculations were carried out on a PDP 11/55 computer using the Enraf Nonius Structure Determination Programs (SDP) [8].

Results and Discussion

The bond distances and bond angles of the complex unit are given in Fig. 1 and Table II. The N1–C2 and the N3–C2 bonds of AdNO have been cleaved

TABLE I. Final Atomic Parameters with Their Estimated Standard Deviations from the Least-squares Refinement. For the anisotropically refined non-hydrogen atoms the isotropic equivalent thermal parameter is given: $B_{\text{eq}} = 4/3 \sum_i \beta_{ij} a_i^2 a_j^2$. Hydrogen atoms were isotropically refined: $\exp[-B \sin^2 \theta / \lambda^2]$.

Atom	x	y	z	B (Å ²)
Cu	0.000	0.20166(2)	0.000	1.696(4)
C4	-0.0752(2)	-0.0614(2)	-0.1223(3)	1.65(3)
C5	-0.0164(2)	0.0122(1)	-0.0713(3)	1.52(3)
C6	0.0871(2)	0.0264(2)	-0.0009(3)	1.61(4)
C8	-0.1592(2)	0.0666(2)	-0.1758(3)	1.89(4)
N1	0.1066(1)	0.1118(1)	0.0363(3)	1.76(3)
N3	-0.0578(1)	-0.1542(1)	-0.1299(3)	1.98(3)
N6	0.1520(2)	-0.0415(1)	0.0202(3)	2.31(4)
N7	-0.0713(1)	0.0921(1)	-0.1042(3)	1.72(3)
N9	-0.1644(1)	-0.0252(1)	-0.1894(3)	1.85(3)
O1	0.2072(1)	0.1297(1)	0.0906(3)	2.22(3)
O2	0.0692(2)	0.2975(1)	0.1562(3)	2.82(4)
O3	0.0772(2)	0.4573(2)	-0.0216(4)	5.44(6)
O4	-0.1124(1)	0.2870(1)	-0.0549(3)	2.12(3)
O5	0.3681(2)	0.0664(1)	0.6706(3)	3.16(4)
O6	0.4204(2)	0.1162(2)	0.0690(3)	3.72(4)
O7	0.1964(1)	0.2540(1)	-0.5317(3)	2.61(3)
O8	0.2424(1)	0.2607(1)	-0.1803(3)	2.48(3)
O9	0.0704(1)	0.2524(1)	-0.3086(3)	2.42(3)
O10	0.1649(1)	0.3892(1)	-0.3495(3)	2.62(3)
S	0.16819(4)	0.28805(3)	-0.34024(8)	1.563(9)
H1	0.224(2)	0.157(2)	0.009(5)	3.1(7)*
H3A	-0.013(2)	-0.176(2)	-0.033(5)	2.5(6)*
H3B	-0.111(2)	-0.189(2)	-0.139(5)	2.5(6)*
H6A	0.215(2)	-0.029(2)	0.066(5)	2.9(6)*
H6B	0.139(2)	-0.090(2)	-0.020(4)	2.7(6)*
H8	-0.204(3)	0.102(2)	-0.210(5)	3.3(7)*
H9	-0.208(3)	-0.054(3)	-0.237(5)	4.1(8)*
H21	0.113(3)	0.282(2)	0.241(5)	3.0(7)*
H22	0.070(3)	0.345(3)	0.107(6)	4.6(9)*
H31	0.112(4)	0.507(4)	0.030(9)	8(1)*
H32	0.096(3)	0.448(3)	-0.137(6)	4.6(8)*
H41	-0.115(3)	0.334(3)	-0.000(5)	3.9(8)*
H42	-0.180(3)	0.269(2)	-0.086(5)	3.6(7)*
H51	0.401(2)	0.021(2)	0.663(5)	3.2(7)*
H52	0.381(2)	0.084(2)	0.777(5)	3.7(7)*
H61	0.471(3)	0.132(3)	0.115(6)	5(1)*
H62	0.392(6)	0.133(6)	0.15(1)	15(3)*

and subsequently N1 has been brought into the coordinating position by a rotation of 180° about the C5–C6 bond. The copper ion is seen to adopt a (4 + 2) octahedral coordination. N7, N1 and two water molecules bind in the equatorial plane while the axial positions are occupied by the sulphate ion and N3 from an adjacent ligand. The bridging ligands are related by *c*-glide translations, forming a polynuclear chain.

The corresponding perchlorate [3] is a square planar, centrosymmetric bis-complex involving N1, N7 coordination as in the present compound. The

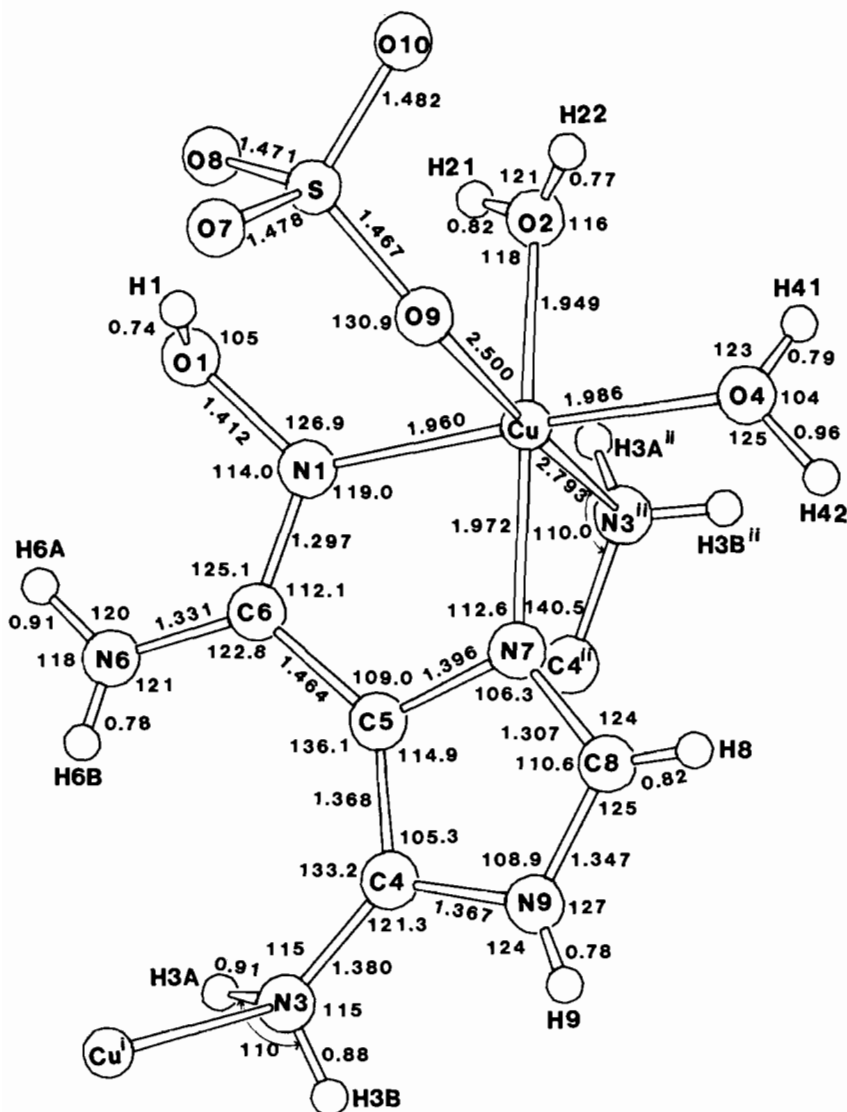


Fig. 1. Interatomic distances (Å) and angles ($^{\circ}$) in the complex unit. The σ 's in bond lengths are: Cu–N(O) and S–O 0.002 Å, C–C(N) and N–O 0.003 Å, N(C)–H 0.03 Å, O–H = 0.04 Å. The σ 's in angles at C(N)(O), not involving H atoms are 0.2° ; those involving H atoms $2\text{--}4^{\circ}$. Bond angles at Cu and S are listed in Table II. Symmetry operations: i: $x, -y, z - \frac{1}{2}$; ii: $x, -y, z + \frac{1}{2}$.

TABLE II. Bond Angles ($^{\circ}$) at Cu and S with Estimated Standard Deviations in Parentheses.

Bond angles at Cu:			
N1–Cu–N3 ⁱⁱ	89.35(6)	N3 ⁱⁱ –Cu–O9	172.90(5)
N1–Cu–N7	80.56(7)	N7–Cu–O2	168.04(8)
N1–Cu–O2	95.61(7)	N7–Cu–O4	95.54(6)
N1–Cu–O4	175.50(7)	N7–Cu–O9	98.96(6)
N1–Cu–O9	88.03(6)	O2–Cu–O4	88.65(8)
N3 ⁱⁱ –Cu–N7	87.11(6)	O2–Cu–O9	92.19(7)
N3 ⁱⁱ –Cu–O2	81.49(7)	O4–Cu–O9	90.37(6)
N3 ⁱⁱ –Cu–O4	92.72(6)		
Bond angles at S:			
O7–S–O8	109.9(1)	O8–S–O9	111.6(1)

TABLE II. (continued)

O7–S–O9	108.9(1)	O8–S–O10	108.6(1)
O7–S–O10	108.0(1)	O9–S–O10	109.7(1)

Symmetry operation: ii: $x, -y, z + \frac{1}{2}$.

lengths of the metal–nitrogen bonds are surprisingly similar in the two complexes, considering the large differences in coordination geometries; Cu–N7 = 1.970(4) Å, Cu–N1 = 1.968(4) Å in the perchlorate compared to 1.972(2) Å and 1.960(2) Å, respectively, in the sulphato complex. The asymmetry seen in the Cu–N bonds in the sulphato complex is matched

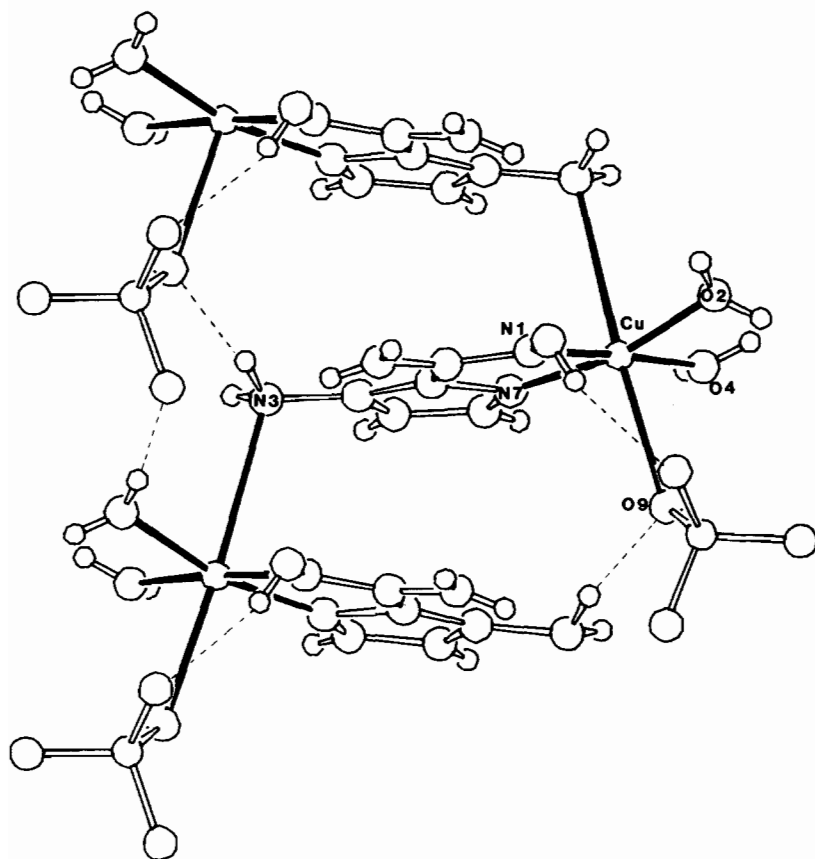


Fig. 2. The vertical stacking of imidazole rings in the polynuclear chain.

TABLE III. Hydrogen Bond Distances and Angles.

D-H...A	Position of acceptor atom	D...A	H...A	\angle D-H...A
N3-H3A...O9	$x, -y, \frac{1}{2} + z$	3.031(2)	2.14(3)	167(3)
N3-H3B...O8	$x - \frac{1}{2}, y - \frac{1}{2}, z$	2.989(2)	2.13(3)	165(3)
N6-H6A...O5	$x, -y, z - \frac{1}{2}$	3.052(3)	2.21(3)	155(3)
N6-H6B...O7	$x, -y, z + \frac{1}{2}$	3.193(2)	2.53(3)	145(3)
N9-H9...O10	$x - \frac{1}{2}, y - \frac{1}{2}, z$	2.777(2)	2.01(4)	171(4)
O1-H1...O8	x, y, z	2.731(2)	2.02(4)	162(3)
O2-H21...O7	$x, y, z + 1$	2.690(2)	1.88(4)	170(3)
O2-H22...O3	x, y, z	2.638(3)	1.87(4)	177(4)
O3-H31...O10	$x, 1 - y, \frac{1}{2} + z$	2.753(3)	1.84(6)	172(5)
O3-H32...O10	x, y, z	2.808(3)	1.99(4)	159(4)
O4-H41...O5	$x - \frac{1}{2}, \frac{1}{2} - y, z - \frac{1}{2}$	2.663(3)	1.88(4)	169(4)
O4-H42...O7	$x - \frac{1}{2}, \frac{1}{2} - y, z + \frac{1}{2}$	2.697(2)	1.79(4)	155(3)
O5-H51...O6	$x, -y, z + \frac{1}{2}$	2.867(3)	2.14(4)	152(3)
O5-H52...O6	$x, y, 1 + z$	2.830(3)	2.06(4)	174(3)
O6-H61...O9	$\frac{1}{2} + x, \frac{1}{2} - y, \frac{1}{2} + z$	2.875(3)	2.19(5)	148(4)
O6-H62...O4	$\frac{1}{2} + x, \frac{1}{2} - y, \frac{1}{2} + z$	2.991(3)	2.35(9)	149(9)

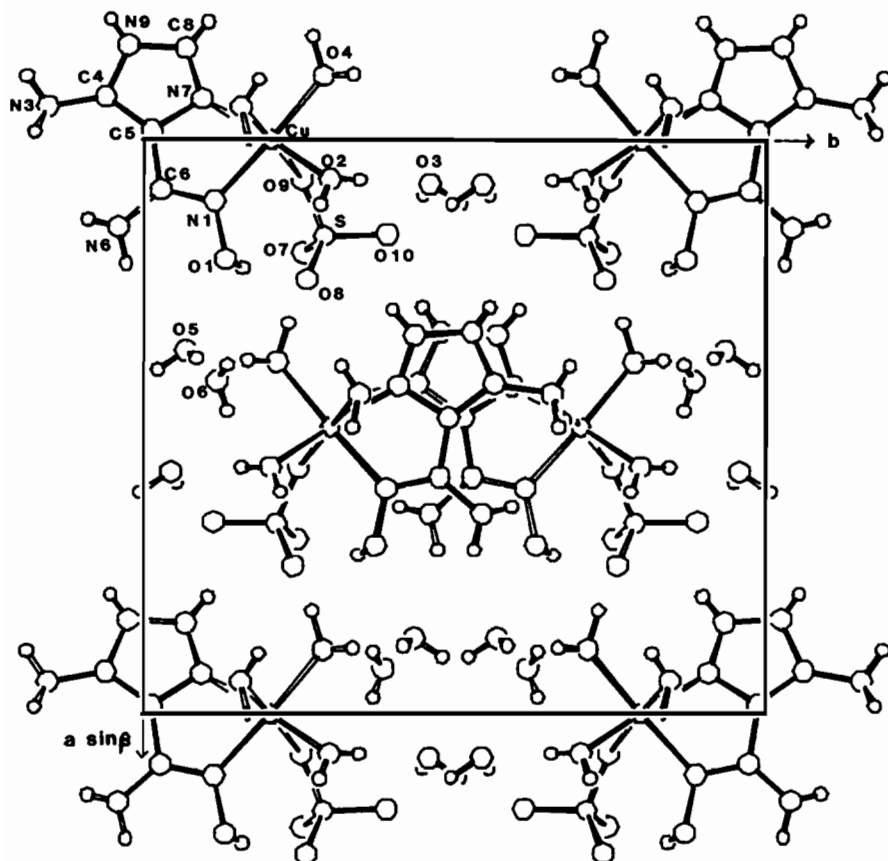


Fig. 3. The crystal packing in the unit cell, viewed down the c -axis.

by a corresponding asymmetry in the water coordination, $\text{Cu}-\text{O}2 = 1.949(2) \text{ \AA}$ and $\text{Cu}-\text{O}4 = 1.986(2) \text{ \AA}$, reflecting slightly different *trans*-effects. The lengths of the $\text{Cu}-\text{O}$ bonds are apparently related to the number of hydrogen bonds formed by the coordinating water molecules. From Table III it is seen that O4 has a complete tetrahedral surrounding, participating in three H bonds, while O2 participates in only two.

The agreements between bond lengths and bond angles in the two compounds are within 1–2 standard deviations except for the $\text{C}4-\text{N}3$ bond which is significantly longer in the sulphate (0.023 \AA). The lengthening is caused by the axial coordination of N3 ($\text{Cu}-\text{N}3 = 2.793(2) \text{ \AA}$). The angles around N3 indicate partial sp^3 hybridization which facilitates metal coordination.

The vertical stacking of imidazole rings is shown in Fig. 2. The ring planes are almost parallel, the dihedral angle being 5.1° . The mean interplanar distance along the stack is 3.26 \AA . Considering the large degree of overlap this is slightly shorter than what is normally found in similar stacking patterns

[9]. There is, of course, a mutual influence between the stacking forces and the axial N3 coordination. The $\text{Cu}-\text{N}3$ distance of 2.793(2) \AA is definitely longer than expected.

The hydrogen bonding network in the crystal involves all acceptor atoms and donor groups (Table III, Fig. 3). The $\text{N}1-\text{O}1-\text{H}1$ group is rotated around $\text{N}1-\text{O}1$ out of the equatorial coordination plane, accommodating an *intramolecular* H bond between O1 and O8 in the sulphate. The amino group is almost coplanar with the five-membered chelate ring. The short contact between the amino proton H6A and O1 ($\text{H}6\text{A}\cdots\text{O}1 = 2.34 \text{ \AA}$, $\angle\text{N}6-\text{H}6\text{A}\cdots\text{O}1 = 100^\circ$) may be characterized as a sterically strained *intramolecular* H bond. The influence of hydrogen bonding on the length of $\text{S}-\text{O}$ bonds has already been pointed out [10]. There seems to exist an inverse relationship between bond length and the extent of H bond involvement. The distances $\text{S}-\text{O}10 = 1.482(1) \text{ \AA}$, $\text{S}-\text{O}7 = 1.478(2)$, $\text{S}-\text{O}8 = 1.471(1) \text{ \AA}$ correspond to three relatively strong H bonds: two strong and one very weak H bonds, and two H bonds, respectively.

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