The hydrogen-bond distances are all in good agreement with the corresponding distances in hydrogen-bonded compounds containing donor ring-NH groups and acceptor carbonyl oxygen atoms while the hydrogen-bond angles are well within the maximum allowed deviation from 180° (Donohue, 1968).

We thank the South African CSIR for the diffractometer data collection. The work was supported by the CSIR and the University of Cape Town's research grants.

References


Crystallographic Studies of Metal--Nucleotide Base Complexes.
III. Dichlorobis-(9-methyl-6-oxypurine)diaquocopper(II) Trihydrate

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\[[(\text{C}_6\text{H}_6\text{N}_4\text{O}_2)^2\text{CuCl}_2\cdot 2\text{H}_2\text{O}].3\text{H}_2\text{O}\] crystallizes as deep-blue prisms from an acidic solution. The space group is \(\text{C}2/c\) with \(a=16.858\), \(b=8.541\), \(c=14.293\) Å, \(\beta=91.02^\circ\), \(Z=4\). The structure determination is based on diffractometer data measured with Nb-filtered Mo Kα radiation. Final \(R\) is 0.027 for the 2029 observed reflexions. The copper ion is located at a centre of symmetry and binds to the purine ring through nitrogen N(7); Cu-N = 2.054 Å. The copper coordination is (4 + 2) with a pair of centro-symmetrically related water molecules completing the equatorial coordination, Cu-O = 1.972 Å, and the axial sites occupied by chloride ions, Cu-Cl = 2.787 Å. The water molecules in the coordination sphere form intramolecular hydrogen bonds to the carbonyl substituent on C(6).

Introduction

The purine bases incorporated in the nucleic acids have several potential coordination sites. The nitrogen atoms N(1), N(3) and N(7) are more or less exposed, and so is the substituent in the 6-position. In the reversible unwinding and rewinding of DNA strands caused by certain transition elements, the coordination...
of the metal may also involve phosphate groups. This is the third in a series of papers dealing with the crystal structures of copper complexes of nucleic acid components. The two previous papers present the structures of copper complexes with unsubstituted adenine and hypoxanthine ligands (Sletten, 1969, 1970).

Table 1. *Observed and calculated structure factors multiplied by 10*
Copper complexes of other simple purines have been described (de Meester & Skapski, 1971, 1973; Carrabine & Sundaralingam, 1970; Terzis, Beauchamp & Rivest, 1973). None of the compounds referred to above is directly related to biological systems of nucleic acids where N(9) carries a ribosyl residue. The present paper describes the crystal structure of a copper–purine complex in which N(9) is blocked by a methyl group. It is expected that the methyl-substituted hypoxanthine molecule will have the same ligand properties at neutral pH as the corresponding nucleoside, inosine. A preliminary account of this work has been published (Sletten, 1971).

Experimental

The compound was synthesized by dissolving 9-methylhypoxanthine in water and adding a 1 M solution of CuCl₂ in excess (Weiss & Venner, 1965). Blue prisms crystallized from the solution the next day. Weissenberg films indicated space group \( \text{Cc} \) or \( \text{C}2/c \). Subsequent refinement confirmed space group \( \text{C}2/c \).

Crystal data

\[ \text{(C}_6\text{H}_6\text{N}_4\text{O})_2\text{CuCl}_2\cdot 2\text{H}_2\text{O}, \text{F.W. 515.8,} \]

\( a = 16.858(4), \quad b = 8.541(4), \quad c = 14.293(11) \text{ Å,} \)

\( \beta = 91.02(5) \degree, \quad D_m = 1.65 \text{ g cm}^{-3}, \)

\( V = 2090 \text{ Å}^3, Z = 4, \lambda(\text{Mo K} \alpha) = 0.71069 \text{ Å,} \)

Cell dimensions were obtained from a least-squares treatment of 2θ settings of 13 reflections as measured on a Siemens AED diffractometer. None of the differences between observed and calculated 2θ values was greater than 0.02°.

The crystal used for data collection had dimensions approximately \( 0.20 \times 0.27 \times 0.32 \text{ mm} \), and was mounted along a°. Integrated intensities were recorded by the moving-crystal moving-counter technique with Nb-filtered Mo Kα radiation at 40 kV and 20 mA. From a preliminary peak count the instrument selects scan rate and attenuation filter. The scan rates and filters are chosen so as to measure all reflexions, except the very weakest, with approximately the same statistical error. The use of attenuation filters also prevents counting losses which appear at high counting rates. The scan ranges were determined according to the tangent relationship (Alexander & Smith, 1964). Within the sphere of reflexion limited at \( \sin \theta/2 = 0.64 \), 2242 unique reflexions were measured. Of these, 228 were less than the threshold value of \( 2\sigma_{\alpha} \), where \( \sigma_{\alpha} \) is the estimated error due to counting statistics.

During data collection three standard reflexions were measured every 100 reflexions to check the stability of crystal and electronics. The averages of the three standards were plotted and showed fluctuations less than ±1 %. The expression used for calculating the random error in any one reflexion is: \( \sigma_f = \sqrt{[\sigma^2 \text{ in counting statistics} + \sigma^2 \text{ in instrumental instability}]} \).

The data were corrected for Lorentz and polarization effects, but not for absorption. The standard deviations in structure factors were calculated from \( \sigma_f = \sigma_{\alpha}/(I_{\text{p}})_{1/2} \).

Structure determination

If the space group is \( \text{C}2/c \), the copper ion must be located on a special position. From a Patterson map the copper coordinates were tentatively chosen as (0,0,0). \( R \) based on copper alone was 0.67 (\( R = \sum |F_o|/|\sum F_o| \)). Even at this high \( R \) value all the non-hydrogen atoms were easily located in the subsequent Fourier map. Refinement proceeded by full-matrix least-squares calculations, minimizing \( \sum w(|F_o| - |F_c|)^2 \) with \( w = 1/\sigma^2_f \). The unobserved reflexions were included in the refinement only when \( |F_c| > |F_o| \). Anisotropic temperature factors were introduced for all atoms, and at an \( R \) of 0.043 the 11 hydrogen atoms were located from a difference map. Two cycles of refinement on all atoms, with isotropic temperature factors for the hydrogen atoms, lowered \( R \) to 0.030.

The data were corrected for secondary extinction according to \( F_{\text{corr}} = K F_{\text{obs}} [1 + (2\beta/\alpha) C |F_{\text{obs}}|] \) (Zachariasen, 1963). The constants \( K \) and \( C \) were determined as 0.99 and 0.155 \( \times 10^{-5} \) by a least-squares procedure. The extinction correction lowered the \( R \) value 0.2 %.

During two final cycles the refinement converged at an \( R \) of 0.028. The weighted \( R \) is 0.033 and the 'goodness of fit', \( [\sum w(|F_o| - |F_c|)^2/(m-n)]^{1/2} \), is 1.14.

A difference map based on all atoms did not show maxima or minima greater than 0.15 e Å⁻³. The few
Table 2. The final atomic parameters

(a) Non-hydrogen atoms (coordinates × 10^5 and temperature parameters × 10^4)

Anisotropic temperature factor = exp \[ -2π²(U_{11}h²a² + U_{22}k²b² + U_{33}l²c² + 2U_{12}hkabc + 2U_{13}hla + 2U_{23}klc) \].

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<th>Z/c</th>
<th>U_{11}</th>
<th>U_{12}</th>
<th>U_{13}</th>
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(b) Hydrogen atoms (parameters × 10^3)

Isotropic temperature factor = \[ \exp \left( -\frac{8\pi^2U}{\sin^2\theta/2^2} \right) \].

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<th>Z/c</th>
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<td>H(32)</td>
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</table>

positive regions of 0.10-0.15 eÅ⁻³ appear in the middle of covalent bonds. These peaks are probably significant, indicating residual bonding electrons.

The observed and calculated structure factors are listed in Table 1. The scattering curves used for Cu, O, N, C are those given in *International Tables for X-ray Crystallography* (1962) and for H that published by Stewart, Davidson & Simpson (1965).

Atomic parameters are listed in Table 2. All calculations were carried out on an IBM 360/50H computer. Some of the programs used have been written by cand. real. K. Maartmann-Moe, and some originate from The Weizmann Institute of Science, Rehovoth, Israel and have been modified by Dr D. Rabinovich, cand. real. K. Åse, and cand. real. L. Milje.

**Description of the structure and discussion**

The structure of the complex is shown in Fig. 1. The copper ion is situated at a centre of symmetry with (4+2) coordination. In the equatorial plane the base nitrogen N(7) and water oxygen O(3) are bonded at 2.054(2) and 1.972(2) Å respectively. The axial positions are occupied by chloride ions at 2.787(1) Å. The sum of the relevant ionic radii is 2.62 Å, thus indicating very weak axial coordination. The coordination octahedron is slightly skewed, the angles C1–Cu–N(7), C1–Cu–O(3), and N(7)–Cu–O(3) being 88.46(5), 86.67(5), and 87.27(6)° respectively. The equatorial plane is tilted 25° relative to the plane through the purine ring to accommodate intramolecular hydrogen bonding between the water molecules in the coordination sphere and the carbonyl oxygen O(6).

![Fig. 2. Stereoscopic illustration of the crystal packing viewed approximately along b, with a parallel to the interocular line. The drawing was made by ORTEP (Johnson, 1970).](image-url)
The hypoxanthine ligand is unidentate. The coordinating orbital on N(7) is bent, the angles Cu–N(7)–C(5) and Cu–N(7)–C(8) being 135-0 and 120-2° respectively. The copper ion is displaced 0-1 Å from the plane through the purine ring.

The possibility of a chelate structure involving both N(7) and O(6) has been invoked on the basis of spectroscopic results (see e.g. Tu & Friedrich, 1968). Recently the structure of a palladium complex of a thionucleoside analogue has been reported where a chelate is formed between S(6), N(7) and Pd (Heitner, Lippard & Sunshine, 1972). The distortion of the ligand geometry to obtain bidentate bonding is appreciable. The donor properties of sulphur far exceed those of oxygen; thus the severely strained five-membered chelate ring is evidently energetically favourable in the case of the palladium complex.

Ultraviolet measurements on cis- and trans-dichlorodiammineplatinum(II) nucleoside complexes have indicated that the ligands are unidentate in the case of guanosine and inosine, but bind bifunctionally between N(7) and the 6-amino group in adenosine (Mansy, Rosenberg & Thomson, 1973). Thus the spectroscopic results point towards unidentate binding for 6-oxy compounds and bidentate for 6-amino compounds. However, an X-ray determination of the latter type of complex shows no tendency to bidentate coordination (Sletten, to be published). Instead an indirect chelation via a water molecule in the coordination sphere seems to be preferred.

The effect of metal bonding on the purine geometry is minor. The ligand is planar within experimental error. The slight bend around C(4)–C(5) observed in most purine structures is barely detectable in the present compound. A comparison between the dimensions in the analogue inosine and the present compound reveals a slight trans effect on the bonds adjacent to the coordination site N(7), the shortening being 0-022 and 0-012 Å in C(5)–N(7) and N(7)–C(8), respectively (Sletten, 1972).

Hydrogen bonding and crystal packing

The molecular packing in the unit cell is shown in a stereo drawing viewed approximately along b (Fig. 2). Hydrogen bonds are listed in Table 3 and are also shown as thin lines in Fig. 2.

The chloride ion participates in three relatively strong hydrogen bonds, one directly to the ring, N(1)–H(1)···Cl, one via a water molecule to the ring, N(3)···H(12)–O(1)–H(11)···Cl, and one connecting two chloride ions via the water molecule located on a twofold axis, Cl···H(21)–O(2)–H(21)···Cl. The water molecule in the coordination sphere forms both an intra- and an intermolecular hydrogen bond. Some-what unexpectedly the two bonds have identical lengths within the limit of error; O(3)···O(6) = 2-634(2) and O(3)···O(1) = 2-643(2) Å. There are no inter-base hydrogen bonds.

The familiar stacking pattern found in most purine structures is also retained in the metal complex. The

Table 3. Hydrogen-bond distances and angles

<table>
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<tr>
<th>Bond</th>
<th>Position of acceptor atom</th>
<th>D···A (Å)</th>
<th>H···A (Å)</th>
<th>Angle (°)</th>
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<td>2-35 (2)</td>
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<td>2-50 (3)</td>
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<td>1-93 (2)</td>
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<td>2-634 (2)</td>
<td>1-90 (3)</td>
<td>165 (3)</td>
</tr>
</tbody>
</table>
interplanar distance between pairs of hypoxanthine ligands related by a screw axis is 3.41 Å. The overlap is seen to be extensive (Fig. 3).

The methyl group is found to be almost exactly eclipsed relative to C(8)-H(8), the H(8)-...H(93) distance being only 2.3 Å. There are no other short intramolecular H···H contacts in the structure.

References


Preparation and Single-Crystal Structure of β-NH₄UF₅, Ammonium Pentafluorouranate(IV)

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And Abraham Rosenzweig

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(Received 14 January 1974; accepted 1 April 1974)

The single-crystal structure of β-NH₄UF₅ has been determined by a three-dimensional X-ray study. It belongs to space group P2₁/c, with dimensions a = 7.799 (5), b = 7.158 (5), c = 8.762 (7) Å, β = 116°45 (5)°. Z = 4, V = 437.9 Å³, dₘ = 5.32, dₒ = 5.3 g cm⁻³. Full-matrix least-squares treatment of 1325 observed intensities, measured by counting techniques, gave an unweighted R value of 0.036, all atoms having anisotropic thermal parameters. The structure is composed of infinite sheets of equivalent UF₄ polyhedra, running parallel to the (100) plane. One fluoride in each polyhedron is unshared, projecting alternatively toward adjacent sheets, but not connecting them. Ammonium ions bind the sheets together. The minimum U-U distances are 3.91 Å within the sheets and 6.33 Å between closest uranium atoms in adjacent sheets. The structure differs greatly from that of isostoichiometric α-NH₄UF₅.

Introduction

Ten years ago it was established (Benz, Douglass, Kruse & Penneman, 1963) that NH₄UF₅ exists in α and β forms. Compounds of 1:1 NH₄F/UF₄ stoichiometry are actually difficult to prepare. The usual result from aqueous precipitation is formation of 7NH₄F.6MF₄. Indeed, many compounds having this special 7:6 molar ratio of alkali fluoride to tetravalent fluoride are known (Thoma, 1962; Penneman, Ryan & Rosenzweig, 1973). The parent structure is that of 7NaF.6ZrF₄ (Burns, Ellison & Levy, 1968). In this structure the tetravalent element is surrounded by eight fluorines in an antiprism, six of which enclose a large cubo-octahedral cavity which accommodates the 'extra' fluoride. We volatilized NH₄F from higher NH₄F/UF₄ complexes and obtained α and β forms of NH₄UF₅ in which the molar ratio of NH₄F to UF₄ was established as unity. The α form has the same X-ray powder diffraction pattern as that of 7NH₄F.6UF₄ and is thus presumed to be an NH₄F-deficient form of it. The structure of the β form was unknown; therefore it was of considerable interest to us that a patent (Allied Chemical Corporation, 1970) disclosed that both α- and β-NH₄UF₅ could be selectively precipitated from hot uranium-bearing aqueous ammonium fluoride solutions upon reduction of U(VI) to U(IV).