distance of 3·7 Å (Pauling, 1960).* The (CH₃)₃Sn group that is closer to a nitrogen atom is also closer to planar, which is consistent, but it is not clear why the nitrogen bridge should be so unsymmetric.

We thank the National Science Foundation for support of this work, R. West for his helpful suggestion, and both R. West and J. S. Thayer for providing the original samples.

### References

COPPENS, P., LEISEROWITZ, L. & RABINOVICH, D. (1965). *Acta Cryst.* **18**, 1035.

\* The van der Waals radius of Sn was estimated by extrapolation of Pauling's values.

*International Tables for X-ray Crystallography* (1959). Vol. III. Birmingham: Kynoch Press.

KASAI, N., YASUDA, K. & OKAWARA, R. (1965). *J. Organometal. Chem.* **3**, 172.

LIPPINCOTT, E. R. & SCHROEDER, R. (1955). *J. Chem. Phys.* **23**, 1099.

PAULING, L. (1960). *The Nature of the Chemical Bond.* 3rd ed. Ithaca: Cornell Univ. Press.

PHILLIPS, D. C. (1954). *Acta Cryst.* **7**, 746.

SCHLEMPER, E. O. & BRITTON, D. (1966). *Inorg. Chem.* **5**, 507.

SUTTON, L. E. (1965). *Interatomic Distances,* Supplement. The Chemical Society, London.

THAYER, J. S. & STROMMEN, D. P. (1966). *J. Organomet. Chem.* **5**, 383.

THAYER, J. S. & WEST, R. (1964). *Inorg. Chem.* **3**, 889.

---

# Stereochemistry of Nucleic Acids and Their Constituents. XXI.* The Crystal and Molecular Structure of Bis-(4-aminoimidazole-5-carboxamidoxime)copper(II) Perchlorate, a Degradation Product of Adenine $N^1$-Oxide

C. D. STOUT, M. SUNDARALINGAM† AND GEORGE HUNG-YIN LIN

*Crystallography Laboratory, Department of Biochemistry, College of Agricultural and Life Sciences, University of Wisconsin, Madison, Wisconsin 53706, U.S.A.*

The crystal and molecular structure of bis-(4-aminoimidazole-5-carboxamidoxime)copper(II) perchlorate, a degradation product of adenine $N^1$-oxide, has been determined by X-ray diffraction. 1458 three-dimensional intensity data were collected on a four-circle diffractometer, using Cu $K\alpha$ radiation. The structure was determined by the usual heavy-atom technique and refined by the method of full-matrix least-squares to a final $R$ value of 0·052. The unit cell is monoclinic, space group $P2_1/c$ with $a = 4·989 \pm 0·001$, $b = 10·883 \pm 0·002$, $c = 16·648 \pm 0·002$ Å and $\beta = 90·24 \pm 0·01°$. The degradation product is formed by expulsion of C(2) of adenine and a rotation around the original C(5)–C(6) bond. This places N(1) in a *cis* planar configuration to N(7). Both N(1) and N(7) and their centrosymmetric partners form a square-planar complex around the copper. The coordination bond lengths are Cu–N(1) = 1·968 Å and Cu–N(7) = 1·970 Å. The N(1)–Cu–N(7) angle is 80·9°. The chelates are stacked in such a manner that the N(6) atoms of the centrosymmetrically related chelates above and below make the shortest contact, 3·136 Å, to the central copper atom. All potential hydrogen atoms are involved in the interionic hydrogen bonding scheme.

## Introduction

As part of a program of research in these laboratories on the interaction of metal ions with nucleic acids and their constituents we have undertaken a study of the crystal structure of bis-(4-aminoimidazole-5-carboxamidoxime)copper(II) perchlorate. Weiss & Venner (1969) who supplied this and several other similar complexes for our X-ray investigation believed that the complexes involved the ligand adenine $N^1$-oxide (Fig. 1). But the X-ray structure determination revealed that the ligand had undergone degradation to 4-aminoimidazole-5-carboxamidoxime with the expulsion of C(2). Apparently, the strong acidic condition and heat em-

* Part XX of this series by J. Abola and M. Sundaralingam, *Acta Cryst.*, to be published. For related papers from these laboratories on metal binding studies, see Carrabine & Sundaralingam (1968, 1969, 1970, 1971), Sundaralingam & Carrabine (1969, 1971), and Sundaralingam, Stout & Hecht (1971).

† To whom correspondence should be addressed.

ployed by Weiss & Venner promoted the degradation of adenine $N^1$-oxide. This in fact had been shown earlier by Stevens & Brown (1958) and independently by Sundaralingam, Stout & Hecht (1971). A possible mechanism for the degradation of adenine $N^1$-oxide to 4-aminoimidazole-5-carboxamidoxime has been given (Sundaralingam et al., 1971).

## Experimental

The complex bis-(4-aminoimidazole-5-carboxamidoxime)copper(II) perchlorate was prepared by dissolving 300 mg of adenine $N^1$-oxide in 6 ml of $1N$ $HClO_4$ and then adding 5 ml $1M$ $Cu(ClO_4)_2$. The mixture was titrated with $1N$ NaOH with warming until the resulting precipitate was no longer soluble ($pH = 2$). The filtrate on standing produced dark brown rod shaped crystals suitable for X-ray structure analysis. This method of preparation of the complex was that of Weiss & Venner, and the crystals for the X-ray study were supplied by them.

The crystal used for recording intensities had the dimensions $0.4 \times 0.15 \times 0.01$ mm$^3$ and was mounted with the crystallographic $a$ axis parallel with that of the goniostat. Preliminary oscillation and Weissenberg photographs showed monoclinic symmetry with extinctions $0k0$ ($k = 2n + 1$) and $h0l$ ($l = 2n + 1$), indicating that the crystal belongs to space group $P2_1/c$. The unit-cell dimensions measured on a four-circle diffractometer are given in Table 1. The density calculated for 2 molecules of $(C_4H_7N_5O)_2$ $Cu(ClO_4)_2$ in the unit cell is $2.002$ g.cm$^{-3}$, which is in agreement with that measured in a mixture of chloroform and bromoform by flotation, $1.998$ g.cm$^{-3}$.

Three-dimensional intensity data were collected on a Picker four-circle automated diffractometer with Ni-filtered Cu $K\alpha$ radiation ($\lambda = 1.5418$ Å). Intensity measurements were made by scanning reflections in the $\theta$–$2\theta$ mode at a speed of $2°$ per minute. A constant scan range of $3.4°$ was used. Background counts of 20 seconds were taken at each end of the scan. 1458 reflections were scanned to a maximum $2\theta$ of $127°$. A reflection with intensity smaller than $1.5$ times its standard deviation was considered unobserved. Accordingly, there were 1136 observed reflections. The standard reflection measured at intervals of 50 reflections showed a
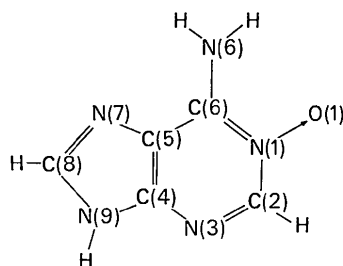


Fig.1. Numbering in adenine $N^1$-oxide.

Table 1. Crystal data for bis-(4-aminoimidazole-5-carboxamidoxime)copper(II) perchlorate

| | |
|---|---|
| Formula | $[(C_4H_7N_5O)_2Cu]^{2+}.2ClO_4^-$ |
| Molecular weight | 544·71 |
| Space group | $P2_1/c$ |
| $a$ | $4.988 \pm 0.001$ Å |
| $b$ | $10.883 \pm 0.002$ |
| $c$ | $16.648 \pm 0.002$ |
| $\beta$ | $90.24 \pm 0.01°$ |
| | 903·73 cm$^3$ |
| $d_{obs}$ | $1.965$ g.cm$^{-3}$ (by flotation in $CHCl_3/CHBr_3$) |
| $d_{calc}$ | $2.002$ g.cm$^{-3}$ |
| $\mu$ | $52.3$ cm$^{-1}$ |

deviation of only $\pm 2\%$ in intensity during the period of data collection. The data were corrected for the usual Lorentz–polarization effects, and no correction for absorption was made.

## Determination and refinement of the structure

The structure was solved by the heavy-atom method. Since there could be only two molecules of $(C_4H_7N_5O)_2Cu(ClO_4)_2$ in a unit cell, the copper must be situated at one of the centers of symmetry. The chlorine was found by inspection of the Patterson map, and the rest of the atoms were found by 3 cycles of structure factor–Fourier synthesis calculations. The initial difficulty encountered in interpreting the Fourier map was mainly due to the fact that the ligand was considered to be adenine $N^1$-oxide. However, it turned out to be its degradation product, 4-aminoimidazole-5-carboxamidoxime, which is formed by the expulsion of C(2) of adenine. This aspect is discussed in detail in a preliminary communication (Sundaralingam et al., 1971).

All the atoms included in the structure factor calculation gave an $R$ value of $0.282$. Two cycles of isotropic and two cycles of anisotropic full-matrix refinement on the 16 nonhydrogen atoms reduced $R$ to $0.062$. All of the hydrogen atoms were located in difference electron density maps. Further refinement of the nonhydrogen atom parameters and positional parameters of hydrogen atoms lowered the $R$ value to $0.052$. The weighting scheme used was $\sigma = 1/\sqrt{w} = 0.978$ for $|F_o| < 15.8$ and $\sigma = 0.489 + 0.0413|F_o|$ for $|F_o| \geq 15.8$, obtained from a plot of $|F_o - F_c|$ versus $|F_o|$. The shift/$\sigma$ ratios were all less than $0.30$. The scattering factors for $Cu^{2+}$, Cl, N, O and C atoms used throughout the analysis were those of Cromer & Waber (1965), while those for H were from Stewart, Davidson & Simpson (1965).

## Results and discussion

The observed and calculated structure amplitudes are given in Table 2. The final positional and thermal parameters for all nonhydrogen atoms and the positional

parameters for hydrogen atoms observed from the difference Fourier map are given in Table 3.

## Bond distances and bond angles of the ligand

The bond distances and bond angles of the cation together with their standard deviations are given in Fig. 2. The bond distances in the imidazole ring are generally in good agreement with those observed in guanine-copper chloride (Carrabine & Sundaralingam, 1970), although interestingly in the latter structure the sites of protonation and metal binding were interchanged. The bond distances in the carboxamidoxime group are in good agreement with those found in formamidoxime (Hall & Llewellyn, 1956). The two amino-group–carbon distances [N(3)–C(4) 1·357 Å, N(6)–C(6) 1·330 Å] are significantly different. The latter is probably involved in a single-bond–double-bond resonance with C(6)–N(1). The observed N(1)–O(1) distance of 1·420 Å is significantly longer than the N–O bonds observed in the oximes such as acetoxime (1·36 Å, Bierlein & Lingafelter, 1951) dimethylglyoxime (1·32 Å, Hamilton, 1961), Ni(II) dimethylglyoxime (1·35, 1·36 Å, Williams, Wohlauer & Rundle, 1959) and Cu(II) dimethylglyoxime (1·34 Å, Frasson, Bardi & Bezzi, 1959). However, the N(1)–O(1) bond distance in the present structure is close to those found in anti- and syn-p-chlorobenzaldoxime (Jensen, 1969), i.e. 1·40 and 1·41 Å respectively.
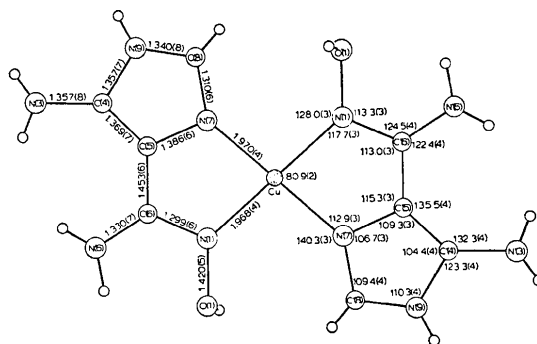


Fig. 2. Bond distances and bond angles in bis-(4-aminoimidazole-5-carboxamidoxime)copper(II) ion. Standard deviations in the least significant digits are given in parentheses.

The oxime N(1)–O(1) bond in this complex is syn with respect to N(6). The torsion angles about N(1)–C(6) are: O(1)–N(1)–C(6)–N(6) −1·5°; O(1)–N(1)–C(6)–C(5) 175·2°.

## The perchlorate group

The perchlorate group shows an approximately tetrahedral geometry with the six O–Cl–O angles from 108·4 to 110·9°. The bond distances in the perchlorate

## Table 2. Observed and calculated structure amplitudes

Columns 1, 2 and 3 represent h, 10|F_o| and 10|F_c| respectively.

are: Cl–O(2) 1·432, Cl–O(3) 1·417, Cl–O(4) 1·442 and Cl–O(5) 1·435 Å. The e.s.d.'s in bond distances are

0·005 Å and in bond angles 0·2°. The negative charge is probably equally distributed on the four oxygen atoms.
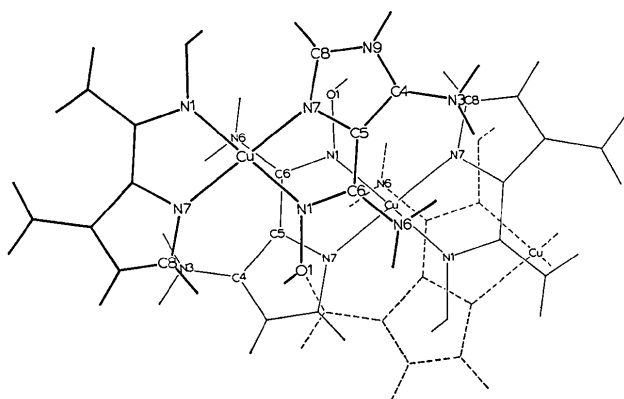


Fig. 3. A view perpendicular to the plane of the cation showing the stacking of the cation planes and the positions of the N(6) atoms on adjacent complexes above and below the copper.

*Metal coordination*

In the present investigation the original N(7) is a metal binding site, Fig. 2. The two other cases where N(7) of adenine participates in metal binding are disodium adenosine triphosphate (Kennard *et al.*, 1970) and zinc adenine complex (Srinivasan & Taylor, 1970). In fact, spectral evidence for N(7) participation in copperguanosine complex has been presented (Eichhorn *et al.*, 1968; Tu & Friederick, 1968). Therefore, from available data it is clear that the preferred metal binding site in the N(9) substituted adenine deviatives is N(7). A lesser preference is exhibited by site N(3) while N(1) seems to show the least preference for metal coordination in the adenine system itself. In the present investigation, both the amino groups N(3) and N(6) do not show affinity for binding to copper.

In addition to N(7), N(1) is also involved in metal binding. Two centrosymmetrically related ligands form a distorted square-planar coordination around the

Table 3

(*a*) Positional parameters and anisotropic thermal parameters of the nonhydrogen atom*†

| | $x$ | $y$ | $z$ | $B_{11}$ | $B_{22}$ | $B_{33}$ | $B_{12}$ | $B_{13}$ | $B_{23}$ |
|---|---|---|---|---|---|---|---|---|---|
| Cu | 0 (0) | 0 (0) | 0 (0) | 388 (6) | 36 (0) | 25 (0) | 4 (0) | − 10 (0) | 0 (0) |
| N(1) | 2680 (9) | − 840 (3) | 674 (2) | 306 (21) | 15 (2) | 24 (1) | − 8 (5) | − 7 (3) | 0 (1) |
| O(1) | 3425 (8) | − 2099 (3) | 659 (2) | 411 (20) | 16 (2) | 31 (0) | − 17 (4) | − 21 (3) | 0 (0) |
| N(3) | 6682 (13) | 2386 (6) | 1929 (3) | 549 (34) | 37 (4) | 29 (1) | − 33 (9) | − 39 (5) | − 2 (2) |
| C(4) | 4665 (11) | 2187 (4) | 1395 (3) | 330 (28) | 28 (3) | 20 (1) | − 8 (7) | 8 (4) | 0 (1) |
| C(5) | 3654 (10) | 1137 (4) | 1058 (3) | 256 (25) | 33 (3) | 15 (1) | 2 (6) | 0 (4) | − 1 (1) |
| C(6) | 4298 (11) | − 163 (4) | 1098 (3) | 257 (26) | 28 (3) | 16 (1) | − 6 (6) | 3 (4) | − 1 (1) |
| N(6) | 6415 (11) | − 587 (4) | 1499 (3) | 365 (27) | 35 (3) | 33 (1) | − 19 (7) | − 45 (6) | 7 (1) |
| N(7) | 1574 (9) | 1442 (3) | 540 (2) | 328 (22) | 23 (2) | 20 (0) | 8 (6) | − 13 (3) | 0 (1) |
| C(8) | 1379 (13) | 2642 (5) | 549 (3) | 384 (30) | 34 (3) | 22 (1) | 14 (8) | − 11 (5) | 5 (1) |
| N(9) | 3202 (12) | 3105 (5) | 1059 (3) | 485 (30) | 13 (3) | 26 (1) | − 6 (7) | − 12 (4) | − 5 (1) |
| Cl | 1697 (3) | 714 (1) | 3379 (1) | 343 (8) | 24 (0) | 21 (0) | − 12 (1) | − 5 (0) | 0 (0) |
| O(2) | 752 (13) | 265 (4) | 4134 (3) | 943 (36) | 72 (3) | 26 (1) | − 86 (8) | 37 (5) | 5 (1) |
| O(3) | 4522 (9) | 609 (4) | 3328 (3) | 348 (24) | 61 (3) | 54 (1) | 12 (6) | − 17 (4) | 3 (1) |
| O(4) | 516 (10) | − 17 (4) | 2748 (3) | 525 (26) | 63 (3) | 32 (0) | − 18 (6) | − 33 (3) | − 19 (1) |
| O(5) | 931 (9) | 1977 (3) | 3286 (3) | 461 (23) | 25 (2) | 52 (1) | 10 (5) | − 15 (4) | 0 (1) |

* For nonhydrogen atoms all parameters and their e.s.d.'s given in parentheses have been multiplied by $10^4$.

† The temperature factor is of the form $\exp[-(B_{11}h^2 + \ldots + 2B_{12}hk + \ldots)]$.

Table 3 (*cont.*)

(*b*) Observed positional parameters of the hydrogen atoms‡

| | $x$ | $y$ | $z$ |
|---|---|---|---|
| H(1) | 184 | − 250 | 85 |
| H(3) | 733 | 174 | 231 |
| H(3') | 718 | 326 | 204 |
| H(6) | 668 | − 151 | 148 |
| H(6') | 730 | − 8 | 176 |
| H(8) | 5 | 314 | 36 |
| H(9) | 341 | 399 | 120 |

‡ Isotropic thermal parameters for all hydrogen atoms were fixed at 4 Å², positional coordinates multiplied by $10^3$.

copper. The process of complexation of site N(1) has been coupled with a rotation of about 180° about the original C(5)–C(6) bond. This can be attributed to the fact that the nitrogen N(1) is more basic than the primary amino nitrogen N(6). This again emphasizes the persistently observed fact that amino groups conjugated to unsaturated systems show little affinity for metal binding (Sundaralingam, 1969; Sundaralingam & Carrabine, 1971).

The coordination bonds Cu–N(7) (1·970 Å) and Cu–N(1) (1·968 Å) are identical within the experimental errors, Fig. 3. These distances fall within the range of

values observed in other Cu(II) complexes of nucleic acid constituents, Table 4. It is seen that the Cu–N distances have a large range 1·945–2·034 Å.The Cu–N distances appear to be a function of the base (purine or pyrimidine) and the size of the ring (six-ring or five-ring). The N(7)–Cu–N(1) angle is 80·9°. The deviation of this angle from 90° is attributable to the geometry of the ligand. The intra-ligand N(1)···N(7) distance is 2·554 Å and the inter-ligand N(1)···N(7) distance is 2·997 Å.

The various least-squares planes are given in Table 5. The cation (plane I) shows significant deviations from planarity, while the atoms of the imidazole ring lie in a plane. The extracyclic atoms C(6), N(6), N(1) and O(1), with the exception of N(3), are all displaced significantly on the same side of the plane of the imidazole ring. The plane N(6)–C(6)–N(1) makes an angle of 8·1° with the imidazole ring.

A projection perpendicular to the cation plane showing the stacking is given in Fig. 3. The interplanar distance is 3·37 Å. The centrosymmetrically related Cu–N(6) distances between adjacent chelates are 3·136 Å, which are shorter than the interplanar distance. The copper may thus be octahedral. It is interesting that N(6) shows the largest deviation (0·19 Å, see Table 5) from the cation plane and towards the copper atom of the adjacent chelate. The angles N(6)···Cu–N(1) = 80·8° and N(6)···Cu–N(7) = 91·5°.

### Hydrogen bonding

All the potential hydrogen atoms are involved in the interionic hydrogen bonding scheme. Each cation is surrounded by six anions. On the other hand, each anion is surrounded by three cations. A projection along the *a* axis showing the packing and hydrogen bonding is given in Fig. 4. The hydrogen bond distances and angles are given in Table 6. All donors are situated on the cation and all four oxygen atoms on the anion act as acceptors, resulting in seven hydrogen bonds. O(3) accepts a hydrogen bond from N(9)–H(9). The same hydrogen, H(9), is at van der Waals contact distance to O(2). O(4) accepts protons from N(6) and N(3) of two different cations, while O(5) is involved in three hydrogen bonds, to O(1) and N(6) of one cation and N(3) of another cation.

### Table 5. *Least-squares planes in the cation*

| | Deviation (Å) from | | |
| | Plane I | Plane II | Plane III |
|---|---|---|---|
| Cu | 0·013* | 0·045 | 0·284 |
| N(1) | −0·024* | 0·023 | −0·006* |
| O(1) | 0·130 | 0·195 | 0·003* |
| N(3) | 0·000 | 0·006 | 0·024 |
| C(4) | −0·011* | −0·005* | 0·130 |
| C(5) | −0·012* | 0·008* | 0·108 |
| C(6) | 0·036 | 0·075 | 0·007* |
| N(6) | 0·191 | 0·239 | −0·003* |
| N(7) | −0·021* | −0·008* | 0·264 |
| C(8) | 0·009* | 0·005* | 0·410 |
| N(9) | 0·009* | 0·000* | 0·327 |
| r.m.s.Δ | 0·019 | 0·006 | 0·005 |

* Atoms defining the plane are marked with asterisks.

### Table 4. Cu–N *bonds in copper complexes with nucleic acid constituents*

| Compound | Bond length (Å) | Bonding site | Coordination geometry | Reference |
|---|---|---|---|---|
| (Cytosine)₂CuCl₂ | 1·945 (12)[e] | N(3) | Octahedral | Carrabine & Sundaralingam (1968, 1971) |
| | 1·967 (11) | N(3) | | |
| (Guanine)CuCl₃.H₂O[a] | 1·976 (5) | N(9) | Trigonal bipyramidal | Carrabine & Sundaralingam (1970, 1971) |
| (6-Hydroxypurine)₂CuCl₂.3H₂O[a],[b] | | | | |
| residue-1 | 2·005 (7) | N(3) | Square- | Sletten (1970) |
| | 1·989 (7) | N(9) | pyramidal | |
| residue-2 | 2·005 (7) | N(3) | Square- | |
| | 1·992 (7) | N(9) | pyramidal | |
| (Adenine)Cu(II).4H₂O[a],[b],[c] | | | | |
| residue-1 | 2·034 (4) | N(3) | Square- | Sletten (1969) |
| | 2·000 (4) | N(9) | pyramidal | |
| residue-2 | 2·031 (4) | N(3) | Square- | |
| | 2·014 (4) | N(9) | pyramidal | |
| (AdenineH)₂Cu₃Cl₈.4H₂O[d] | 2·027 (7) | N(3) | Octahedral | de Meester *et al.* (1970) |
| | 2·028 (7) | N(9) | Trigonal bipyramidal | |
| (Adenine)₂CuCl₂.3H₂O[a] | 2·041 (11) | N(3) | Square- | de Meester *et al.* (1971) |
| | 2·008 (11) | N(9) | pyramidal | |
| (C₄H₇N₅O)₂Cu(ClO₄)₂ | 1·970 (4) | N(7) | Square- | This work |
| | 1·968 (4) | N(1) | planar | |
| Average | 2·000 | | | |

(*a*) A dinuclear complex.
(*b*) A dimeric structure.
(*c*) Anion not reported.
(*d*) A trinuclear complex.
(*e*) Standard deviations given in parentheses are in the least significant digits.

## Conclusion

The participation of N(7) in metal binding is of special interest in elucidating the mode of binding of metal ions to nucleic acids. The copper induced denaturation of DNA is attributed to the selective attack of the guanine–cytosine base pairs (Venner & Zimmer, 1966; Hiai, 1965). X-ray crystallographic studies of metal-base complexes have now provided definitive evidence of the participation of N(3) of cytosine and N(7) of adenine in metal binding (Carrabine & Sundaralingam, 1969; Sundaralingam & Carrabine, 1971). Spectral evidence is also available for the participation of these sites in copper complexes (Eichhorn et al., 1968; Tu & Frederick, 1968). Based on these sites, various coor-
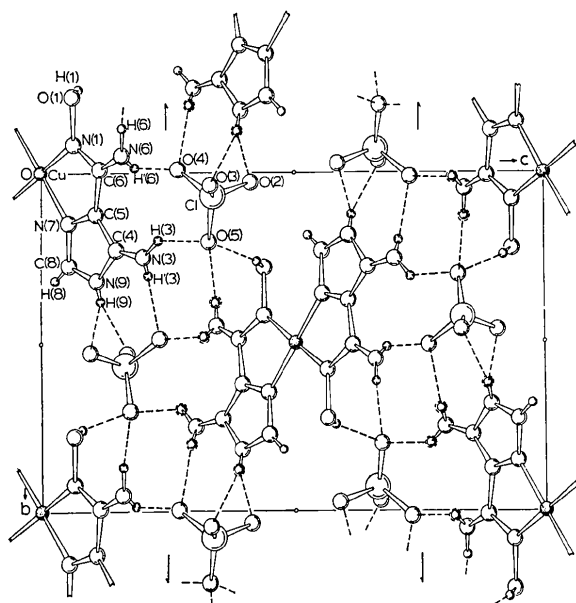
dination models involving N(7) of guanine and N(3) of cytosine have recently been proposed for the mechanism of guanine–cytosine selective denaturation of DNA by copper (Sundaralingam & Carrabine, 1971). It is worthwhile to point out that in vitamin $B_{12}$ (Hodgkin, Pickworth & Robertson, 1959) the corresponding N(7) site of the dimethylbenzoimidazole base is engaged in binding to the cobalt atom at the center of the corrin ring.

Fig. 4. A projection along the $a$ axis showing the hydrogen bonding scheme.

## References

BIERLEIN, T. K. & LINGAFELTER, E. C. (1951). Acta Cryst. 4, 450.
CARRABINE, J. A. & SUNDARALINGAM, M. (1968). Chem. Commun. p. 746.
CARRABINE, J. A. & SUNDARALINGAM, M. (1969). Acta Cryst. A25, 179.
CARRABINE, J. A. & SUNDARALINGAM, M. (1970). J. Amer. Chem. Soc. 92, 369.
CARRABINE, J. A. & SUNDARALINGAM, M. (1971). Biochemistry, 10, 292.
CROMER, D. T. & WABER, J. T. (1965). Acta Cryst. 18, 104.
EICHHORN, G. L. & SHIN, Y. A. (1968). J. Amer. Chem. Soc. 90, 7323.
FRASSON, E., BARDI, R. & BEZZI, S. (1959). Acta Cryst. 12, 201.
HALL, D. & LLEWELLYN, F. J. (1956). Acta Cryst. 9, 108.
HAMILTON, W. C. (1961). Acta Cryst. 14, 95.
HIAI, S. (1965). J. Mol. Biol. 11, 672.
HODGKIN, D. C., PICKWORTH, J. & ROBERTSON, J. H. (1959). Proc. Roy. Soc. A251, 306.
JENSEN, K. G. (1969). Acta Cryst. A25, part S3, S148.

Table 6. Hydrogen bonds (Å) and angles (°)

| Bond type $A \cdots H-B$ | Symmetry code for atom $B$ | $A \cdots B$ distance | $A \cdots H$ distance | $A \cdots H-B$ angle |
|---|---|---|---|---|
| O(2)···H(9)–N(9) | I | 3·084 | 2·56* | 113 |
| O(3)···H(9)–N(9) | II | 3·121 | 2·18 | 156 |
| O(4)···H(6′)-N(6) | III | 2·976 | 2·29 | 141 |
| O(4)···H(3′)-N(3) | I | 3·197 | 2·23 | 163 |
| O(5)···H(1)–O(1) | IV | 2·974 | 2·08 | 155 |
| O(5)···H(3)–N(3) | III | 3·123 | 2·43 | 126 |
| O(5)···H(6)–N(6) | V | 2·983 | 2·06 | 149 |

| Symmetry code: | | | |
|---|---|---|---|
| I | $\bar{x}$ | $y-\frac{1}{2}$ | $\frac{1}{2}-z$ |
| II | $1-x$ | $y-\frac{1}{2}$ | $\frac{1}{2}-z$ |
| III | $x-1$ | $y$ | $z$ |
| IV | $\bar{x}$ | $\frac{1}{2}+y$ | $\frac{1}{2}-z$ |
| V | $x+1$ | $y$ | $z$ |

* This probably represents a van der Waals contact rather than a hydrogen bond.

KENNARD, O., ISAACS, N. W., COPPOLA, J. C., KIRBY. A. J., WARREN, S., MOTHERWELL, W. D. S., WATSON, D. G., WAMPLER, D. L., CHENERY, D. H., LARSON, A. C., KERR, K. A. & RIVA DI SANSEVERINO, L. (1970). *Nature, Lond.* **225**, 333.

MEESTER, P. DE, GOODGAME, D. M. L., PRICE, K. A. & SKAPSKI, A. C. (1970). *Chem. Commun.* p. 1573.

MEESTER, P. DE, GOODGAME, D. M. L., PRICE, K. A., & SKAPSKI, A. C. (1971). *Nature, Lond.* **229**, 191.

SLETTEN, E. (1969). *Acta Cryst.* B**25**, 1480.

SLETTEN, E. (1970). *Acta Cryst.* B**26**, 1609.

SRINIVASAN, L. & TAYLOR, M. R. (1970). *Chem. Commun.*, p. 8.

STEVENS, M. A. & BROWN, G. B. (1958). *J. Amer. Chem. Soc.* **80**, 2759.

STEWART, R. F., DAVIDSON, E. R. & SIMPSON, W. T. (1965). *J. Chem. Phys.* **42**, 3175.

SUNDARALINGAM, M. *Biopolymers* (1969). **7**, 821.

SUNDARALINGAM, M. & CARRABINE, J. A. (1969). *Acta Cryst.* A**25**, 179.

SUNDARALINGAM, M. & CARRABINE, J. A. (1971). *J. Mol. Biol.* **61**, 287.

SUNDARALINGAM, M., STOUT, C. D. & HECHT, S. M. (1971). *Chem. Commun.* p. 240.

TU, A. T. & FRIEDERICK, C. G. (1968). *Biochemistry*, **5**, 245.

VENNER, H. & ZIMMER, C. H. (1966). *Biopolymers*, **4**, 321.

WEISS, R. & VENNER, H. (1969). *Z. physiol. Chem.* **350**, 230.

WILLIAMS, D. E., WOHLAUER, G. & RUNDLE, R. E. (1959). *J. Amer. Chem. Soc.* **81**, 755.

# Stereochemistry of Nucleic Acids and Their Constituents. XXV. Crystal and Molecular Structure of Adenine N¹-Oxide–Sulfuric Acid Complex*

BY P. PRUSINER AND M. SUNDARALINGAM†

*Department of Biochemistry, College of Agricultural and Life Sciences, University of Wisconsin, Madison, Wisconsin 53706, U.S.A.*

Adenine $N^1$-oxide is an oxidation product of adenine. Current interest in the $N$-oxide derivatives of purines stems from the fact that they possess spontaneous cancer induction properties. Crystals of the sulfuric acid complex of adenine $N^1$-oxide belong to the orthorhombic space group $P2_12_12_1$, with four molecules in the unit cell of dimensions: $a = 10\cdot224$ (1), $b = 14\cdot944$ (2), $c = 5\cdot639$ (1) Å; $D_{calc} = 1\cdot921$, $D_{obs} = 1\cdot910$ g.cm$^{-3}$. The tangent method for noncentrosymmetric crystals was used to obtain the structural solution with initial phasing on the sulfur atom. The structure was refined to a final $R$ value of 0·042 using 838 reflections collected on a diffractometer. The protonated sites in the base are O(1), N(9) and N(7). The bond distances and bond angles, with average standard deviations of 0·005 Å and 0·3°, are in good agreement with other protonated adenine derivatives. The O(1) of the base is involved in a possible symmetric hydrogen bond to O(4) of the sulfate, of 2·54 Å. The compound provides an example of a C–H···O interaction involving the C(8) position of the base and a sulfate oxygen. Other hydrogen bonds involve the N(7), N(9), and the amino group of the base and the sulfate. The S–O bond distances range from 1·455 to 1·494 Å and are correlated with the strengths of the hydrogen bonds involving the sulfate oxygen atoms. The crystal packing arrangement consists of seven negatively charged sulfate groups surrounding each positively charged base, and *vice versa*.

## Introduction

The crystal structure of the adenine $N^1$-oxide–sulfuric acid complex has been determined as part of a program of research in our laboratory on the molecular structures of the nucleic acid constituents and their derivatives. Our attention was focused on adenine $N^1$-oxide (1) when it was shown by Cramer, Doepner, Haar, Schlimme & Seidel (1968) that the exposed ade-

* For part XXIV of this series, see M. Sundaralingam, in Fourth Jerusalem Symposium on 'Purines: Theory and Experiment' (April 1971). Published in New York by the Israeli Academy of Sciences and Humanities and Academic Press.

† To whom correspondence should be addressed.

nine bases in transfer ribonucleic acid (tRNA) can be selectively oxidized by monoperphthalic acid. Weiss & Venner (1969) had reported that 1 forms crystalline metal complexes. We felt, therefore, that these experiments would be suited to the preparation of isomorphous heavy-atom derivatives of tRNA which would then serve in the solution of its crystallographic 'phase problem'. In this connection we were initially interested in the copper perchlorate complex of 1. Our X-ray study of the complex revealed that 1 had undergone degradation with the expulsion of carbon C(2) and the resulting product served as the ligand in the complexing with copper (Sundaralingam, Stout & Hecht, 1971). Apparently, the highly acidic conditions