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[(Glycylglycinato) (cytosine)copper(II)]. A Model for Enzyme–Metal–Nucleic Acid Ternary Complexes*

BY THOMAS J. KISTENMACHER, DAVID J. SZALDA AND LUIGI G. MARZILLI

Department of Chemistry, The Johns Hopkins University, Baltimore, Maryland 21218, *U.S.A.*

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The synthesis and crystal structure of the complex [(glycylglycinato) (cytosine)copper(II)], $CuO_4N_5C_8H_{11}$, are reported. The complex crystallizes as the dihydrate in the monoclinic system, space group $P2_1/n$, with $a=10{\cdot}695$ (4), $b=8{\cdot}077$ (1), $c=14{\cdot}756$ (7) Å, $\beta=92{\cdot}38$ (3)°, $Z=4$, $D_m=1{\cdot}78$ (1), $D_c=1{\cdot}78$ g cm^{-3}. Intensities for 2951 symmetry-averaged reflections were collected in the θ–2θ mode by counter methods. The structure was solved by standard heavy-atom Patterson and Fourier methods. Full-matrix least-squares refinement has led to a final R value of 0·084. The final weighted R value and goodness-of-fit are 0·042 and 1·3, respectively. The primary coordination sphere about the copper is approximately square planar with the tridentate glycylglycine dianion and N(3) of cytosine occupying the four coordination sites. The copper also forms two weak, axial interactions with O(2) of cytosine, one intramolecular, Cu···O(2) 2·819 (3) Å, and one intermolecular, Cu···O(2) 2·713 (3) Å. The crystal structure is dominated by columnar stacks of complexes about the twofold screw axis along **b** with intracolumn interactions *via* the weak Cu···O(2) intermolecular bond and hydrogen bonds of the type N(4) [cytosine]···O(2) [cytosine] and N(10) [glycylglycine]···O(7) [glycylglycine]. The columns are directly linked by hydrogen bonds involving N(4) and N(1) of cytosine and O(8) and O(9) of glycylglycine and further coupled by hydrogen bonds through the waters of crystallization.

Introduction

As part of a program designed to provide detailed information about the role of secondary forces in determining the preferential site for complexation in nucleic acids, we have synthesized and determined the molecular structure of a variety of metal-chelate complexes of purines and pyrimidines (see Marzilli, Kistenmacher, Darcy, Szalda & Beer (1974) for example). It is now clear that the affinity of metal ions for the base binding sites in nucleic acids cannot be solely a function of the nucleophilicity of the coordination site (Eichhorn, 1973). The selectivity of metal-containing or metal-mediated systems for one of the four purine or pyrimidine bases must then arise from factors other than the electronic properties of the donor sites on these bases.

Enzymes with functions related to nucleic acid synthesis, repair and transcription often require the presence of metal ions, probably in a ternary complex of the type enzyme–metal–nucleic acid (Daune, 1974; Eichhorn, 1973). We are interested in models of such ternary systems for two reasons. First, great difficulty can be expected in the isolation and detailed study of the naturally occurring systems. Therefore, models might serve to provide insight into binding sites and other modes of interaction in these species. Second, such metal–enzyme complexes are rather specific (Daune, 1974; Eichhorn, 1973; Zimmer, Luck & Triebel, 1974), and we have been interested in developing specific metal-containing probes which may serve to elucidate the solution geometry of nucleic acids or alternately provide a means for nucleic acid sequencing by electron microscopy (Wiggins & Beer, 1972).

In an attempt to study models for enzyme–metal–nucleic acid ternary species, we have recently initiated a systematic study of several complexes obtained by the reaction of glycylglycinatocopper(II) with nucleic acid bases and nucleosides (Marzilli & Kistenmacher, 1974; Kistenmacher, Szalda & Marzilli, 1975*a*). As part of this effort, we have synthesized and determined the crystal and molecular structure of the complex [(glycylglycinato) (cytosine)copper(II)]. Our efforts have apparently been in parallel with those of Saito, Terashima, Sakaki & Tomita (1974), hereinafter STST. Our results, however, differ in detail from those of STST and are described below.

Experimental

The complex was prepared by the addition of cytosine (0·1 g, 1 mmole) to an aqueous solution (12·5 ml) of glycylglycinatocopper(II) (Manyak, Murphy & Martell (1955); 0·2 g, 1 mmole). The solution was heated for about $\frac{1}{2}$ h on a steam bath (75–80°) and then reduced in volume until a purple precipitate was obtained. Crystals were grown by redissolving the material in water and allowing the solvent to slowly evaporate.

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The crystals are elongated monoclinic prisms with [010] along the prism axis. Preliminary diffraction photographs showed the crystal system to be monoclinic with systematic absences ($0k0$, $k=2n+1$; $h0l$, $h+l=2n+1$) consistent with the space group $P2_1/n$. Unit-cell dimensions and their associated standard deviations were derived from a least-squares fit to the 2θ, ω and χ values for 14 carefully-centered reflections on a Syntex $P\bar{1}$ computer-controlled diffractometer. The crystal density was measured by neutral buoyancy methods and indicated one formula unit plus two waters of crystallization per asymmetric volume. Complete crystal data are given in Table 1.

7069 reflections (the $+h$-hemisphere to $2\theta=55°$) were measured on the diffractometer; molybdenum graphite-monochromatized radiation was employed. The crystal used in data collection was $0{\cdot}20\times0{\cdot}06\times0{\cdot}06$ mm with the long axis approximately aligned along the φ axis. Intensity data were collected in the θ–2θ scan mode; individual scan speeds were determined by a rapid scan at the calculated Bragg peak, and the rate of scanning varied from 1·0° min^{-1} (less than 100 counts in the rapid scan) to 12·0° min^{-1} (more than 1000 counts in the rapid scan). Three standards were monitored after every 100 reflections, and their intensities showed no unusual variation over the course of the experiment. The 7069 measured intensities, which included standards and systematic absences, were then averaged to yield a set of 2951 independent values. All reflections were assigned observational variances based on the following equation: $\sigma^2(I)=S+(B_1+B_2)(T_S/2T_B)^2+(pI)^2$, where S, B_1 and B_2 are the scan and extremum background counts, T_S and T_B are the scan and individual background counting times ($T_B=\frac{1}{4}T_S$ for all reflections), and $p=0{\cdot}03$ and represents the expected error proportional to the diffracted intensity (Busing & Levy, 1957). The intensities and their standard deviations were corrected for Lorentz and polarization effects; the amplitudes of reflections with negative intensities were set equal to zero. No correction for absorption was deemed necessary ($\mu=18{\cdot}2$ cm^{-1}); the maximum error introduced by the neglect of absorption effects was estimated to be 3% in I. The intensities were placed on an absolute scale by the method of Wilson (1942).

Table 1. *Crystal data for [(glycylglycinato) (cytosine)copper(II)] dihydrate*

KSM*	STST†
a = 10·695 (4) Å	10·642 (1) Å
b = 8·077 (1)	8·081 (1)
c = 14·756 (7)	14·711 (1)
β = 92·38 (3)°	92·40 (1)°
$V=1273{\cdot}6$ Å^3	1264·0 Å^3
$P2_1/n$	
$Cu(O_4N_5C_8H_{11}).2H_2O$	
M.W. 340·78	
$D_m=1{\cdot}78$ (1) g cm^{-3}	
$D_c=1{\cdot}78$ g cm^{-3}	1·79 g cm^{-3}
$Z=4$	
$\mu=18{\cdot}2$ cm^{-1}	
Mo $K\alpha$ (0·71069 Å)	Cu $K\alpha$ (1·5418 Å)
2951 independent data	1758 independent data
$R=0{\cdot}084$	0·09

* This investigation.
† Derived from the $P2_1/c$ cell of Saito, Terashima, Sakaki & Tomita (1974).

Solution and refinement of the structure

The position of the copper atom was derived from an unsharpened Patterson map. A subsequent structure factor-Fourier calculation led to the positioning of the remaining 19 non-hydrogen atoms (a potential ambiguity exists in the assignment of the exocyclic atoms at C(2) and C(4) on the cytosine ring; a clear distinc-

Table 2. *Final atomic parameters*

Fractional coordinates ($\times10^4$) and heavy-atom anisotropic thermal parameters ($\times10^4$). The ellipsoid equation is:

$$\exp\left[-(B_{11}h^2+B_{22}k^2+B_{33}l^2+2B_{12}hk+2B_{13}hl+2B_{23}kl)\right].$$

	x	y	z	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
Cu	2069 (0·4)	93 (0·6)	2917 (0·3)	35 (0·3)	84 (0·7)	15 (0·2)	6 (0·5)	2 (0·2)	−0 (0·4)
O(2)	3830 (2)	1961 (3)	1981 (2)	59 (2)	109 (5)	22 (1)	−22 (3)	−3 (1)	−7 (2)
O(7)	3670 (2)	−935 (3)	3347 (2)	45 (2)	111 (4)	20 (1)	15 (3)	1 (1)	0 (2)
O(8)	4605 (2)	−1952 (3)	4592 (2)	66 (3)	130 (5)	29 (1)	26 (3)	−7 (2)	11 (2)
O(9)	651 (2)	1782 (3)	5218 (2)	57 (2)	112 (5)	21 (1)	13 (3)	9 (1)	−8 (2)
O(15)	3779 (3)	−184 (5)	7322 (3)	75 (3)	218 (7)	89 (2)	24 (5)	4 (2)	25 (4)
O(16)	1588 (3)	1592 (4)	7031 (2)	85 (3)	185 (6)	43 (2)	24 (4)	−6 (2)	−6 (3)
N(1)	3620 (3)	1194 (4)	504 (2)	56 (3)	102 (5)	19 (1)	−18 (3)	7 (2)	−2 (2)
N(3)	2365 (2)	8 (4)	1603 (2)	40 (2)	79 (4)	14 (1)	−0 (4)	1 (1)	−3 (3)
N(4)	737 (3)	−1721 (4)	1177 (2)	60 (3)	108 (5)	19 (1)	−26 (3)	−1 (2)	−2 (2)
N(8)	1873 (3)	508 (3)	4165 (2)	39 (2)	88 (5)	19 (1)	13 (3)	3 (1)	0 (2)
N(10)	374 (3)	1161 (4)	2769 (2)	50 (3)	111 (6)	22 (1)	18 (3)	1 (2)	4 (2)
C(2)	3298 (3)	1100 (4)	1392 (2)	37 (3)	71 (6)	19 (2)	6 (3)	4 (2)	2 (3)
C(4)	1671 (3)	−765 (4)	949 (2)	39 (3)	65 (5)	18 (2)	5 (3)	−2 (2)	3 (2)
C(5)	1950 (3)	−533 (4)	10 (2)	61 (3)	78 (6)	16 (2)	−8 (4)	−1 (2)	−6 (2)
C(6)	2941 (4)	402 (5)	−172 (2)	75 (4)	104 (7)	15 (1)	−11 (4)	6 (2)	1 (2)
C(7)	3780 (3)	−1100 (4)	4217 (2)	37 (3)	66 (6)	26 (2)	−7 (3)	−1 (2)	4 (3)
C(8)	2850 (3)	−152 (5)	4782 (2)	49 (3)	91 (6)	19 (1)	−2 (4)	−1 (2)	5 (3)
C(9)	909 (3)	1354 (4)	4422 (2)	40 (3)	70 (6)	22 (2)	−4 (3)	5 (2)	−1 (3)
C(10)	42 (3)	1908 (5)	3636 (2)	41 (3)	95 (5)	27 (2)	13 (4)	4 (2)	1 (3)

Table 2 (*cont.*)

Fractional coordinates ($\times 10^3$) and unscaled isotropic thermal parameters for the hydrogen atoms.

	x	*y*	*z*	*B*
H(1)	429	179	36	2·5
H(3)	27	−224	76	2·5
H(4)	55	−184	175	2·5
H(5)	143	−103	−46	2·5
H(6)	317	52	−80	2·5
H(7)	325	71	512	2·5
H(8)	248	−90	521	2·5
H(9)	−81	164	376	2·5
H(10)	9	310	359	2·5
H(11)	−20	41	260	2·5
H(12)	37	191	234	2·5
H(14)	462	31	721	6·0
H(15)	375	−103	790	6·0
H(16)	238	125	667	4·5
H(17)	112	219	652	4·5

tion was evident, however, from the size of the peaks on the Fourier map and bond lengths and angles at each site). Four cycles of isotropic least-squares calculations, minimizing the quantity $\sum w(|F_o|-|F_c|)^2$ where $w=1/\sigma^2(F_o)$, reduced the *R* value ($\sum||F_o|-|F_c||/\sum|F_o|$) to 0·136. A difference map was then computed, and all 15 independent hydrogen atoms located.

The refinement was continued with the addition of anisotropic thermal parameters for the non-hydrogen atoms. Three cycles of least squares in this mode led to a final *R* of 0·084. The final weighted *R* [$(\sum w(|F_o|-|F_c|)^2/\sum w|F_o|^2)^{1/2}$] and goodness-of-fit [$(\sum w(|F_o|-|F_c|)^2/(NO-NV))^{1/2}$ where NO = 2951 independent observations and NV = 181 parameters] are 0·042 and 1·8, respectively.

The scattering factors for all non-hydrogen atoms were taken from the compilation of Hanson, Herman, Lea & Skillman (1964); the form factor for H was that of Stewart, Davidson & Simpson (1965). The real part of the scattering curve for Cu was corrected for anomalous dispersion effects (Cromer, 1965). Final atomic parameters are collected in Table 2.*

The structure factor and Fourier calculations were done with the X-RAY 67 package of programs (Stewart, 1967); the least-squares refinements were performed with an extensively modified version of *ORFLS* (Busing, Martin & Levy, 1962); best planes were computed with the program of Pippy & Ahmed (1968); the illustrations were prepared with the aid of the computer program *ORTEP* (Johnson, 1965). All other calculations were performed with locally written programs.

Discussion

(i) *Molecular geometry*

[(Glycylglycinato) (cytosine)copper(II)] exists as a slightly distorted, square-planar complex with the four coordination sites occupied by the tridentate glycylglycine dianion and N(3) of cytosine (Fig. 1). The N(3) position of the cytosine ring is accessible for coordination in nucleosides, nucleotides and nucleic acids (Eichhorn, 1973), and we therefore expect that the mode of binding shown in Fig. 1 is possible in such systems and, in fact, has been shown to be so in the cytidine complex of glycylglycinatocopper(II) (Szalda, Marzilli & Kistenmacher, 1975*a*). Furthermore, the presence of the dipeptide ligand in the coordination sphere makes the complex a likely model for the type of interactions which may occur in enzyme–metal–nucleic acid ternary complexes (Eichhorn, 1973; Daune, 1974).

A point of particular interest in such studies is the elucidation of secondary interactions in these complexes. Sundaralingam & Carrabine (1971) first noted

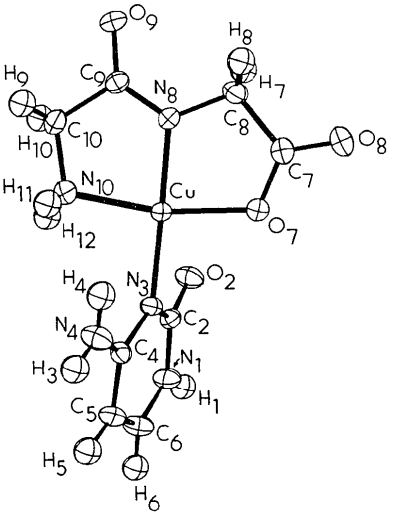

Fig. 1. A perspective view of the [(glycylglycinato) (cytosine)-copper(II)] complex. The view direction is approximately normal to the plane defined by the copper and its four coordinated atoms. The thermal ellipsoids are drawn at the 50% probability level.

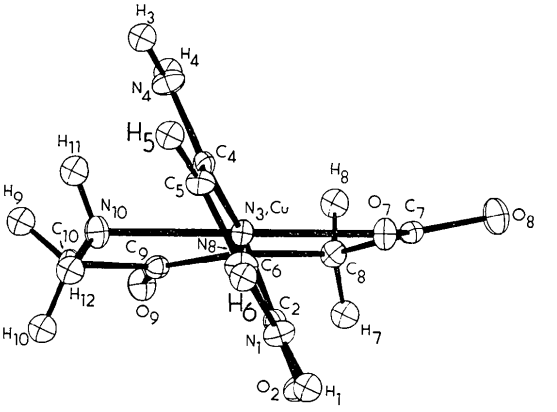

Fig. 2. A projection of the complex down the N(3)–Cu bond. Note in particular the disposition of the cytosine plane relative to that of the tridentate glycylglycine dianion.

* A list of structure factors has been deposited with the British Library Lending Division as Supplementary Publication No. SUP 31021 (18 pp., 1 microfiche). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

in the structure of [(dichloro) (bis(cytosine))copper(II)] that a significant intramolecular interaction existed between the exocyclic oxygen, O(2), on the cytosine ring and the copper atom [Cu···O(2) distances of 2·74 (1) and 2·88 (1) Å to the two independent cytosine ligands in the complex]. Subsequent structural studies on square-planar copper(II) complexes of cytosine (or cytidine) (Szalda, Marzilli & Kistenmacher, 1975*a*,*b*; STST, 1974; and the present work) all clearly show an axial, intramolecular Cu···O(2) interaction. The constancy (Szalda *et al.*, 1975*a*) of the geometrical parameters in this interaction in the range of complexes studied [Cu–N(3)$_{AVE}$ 1·99 (1), 1·979 (3) Å in this study; Cu···O(2)$_{AVE}$ 2·77 (1), 2·819 (3) Å in this study; angle Cu···O(2)–C(2)$_{AVE}$ 76 (1)°, 75·5 (2)° in this study] suggests that this type of interaction may be specific for square-planar copper(II) complexes of cytosine (cytidine) and may play some role in the recognition of cytosine residues in nucleic acids by copper(II).

Furthermore, there would seem to be some theoretical justification for the semi-chelation of cytosine (cytidine) to Cu(II) ions: a molecular electrostatic potential calculation for cytosine (Bonaccorsi, Pullman, Scrocco & Tomasi, 1972) shows that the presence of the carbonyl group, C(2)–O(2), adjacent to the pyrimidine nitrogen, N(3), establishes a wide attractive region for electrophilic agents with two deep minima, one in the direction of the lone pair at N(3) and one at an angle of 55° to the C(2)–O(2) bond. The minima at N(3) and O(2) are deeper than similar sites in adenine or thymine, respectively, and the simultaneous interaction of Cu(II) ions with N(3) and O(2) may be thought of then as a natural consequence of the electrostatic potential distribution inherent to the cytosine framework. The orientation of the cytosine ring about the N(3)–Cu bond is illustrated in Fig. 2. The relationship of the cytosine plane to that of the glycylglycine dianion does not appear to be critical. In the cytosine complex the dihedral angle between the dipeptide plane and that of the cytosine is 68·1 (3)°, while in the cytidine complex (Szalda *et al.*, 1975*a*) this dihedral angle is 104 (1)°, but as noted above the geometrical parameters in the intramolecular Cu···O(2) interaction remain essentially constant.

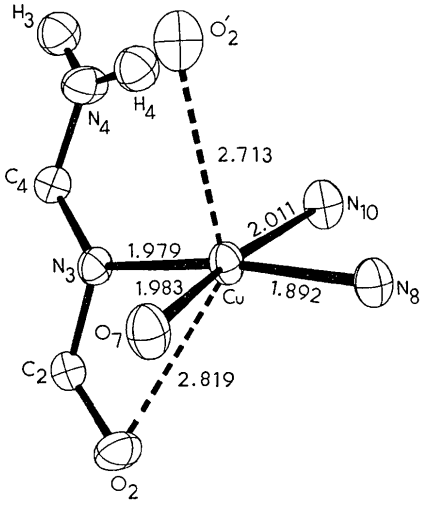

Fig. 3. The primary and secondary coordination sphere about the copper atom. O(2)′ is related to O(2) by the twofold screw axis along y [$\frac{1}{2}-x, -\frac{1}{2}+y, \frac{1}{2}-z$]. O(2)′ is also involved in a hydrogen bond with H(4).

The copper atom further extends its coordination sphere to the so-called (4+2) coordination geometry (Hathaway, 1973) *via* a Cu···O(2) interaction involving a twofold-screw related complex [Cu···O(2) distance of 2·713 (3) Å]. The presence of both intramolecular and intermolecular Cu···O(2) interactions is unique to this complex, and is probably not suggestive for biologically interesting systems. The complete coordination sphere about the copper is illustrated in Fig. 3.

(ii) *Molecular dimensions*

(*a*) *The glycylglycine dianion.* The glycylglycine dianion has approximately the same molecular dimensions, Table 3, as observed, for example, in the dihydrate (Kistenmacher & Szalda, 1975) and the trihydrate (Hermodsson & Strandberg, 1957; Strandberg, Lindqvist & Rosenstein, 1961; Freeman, 1967, 1974) complexes of glycylglycinatocopper(II) where in each case a water molecule completes the square-planar coordination about the copper atom and a second water molecule occupies an approximate axial position. There have been significant adjustments [to a maximum of about 3° in O(7)–Cu–N(10)] in some of the angles about the copper atom, but, as expected, the chelate 'bite' angles, O(7)–Cu–N(8) and N(10)–Cu–N(8), have maintained approximately constant values [83·8 (4) and 83·9 (4)° in this study; 82·7 (3) and 83·5 (3)° in the dihydrate; 82·9 (5)$_{AVE}$ and 83·3 (5)$_{AVE}$ for the average values in the two independent complexes in the trihydrate].

A point of some interest is the planarity of the coordinated dipeptide system. It is well known that the substitution of the coordination bond for the proton at the peptide-nitrogen atom N(8) causes the ligand system to be approximately planar (Strandberg *et al.*, 1961; Freeman, 1967). The cytosine complex, Table 4, retains this feature, although the planarity is less than that observed in the dihydrate and the trihydrate. The copper atom lies somewhat out of this plane, and that of the primary coordination sphere plane, Table 4, toward the O(2) atom involved in the intermolecular Cu···O(2) interaction. As in the hydrated complexes, there is a folding of the dipeptide chelate system about the Cu–N(8) bond, dihedral angle of 4·4 (3)° *versus* a value of 5·3 (3)° in the dihydrate, so that the two halves of the chelate system are more planar than the ligand system as a whole. The carboxylate and peptide groups have retained their expected planarity, Table 4.

(*b*) *The cytosine ligand.* The bond lengths and angles in the cytosine ligand are, in general, in reasonable agreement with other determinations (Sundaralingam & Carrabine, 1971; Szalda *et al.*, 1975*b*).

Table 3. *Heavy-atom interatomic distances and angles*

(*a*) Primary coordination sphere about the copper atom

Cu–O(7)	1·983 Å	Cu–N(8)	1·892 Å
Cu–N(3)	1·979	Cu–N(10)	2·011
O(7)–Cu–N(3)	97·3°	N(3)–Cu–N(8)	171·3°
O(7)–Cu–N(8)	83·8	N(3)–Cu–N(10)	95·1
O(7)–Cu–N(10)	167·6	N(8)–Cu–N(10)	83·9

(*b*) The glycylglycine chelate ligand

C(8)–O(7)	1·291 Å	C(9)—N(8)	1·306 Å
C(7)–O(8)	1·232	C(9)—O(9)	1·266
C(7)–C(8)	1·530	C(9)—C(10)	1·522
C(8)–N(8)	1·458	C(10)–N(10)	1·471
Cu—O(7)–C(7)	113·8°	Cu—N(8)—C(9)	119·7°
O(7)–C(7)–O(8)	122·6	C(8)–N(8)—C(9)	124·3
O(7)–C(7)–C(8)	117·1	O(9)–C(9)—N(8)	128·1
O(8)–C(7)–C(8)	120·3	O(9)–C(9)—C(10)	118·5
C(7)–C(8)–N(8)	107·9	N(8)–C(9)—C(10)	113·3
Cu—N(8)–C(8)	116·0	C(9)–C(10)–N(10)	112·4
		Cu—N(10)–C(10)	109·3

(*c*) The cytosine ligand

N(1)–C(2)	1·371 Å	N(4)–C(4)	1·317 Å
N(1)–C(6)	1·368	C(2)–O(2)	1·234
N(3)–C(2)	1·377	C(4)–C(5)	1·442
N(3)–C(4)	1·346	C(5)–C(6)	1·338
C(2)–N(1)–C(6)	121·6°	N(1)–C(2)–N(3)	117·7°
C(2)–N(3)–C(4)	121·2	N(3)–C(4)–N(4)	119·4
Cu—N(3)–C(2)	110·3	N(3)–C(4)–C(5)	119·9
Cu—N(3)–C(4)	127·8	N(4)–C(4)–C(5)	120·7
N(1)–C(2)–O(2)	121·0	C(4)–C(5)–C(6)	117·6
N(3)–C(2)–O(2)	121·3	N(1)–C(6)–C(5)	121·2

Estimated standard deviations: bond lengths, Cu–N(O) 0·003 Å; C–C(N,O) 0·006 Å. bond angles, N–Cu–N(O) 0·2°; C(N)–C(N)–C(O,N) 0·4°.

As we have noted previously (Marzilli, Kistenmacher & Chang, 1973; Marzilli *et al.*, 1974; Kistenmacher *et al.*, 1975*b*), there is considerable dissymmetry in the exocyclic bond angles at the hetero atom to which the metal atom is bonded in transition-metal purine complexes where interligand hydrogen bonding or chelation [see, for example, Heitner & Lippard (1974)] takes place. The present structure also shows this feature, Cu–N(3)–C(2) 110·3 (3)° and Cu–N(3)–C(4) 127·8 (3)°. This dissymmetry of the exocyclic angles at N(3) is also a common feature of the other copper(II)–cytosine (cytidine) complexes (Sundaralingam & Carrabine, 1971; Szalda *et al.*, 1975*a*,*b*).

The six-atom framework of the cytosine ligand is planar, Table 4. A particular feature of the present complex is the large out-of-plane deviation of O(2), 0·19 Å. This out-of-plane deviation is unique to this complex with the other known cytosine complexes showing minimal deviations of about 0·02–0·03 Å. A more common occurrence is a substantial deviation of N(4), 0·11 Å in [(dichloro) (bis(cytosine))copper(II)] (Sundaralingam & Carrabine, 1971) and 0·17 Å in the cytidine complex of glycylglycinatocopper(II) (Szalda *et al.*, 1975*a*). It seems likely then that the out-of-plane deviation of O(2) in this complex is due to the presence of both an intramolecular and an intermolecular Cu···O(2) interaction.

(iii) *Crystal packing*

The crystal packing is illustrated in Fig. 4, which is a projection of the unit-cell contents down the short *b* axis. The crystal packing is dominated by two principal features: (1) helical arrays of neutral complexes about twofold screw axes; (2) columns of water molecules about alternate twofold screw axes. The stacking

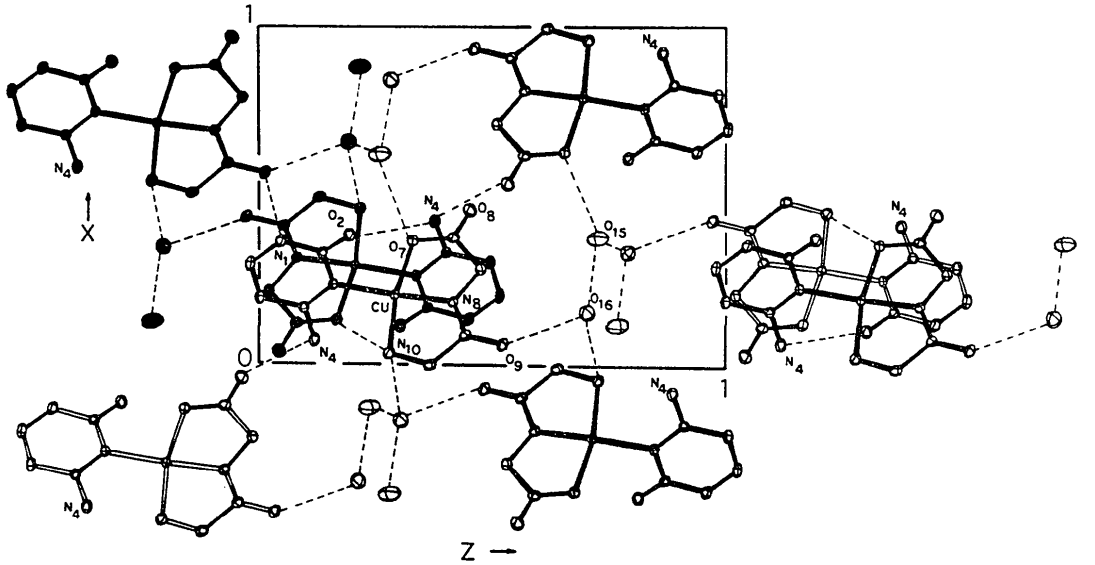

Fig. 4. A projection of the unit cell contents down the *b* axis. The labeled molecule has the atomic coordinates given in Table 2. The relative heights of the molecules are indicated by the following shading scheme: (1) unshaded, $y \simeq -0{\cdot}5$; (2) shaded bonds, $y \simeq 0{\cdot}0$; (3) shaded bonds and atoms, $y \simeq 0{\cdot}5$.

in the array of complexes is *via* the intermolecular Cu···O(2) interaction and hydrogen bonds involving the exocyclic amine and O(2) of the cytosine ring and the primary amine nitrogen, N(10), and coordinated oxygen, O(7), of the glycylglycine dianion. The water columns contain hydrogen bonds of the type O(15)–H(15)···O(16) and O(16)–H(16)···O(15).

Both direct, N(4)–H(3)···O(8) and N(1)–H(1)···O(9), and indirect hydrogen bonds through the water molecules [O(15)–H(14)···O(7), O(16)–H(17)···O(9) and N(10)–H(11)···O(16)] serve to interconnect the arrays of complexes and produce a three-dimensional network of attractive forces. Details of these hydrogen bonds are given in Table 5.

Table 4. *Least-squares planes and the deviations of individual atoms from these planes*

In each of the equations of the planes, the X, Y and Z are coordinates (Å) referred to the orthogonal axes a, b and c^*. Atoms indicated by an asterisk (*) were given zero weight in calculating the planes; other atoms were equally weighted.

(*a*) The complete eleven atom equatorial plane

$0{\cdot}5267X+0{\cdot}8493Y-0{\cdot}0362Z=1{\cdot}0299$ Å

Cu	−0·050 Å	N(10)	−0·260 Å
O(7)	0·109	C(7)	−0·016
O(8)	−0·168	C(8)	0·062
O(9)	0·112	C(9)	0·032
N(3)	0·170	C(10)	−0·009
N(8)	0·017	O(2)′	−2·714*†

(*b*) The copper and its four ligated atoms

$0{\cdot}4948X+0{\cdot}8689Y-0{\cdot}0098Z=1{\cdot}1346$ Å

Cu	−0·105 Å	N(10)	0·026 Å
O(7)	0·001	N(3)	0·051
N(8)	0·026	O(2)	2·180*
		O(2)′	−2·784*†

(*c*) The copper and the two halves of the tridentate glycylglycinato chelate

(1) The carboxylate half

$0{\cdot}5073X+0{\cdot}8604Y-0{\cdot}0487Z=0{\cdot}9253$ Å

Cu	−0·038 Å	C(7)	−0·073 Å
O(7)	0·072	C(8)	0·024
N(8)	0·016	O(8)	−0·256*

(2) The peptide half

$0{\cdot}4986X+0{\cdot}8577Y-0{\cdot}1259Z=0{\cdot}4834$ Å

Cu	0·054 Å	C(9)	−0·017 Å
N(8)	−0·033	C(10)	0·075
N(10)	−0·078	O(9)	−0·030*

(*d*) The carboxylate group

$-0{\cdot}6137X-0{\cdot}7883Y-0{\cdot}0441Z=-1{\cdot}9027$ Å

O(7)	−0·002 Å	C(7)	0·007 Å
O(8)	−0·002	C(8)	−0·002

(*e*) The peptide group

$0{\cdot}5312X+0{\cdot}8426Y-0{\cdot}0890Z=0{\cdot}7240$ Å

O(9)	0·004 Å	C(9)	−0·010 Å
N(8)	0·004	C(10)	0·003

(*f*) The cytosine plane

$-0{\cdot}6197X+0{\cdot}7804Y-0{\cdot}0835Z=-1{\cdot}6634$ Å

N(1)	−0·026 Å	C(5)	0·034 Å
N(3)	−0·035	C(6)	−0·018
C(2)	0·052	O(2)	0·192*
C(4)	−0·007	N(4)	−0·010*
		Cu	0·102*

† O(2)′ is related to O(2) by the twofold screw axis along $y[\frac{1}{2}-x,-\frac{1}{2}+y,\frac{1}{2}-z]$.

Table 5. *Distances and angles in the intermolecular interactions of the type D–H···A*

D	H	*D*–H	*A*	*D*···*A*	H···*A*	∠*D*–H···*A* (∠H–*D*···*A*)
N–H···O and O–H···O hydrogen bonds						
N(1)	H(1)	0·90 Å	O(9)[a]	2·765 Å	1·88 Å	171° (6°)
N(4)	H(3)	0·88	O(8)[b]	2·802	1·95	162 (13)
N(4)	H(4)	0·88	O(2)[c]	2·938	2·19	143 (27)
N(10)	H(11)	0·89	O(16)[d]	3·080	2·28	150 (22)
N(10)	H(12)	0·88	O(7)[e]	3·066	2·28	149 (22)
O(15)	H(14)	1·01	O(7)[f]	3·075	2·09	164 (11)
O(15)	H(15)	1·07	O(16)[g]	2·807	1·96	134 (30)
O(16)	H(16)	1·05	O(15)[h]	2·766	2·10	119 (42)
O(16)	H(17)	1·01	O(9)[h]	2·822	1·99	138 (28)
C–H···O interactions						
C(5)	H(5)	0·96	O(8)[b]	3·266	2·54	132
C(8)	H(7)	0·95	O(8)[f]	3·308	2·52	140

(*a*)	$\frac{1}{2}+x, \frac{1}{2}-y, -\frac{1}{2}+z$	(*e*)	$\frac{1}{2}-x, \frac{1}{2}+y, \frac{1}{2}-z$
(*b*)	$-\frac{1}{2}+x, -\frac{1}{2}-y, -\frac{1}{2}+z$	(*f*)	$1-x, -y, 1-z$
(*c*)	$\frac{1}{2}-x, -\frac{1}{2}+y, \frac{1}{2}-z$	(*g*)	$\frac{1}{2}-x, -\frac{1}{2}+y, \frac{3}{2}-z$
(*d*)	$-x, -y, 1-z$	(*h*)	x, y, z

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The Crystal Structure of Nambulite (Li,Na)$Mn_4Si_5O_{14}(OH)$

BY HAJIME NARITA, KICHIRO KOTO AND NOBUO MORIMOTO

The Institute of Scientific and Industrial Research, Osaka University, Suita, Osaka 565, *Japan*

AND MORIMASA YOSHII

Geological Survey of Japan, Kawada-cho, Shinjuku, Tokyo 162, *Japan*

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Nambulite, (Li,Na)$Mn_4Si_5O_{14}(OH)$, is triclinic with $a=7{\cdot}621$ (5), $b=11{\cdot}761$ (8), $c=6{\cdot}731$ (5) Å, $\alpha=92°46$ (3)′, $\beta=95°05$ (3)′, $\gamma=106°52$ (5)′ and $D_x=3{\cdot}55$ g cm^{-3}. The space group is $P\bar{1}$ and $Z=2$. The crystal structure has been determined by the Patterson method and refined to an R value of 0·086 for all 2233 reflexions collected by the counter method. The structure consists of infinite silicate chains with a repeat unit of five tetrahedra, and Mn polyhedral bands, both parallel to [110]. The mean Mn–O distances are 2·233, 2·242, 2·188 and 2·410 Å for crystallographically independent Mn polyhedra. The mean (Li,Na)–O distance is 2·487 Å for (Li,Na) polyhedra. The mean Si–O distances are 1·621, 1·623, 1·623, 1·626 and 1·630 Å for independent Si tetrahedra. In spite of the difference in the number of cations, nambulite is more closely related to baringtonite, $Ca_2Fe^{2+}Fe^{3+}Si_5O_{14}(OH)$, than to rhodonite, $CaMn_4Si_5O_{15}$, in the arrangement of silicate chains and polyhedral bands.

Introduction

Nambulite is a new mineral with the ideal formula $LiNaMn_8Si_{10}O_{28}(OH)_2$ (Yoshii, Aoki & Maeda, 1972). Because of the similarity of the cell dimensions and chemical composition of nambulite and rhodonite, $CaMn_4Si_5O_{15}$ (Liebau, Hilmer & Lindemann, 1959; Peacor & Niizeki, 1963), Yoshii *et al.* (1972) considered that both minerals should have essentially the same crystal structure. However, they suspected that Li and Na atoms might occupy independent positions in the structure of nambulite, because of the difference in the ionic radii of Li and Na atoms. In a study of the crystal chemistry of the system Li_2SiO_3–Mn_2SiO_4–SiO_2–H_2O, Ito (1972) reported that the maximum substitution of Na for Li in synthetic hydrorhodonite, $LiMn_4Si_5O_{14}(OH)$, did not exceed 30% of the total Li.

Nambulite also has some similarity in cell dimensions and chemical composition to babingtonite, $Ca_2Fe^{2+}Fe^{3+}Si_5O_{14}(OH)$, though the numbers and species of large cations in the two minerals are different. The structure of babingtonite has been determined by Araki & Zoltai (1972) and found to have the *Fünferketten pyroxenoid structure*.

In this investigation the crystal structure of nambulite has been studied to determine the arrangement of Li and Na atoms in the structure, and to elucidate the structural relationships between nambulite, rhodonite and babingtonite.

Experimental

Single crystals of nambulite from the Funakozawa Mine, Iwate, Japan, were used in this study. They are triclinic. The cell dimensions, obtained with a four-