The Crystal Structure of Cupric Complex with Succinimide I. Cesium Tetrakis(succinimidato)copper(II) Dihydrate

Tomitake TSUKIHARA, Yukiteru KATSUBE, Kumiko FUJIMORI, and Toshiaki ITO

Faculty of Engineering, Tottori University, Koyama-cho, Tottori

(Received February 23, 1972)

The crystal structure of cesium tetrakis(succinimidato) copper(II) dihydrate, $Cs_2(Cu(sucim)_4).2H_2O$, has been determined by means of X-ray analysis. The crystals are violet rhombic plates. Dimensions of the triclinic unit cell are $a=9.19$, $b=15.32$, $c=8.39$ Å, $\alpha=88.7°$, $\beta=92.0°$, $\gamma=93.8°$, and $z=2$. The space group is $C\bar{1}$. The structure has been determined by the Patterson synthesis, a series of Fourier syntheses and the least-squares method. The coordination around the copper atom is a square planar. Two independent cesium ions have a quite different environment. Complex anions, $(Cu(sucim)_4)^{2-}$, are linked with each other through the hydrogen bonds between water and carboxyl oxygen atoms.

Succinimide forms complexes with various metallic ions. A number of cupric compounds with succinimide having the general formula $M_2^+[Cu(sucim)_4]^{2-}.nH_2O$ and a red or violet color in solid state have been reported.

A structural investigation of compounds of this type is thought to be of interest from the viewpoint of the coordination chemistry of cupric complexes. Some of these complexes have been studied spectroscopically.[1]

As a part of studies of the crystal structure of such complexes, a detailed description of the crystal structure of cesium tetrakis(succinimidato)copper(II) dihydrate is given in this paper.

Experimental

The crystals are violet rhombic plates. Preliminary Weissenberg and oscillation photographs established that the crystal was triclinic with axis *a* along an edge of the plate and axes *b* and *c* along the diagonals of the rhombic plane (Fig. 1). By the systematic extinction of *hkl* for odd $h+k$ the space group was restricted to $C1$ or $C\bar{1}$. The cell dimensions were obtained by means of the least-squares method. The crystal data were collected on a Rigaku Denki Computer-controlled four-circle diffractometer, using Ni-filtered Cu$K\alpha$ radiation. All the intensities were obtained from a crystal with dimensions $0.25\times0.25\times0.08$ mm³. Reflections with 2θ values up to 120° in octants of *(hkl)*, *($\bar{h}$kl)*, *(h$\bar{k}$l)*, and *($\bar{h}\bar{k}$l)* were measured by ω-2θ scanning technique at a scan rate of 2° per minute. The scan range of ω for each reflection was calculated by the formula $\omega=0.90°+0.15°\tan\theta$, and the backgrounds were measured at both ends of the scan range for 10.0 seconds. Attenuators were inserted automatically when the maximum counting rate exceeded 8000 cps. Reflections whose counts at mid point of the scan range were less than 10 cps were not measured. The intensities of two reference reflections $I(006)$ and $I(008)$ were measured after every fifty reflections. Owing to sublimation of the crystal, the intensities of these two reflections decreased gradually during the course of measurement. Correction was made for a decay of the crystal by multiplying each reflection by a factor found from the normalized plot of the intensities of the reference reflections. Application of Lotrentz-polarization factors was made but no correction for absorption.

TABLE 1. CRYSTAL DATA

$Cs_2CuC_{16}H_{20}N_4O_{10}$	Mw=748.71	
Triclinic:	$C\bar{1}$	
a=9.189 Å	$b=15.315$ Å	$c=8.387$ Å
$\alpha=88.7°$	$\beta=92.0°$	$\gamma=93.8°$
$D_{cal}=2.11$ g/cm³		
$D_{obs}=2.13$ g/cm³ (by flotation)		

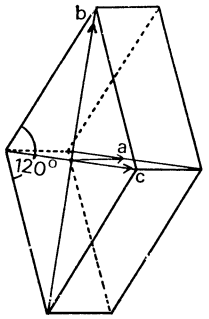

Fig. 1. The crystal shape and the orientation of the axes.

Structure Determination and Refinement

A sharpened three-dimensional Patterson function showed that a copper atom and two cesium ions should be located on the special positions (0,0,0), (1/4,1/4,0) and (1/4,1/4,1/2), respectively. The space group was restricted to $C\bar{1}$ by an interpretation of the Patterson function.

The remaining light atoms were located by successive cycles of structure factor calculations and difference Fourier synthesis. The trial structure was refined by a diagonal least-squares procedure with the positional and isotropic thermal parameters. The isotropic refinement converged the reliability index ($R=\Sigma||F_o|-|F_c||/\Sigma|F_o|$) to 0.19. Further refinement was carried out by the least-squares of block-diagonal matrix approximation with the positional parameters for all the non-hydrogen atoms, the anisotropic thermal parameters for three metal atoms and the isotropic thermal parameters for the other atoms. The final value of R was 0.11. The atomic scattering factors were taken from the literature.[2] Those of copper and cesium atoms were corrected for real and

1) S. Yamada and S. Miki, This Bulletin, **36**, 680 (1963).

2) "International Tables for X-Ray Crystallography," Vol. III, Kynoch Press, Birmingham (1962), p. 202 and p. 211.

Table 2. Final atomic parameters

Atom	x	y	z	Atom	x	y	z
Cs1	0.2500	0.2500	0.0000	CB3	0.2199	−0.0130	−0.4505
Cs2	0.2500	0.2500	0.5000	CB4	0.1722	0.0291	−0.2924
Cu	0.0000	0.0000	0.0000	OA1	0.0693	−0.1990	0.1219
CA1	0.1712	−0.1410	0.1304	OA2	0.3311	0.0648	0.1220
CA2	0.3272	−0.1685	0.1995	OB1	−0.0426	−0.1617	−0.2507
CA3	0.4127	−0.0788	0.1989	OB2	0.2178	0.1033	−0.2548
CA4	0.3047	−0.0139	0.1363	OW1	0.0076	−0.3368	0.3282
CB1	0.0410	−0.0980	−0.2906	NA1	0.1708	−0.0570	0.1019
CB2	0.1306	−0.1033	−0.4481	NB1	0.0746	−0.0258	−0.2136

Atom	B_{11} or B	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
Cs1	0.0068	0.0017	0.0130	−0.0011	0.0028	0.0000
Cs2	0.0192	0.0043	0.0183	−0.0080	−0.0122	0.0050
Cu	0.0045	0.0013	0.0089	0.0001	0.0025	0.0006
CA1	7.12					
CA2	7.76					
CA3	7.08					
CA4	6.56					
CB1	6.47					
CB2	7.44					
CB3	6.94					
CB4	5.89					
OA1	3.91					
OA2	3.55					
OB1	3.07					
OB2	3.04					
OW1	6.33					
NA1	1.44					
NB1	1.29					

Temperature Factor

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

or

$$=\exp[-B(\sin\theta/\lambda)^2]$$

Table 4. Bond distances and angles with their e.s.d.

Bond	Length	e.s.d.	Bond	Length	e.s.d.
Cu-NA1	2.00 Å	0.02 Å	Cu-NB1	2.00 Å	0.02 Å
CA1-CA2	1.61	0.04	CB1-CB2	1.59	0.03
CA1-NA1	1.31	0.03	CB1-NB1	1.31	0.03
CA2-CA3	1.54	0.03	CB2-CB3	1.56	0.04
CA3-CA4	1.52	0.03	CB3-CB4	1.58	0.03
CA1-OA1	1.25	0.03	CB1-OB1	1.26	0.03
CA4-OA2	1.22	0.03	CB4-OB2	1.22	0.03
CA4-NA1	1.38	0.03	CB4-NB1	1.38	0.03

	Angle	e.s.d.		Angle	e.s.d.
CA2-CA1-OA1	118°	2°	CB2-CB1-OB1	119°	2°
CA2-CA1-NA1	112	2	CB2-CB1-NB1	112	2
OA1-CA1-NA1	130	2	OB1-CB1-NB1	128	2
CA1-CA2-CA3	100	2	CB1-CB2-CB3	102	2
CA2-CA3-CA4	105	2	CB2-CB3-CB4	102	2
CA3-CA4-OA2	125	2	CB3-CB4-OB2	121	2
CA3-CA4-NA1	110	2	CB3-CB4-NB1	111	2
OA2-CA4-NA1	125	2	OB2-CB4-NB1	128	2
Cu-NA1-CA1	123	1	Cu-NB1-CB1	124	1
Cu-NA1-CA4	124	1	Cu-NB1-CB4	123	1
NA1-Cu-NB1	89	1	NA1-Cu-NB1	89	1
CA1-NA1-CA4	112	2	CB1-NB1-CB4	112	2

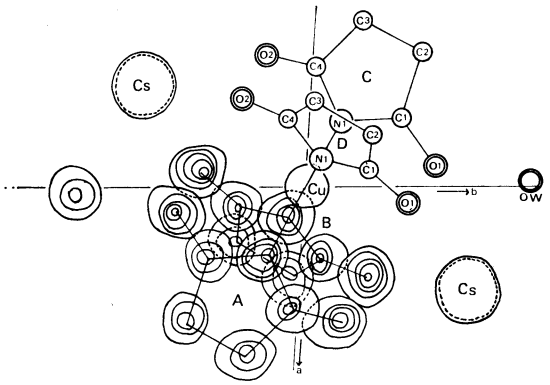

Fig. 2. The composite electron density map of $Cs_2(Cu(sucim)_4)\cdot 2H_2O$, contours are drawn at intervals of 1.0 e/Å^3 starting at 2.0 e/Å.

imaginary parts of anomalous dispersion: $\Delta f_{Cu}'=-2.1$, $\Delta f_{Cu}''=0.7$, $\Delta f_{Cs}'=-1.8$, and $\Delta f_{Cs}''=8.0$. The composite electron density map is given in Fig. 2, and the final atomic parameters in Table 2. The standard deviations of the positional parameters are 0.02 Å for oxygen, nitrogen, and carbon atoms. Table 3 containing the observed and calculated structure factors is kept as Document No. 7208 at the Chemical Society of Japan.

Description and Discussion of the Structure

The bond distances and angles are given in Table 4. The structure of the complex anion $(Cu(sucim)_4)^{2-}$ is centrosymmetric about the copper atom. Four nitrogen atoms of four succinimides take a square planar arrangement around the copper atom with a mean Cu–N distance of 2.00 Å. The distance is in good agreement with that generally found in the planar part of other Cu(II)-complexes: 1.963 Å in ethyl-

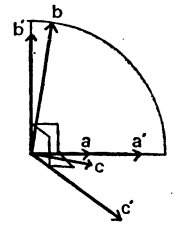

Fig. 3—1. The orientation of the orthogonal axes, a', b', and c' related to the crystal axes, a, b, and c.

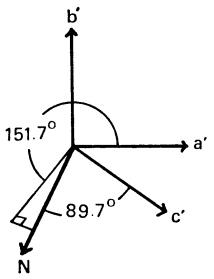

Fig. 3—2. The orientation of the coordination-plane related to the orthogonal axes. Symbol N represents the normal line of the plane.

Table 5. Equations of the least-squares plane through atoms

Equation	Atom	Deviation
Succinimide group of A		
$0.3037x'-0.1584y'-0.9395z'+0.2122=0$	NA1	0.0303 Å
	CA1	0.0332
	CA2	−0.0093
	CA3	−0.0106
	CA4	0.0110
	OA1	−0.0259
	OA2	−0.0151
	*Cu	0.2122
Succinimide group of B		
$0.7564x'-0.3965y'+0.5202z'+0.2095=0$	NB1	0.0353
	CB1	−0.0181
	CB2	0.0001
	CB3	−0.0057
	CB4	0.0183
	OB1	−0.0024
	OB2	−0.0179
	*Cu	0.2095
Succinimide group of C		
$-0.3037x'+0.1584y'+0.9395z'+0.2122=0$		
Succinimide group of D		
$-0.7564x'+0.3965y'-0.5202z'+0.2095=0$		
The plane of the coordination square		
$-0.4744x'-0.8803y'+0.0061z'+0.0000=0$		

where $x'=ax+by\cos\gamma+cz\cos\beta$, $y'=by\sin\gamma-cz\sin\beta\cos\alpha^*$, $z'=cz\sin\beta$

* Atom not included in the least-squares calculations.

enebidiguanide copper(II) chloride monohydrate,[3] 2.01 Å in Bis(pyridine–2–acetamide)copper(II) perchlorate[4] and 2.003 Å in copper(II) complex with *o*-hydroxyacetophenone isobutylimine.[5] Since the copper atom is located at the center of symmetry, it is exactly on a coordination-plane defined by the four nitrogen atoms. An orientation of the coordination-plane is given in Fig. 3.

The dimensions of the succinimides in the complex anion are consistent with those of the free molecule.[6] Each succinimide ring is planar within a limit of error. The best planes determined by the least-squares calculation are given in Table 5. The dihedral angle between the coordination-plane and the A-ring of succinimide is 90.6° and that for the B-ring 90.4°. Four succinimide rings are therefore almost perpendicular to the coordination-plane. Thus, the complex anion has approximate symmetry of D_{4h}. This configuration agrees with that proposed spectroscopically for $K_2(Cu(II)(sucim)_4)\cdot 6H_2O$ by Yamada and Miki.[1] The structure of the complex anion is given in Fig. 4.

Two independent cesium ions exist in the structure. That at (1/4,1/4,0), Cs1, has eight oxygen atoms situated at the corners of an almost perfect tetragonal prism with dimensions $3.32\times3.34\times4.09$ Å^3. These atoms belong to the carbonyl groups. This arrangement may be compared to the CsCl-type structure of eight-coordination. The cesium ion at (1/4,1/4,1/2), Cs2, fits into a cavity in the crystal, and is surrounded by six oxygen atoms which form a somewhat distorted octahedron. Two of these belong to water molecules and the other four are carbonyl oxygen atoms. The Cs2 ion is also at the center of symmetry with respect to the six oxygen atoms. The mean value 3.04 Å

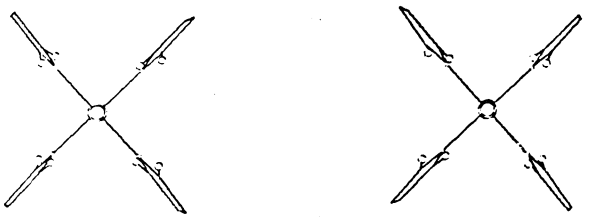

Fig. 4. The complex anion of $(Cu(sucim)_4)^{2-}$ shown by a stereo pair.

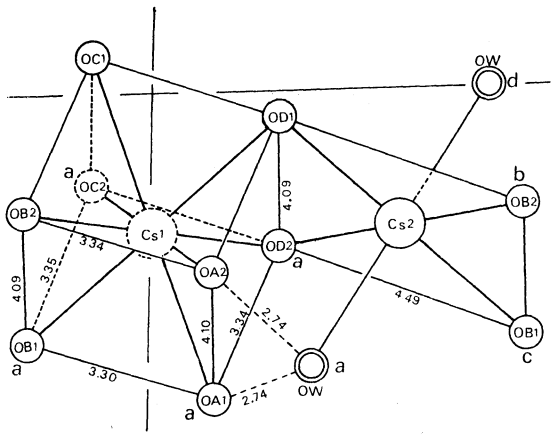

Fig. 5—1. The arrangement of oxygen atoms around two independent cesium ions. Small letters, *a*, *b*, and *c* indicate the symmetry operations in Table 6.

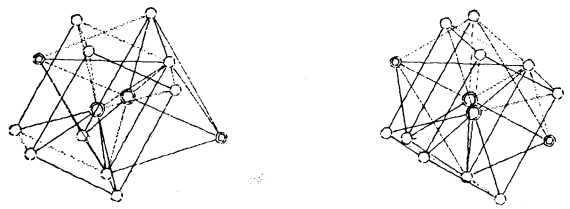

Fig. 5—2. The arrangement of oxygen atoms around two cesium ions shown by a stereo pair.

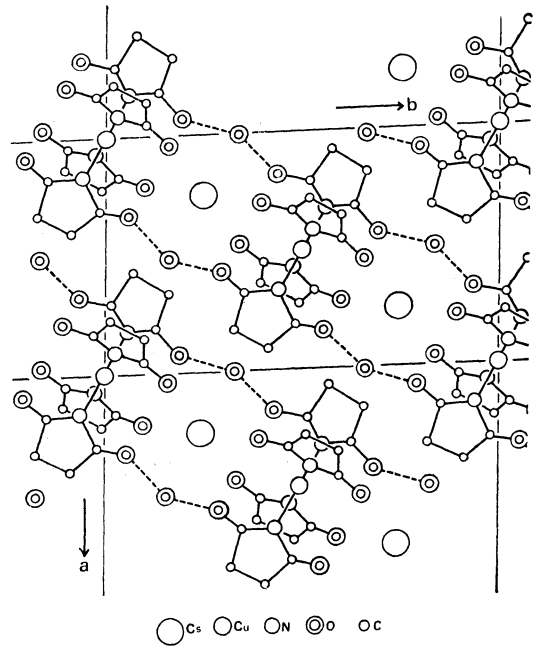

Fig. 6—1. The crystal structure of $Cs_2(Cu(sucim)_4)\cdot 2H_2O$ projected along the *c* axis. Hydrogen bonds are indicated by broken lines.

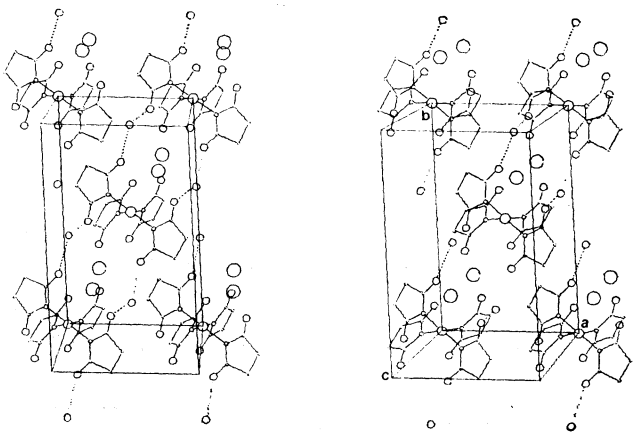

Fig. 6—2. The crystal structure of $Cs_2(Cu(sucim)_4)\cdot 2H_2O$ shown by a stereo pair.

3) M. Matthew and N. R. Kunchur, *Acta Crystallogr.*, **B26**, 2054 (1970).
4) M. Sekizaki, F. Marumo, K. Yamasaki, and Y. Saito, This Bulletin, **44**, 1731 (1971).
5) C. A. Ghilardi and E. C. Lingafelter, *Acta Crystallogr.*, **B26**, 1807 (1970)
6) R. Mason, *ibid.*, **9**, 405 (1956).

Table 6. Environment of cesium ions and water molecules

Atom	Neighbor atom		Distance	Atom	Neighbor atom		Distance
Cs1	OA2	or OC2(a)	3.12 Å	Cs1	OB2	or OD2(a)	3.13 Å
Cs1	OC1	OA1(a)	3.13	Cs1	OD1	OB1(a)	3.12
Cs2	OD1	OB1(c)	3.06	Cs2	OD2 (a)	OB2(b)	3.02
Cs2	OW1(a)	OW1(d)	3.19	Cs1	Cs2		4.19

Hydrogen bonds

OA2···OW1(a)	2.74 Å	OA1···OW1	2.74 Å

Angles

OA2-Cs1-OB2		or	OC2(a)-Cs1-OD2(a)	65°
OB2-Cs1-OC1			OD2(a)-Cs1-OA1(a)	65
OC1-Cs1-OD1			OA1(a)-Cs1-OB1(a)	64
OA2-Cs1-OD1			OC2(a)-Cs1-OB1(a)	65
OA2-Cs1-OA1(a)			OC2(a)-Cs1-OC1	82
OB2-Cs1-OB1(a)			OD2(a)-Cs1-OD1	82
OB2-Cs1-OD1			OD2(a)-Cs1-OB1(a)	98
OA2-Cs1-OC1			OC2(a)-Cs1-OA1(a)	98
OD1-Cs2-OD2(a)			OB1(c)-Cs2-OB2(b)	85
OD1-Cs2-OB2(b)			OB1(c)-Cs2-OD2(a)	95
OD1-Cs2-OW1(a)			OB1(c)-Cs2-OW1(d)	87
OD2(a)-Cs2-OW1(a)			OB2(b)-Cs2-OW1(d)	87
OD1-Cs2-OW1(d)			OB1(c)-Cs2-OW1(a)	93
OD2(a)-Cs2-OW1(d)			OB2(b)-Cs2-OW1(a)	93
OB2-OA2-OD1	90°		OA2-OD1-OC1	90°
OD1-OC1-OB2	90		OC1-OB2-OA2	90
OB2-OB1(a)-OA1(a)	91		OB1(a)-OA1(a)-OA2	90
OA1(a)-OA2-OB2	90		OA2-OB2-OB1(a)	90
OD1-OA2-OA1(a)	90		OA2-OA1(a)-OD2(a)	90
OA1(a)-OD2(a)-OD1	90		OA2-OD1-OD2(a)	90
OD1-OD2(a)-OB1(c)	91		OB2(b)-OD1-OC1	175

Key for molecular position

a: $(0.5+x, 0.5+y, z)$ b: $(x, y, 1.0+z)$ c: $(0.5+x, 0.5+y, 1.0+z)$, d: $(-x, -y, 1.0-z)$

of the Cs2-O(carbonyl) is slightly less than 3.12 Å of Cs1-O(carbonyl). The arrangement around the Cs2 ion may be compared to the six-coordination NaCl-type structure. The Cs-O distances are in fairly good agreement with the sum of ionic radii, 3.09 Å. Thus all the oxygen atoms gather around the cesium ions whose positive charges are probably neutralized by negative charges of the oxygen atoms. The environment is illustrated in Fig. 5 and Table 6.

The complex anions are linked to the neighbouring anions in the [110] direction through the hydrogen bonds between the water molecules and carbonyl oxygen atoms and through the ionic contacts between the cation of Cs1 and carbonyl oxygen atoms. The complex anions are also linked together by Cs2-O(carbonyl) contacts in the direction of axis *c*.

The crystal structure is shown in Fig. 6.

The authors express their thanks to Dr. S. Komorita for valuable discussions and the kind supply of crystals, and to Dr. T. Ashida for permission to use his program.