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Crystal Structure of Bis(iminodiacetamide)copper(II) Perchlorate[1]

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Bis(iminodiacetamide)copper(II) perchlorate was newly synthesized, and the crystal structure was determined from three-dimensional X-ray data collected on a diffractometer. The structure was refined by block-diagonal least-squares methods to give $R=0.08$ for the 950 observed reflections. The crystals are monoclinic with the space group of $P2_1/c$. There are two formula units per unit cell with $a=6.183$, $b=17.617$, $c=8.900$ Å, and $\beta=110.2°$. The complex is centrosymmetric, in which the two ligand molecules coordinate to the central copper atom through two imino nitrogen atoms and two of the four amide oxygen atoms in *trans* positions, exhibiting a square-planar coordination. The other two amide oxygen atoms are weakly bonded to the copper atom above and below this square-plane, thus completing an *s-facial* distorted (elongated) octahedral coordination. The complex cations are held together through hydrogen bonds to form infinite chains along the *a* axis. These chains are connected with one another by perchlorate ions through hydrogen bonds, thus forming three-dimensional networks.

A number of bivalent copper complexes of bidentate ligands exhibit an elongated octahedral structure of D_{2h} symmetry.[2–7] There are some complexes of terdentate ligands in which the length of the four coordination bonds in the same plane are longer than those of the other two coordination bonds, such as $[Cu(dien)_2](NO_3)_2$ (dien=diethylenetriamine).[8] Such an unusual structure is sometimes called a "compressed" distorted octahedral structure.[9] The complex of the other terdentate ligand, such as $[Cu(ida)_2]^{2-}$ (ida=iminodiacetate), was, however, reported on the basis of a spectroscopic investigation, to have an elongated octahedral structure.[10] Two of the factors that differentiate the structures of these complexes may be as follows: the iminodiacetate ion[11] has a smaller stability constant of complex formation than diethylenetriamine,[12] and the force constant of Cu–O is generally smaller than that of Cu–N.[13]

Iminodiacetamide, $HN(CH_2CONH_2)_2$, (abbreviated as $idaaH_2$) can act as a terdentate ligand. It can also function as a neutral ligand, forming a cationic complex like diethylenetriamine. It can coordinate to a metal atom through two oxygen and one nitrogen atoms like the iminodiacetate ion. It is difficult to decide by the spectroscopic method whether or not the distorted octahedral coordination around the copper atom is "compressed." A copper complex of iminodiacetamide, $Cu(idaaH_2)_2(ClO_4)_2$, was subjected to X-ray crystal analysis in order to clarify this point and to facilitate the assignments of the infrared spectra.

Experimental

Preparations. Iminodiacetamide was prepared as white needles by the reaction of diethyliminodiacetate and ammonia in ethanol. The melting point, 142 °C, and the results of chemical analysis agreed with the reported values.[14]

The complex was prepared by mixing 0.07 g of the ligand with 0.09 g of copper(II) perchlorate dissolved in water and then by concentrating the mixture *in vacuo* at room temperature. The crystals thus obtained were washed with a small amount of water. Yield, 0.06 g.

Found: C, 18.00; H, 3.46; N, 15.67; Cu, 11.90%. Calcd for $C_8H_{18}N_6O_4Cu(ClO_4)_2$: C, 18.00; H, 3.56; N, 15.75; Cu, 11.92%.

Determination of the Cell Constants and Collection of the Intensity Data. The cell constants were determined by the least-squares methods based on the 2θ values measured on a single-crystal diffractometer using Cu$K\alpha$ radiation ($\lambda=1.5418$ Å). A crystal with a diameter of about 0.2 mm was sealed in a glass capillary. The intensities were collected on a Hilger-Watts automatic four-circle diffractometer, using Ni-filtered Cu$K\alpha$ radiation. The ω-2θ step-scan technique with $\Delta\omega=0.02°$ and a counting time of 1 sec per step were used. The scan range was 0.8° in the 0—57° region and 1.2° in the 57—75° region. At each end of the scan, the backgrounds were measured for 10 sec in the $\theta \leqq 57°$ region and for 15 sec in the $\theta > 57°$ region. The fluctuations in intensity of the three standard reflections measured every 100 reflections were about 2% during the data collection. A total of 1600 independent reflections were measured up to $\theta=75°$; of them, 650 had an intensity less than σ's above the background. Thus, 950 independent non-zero reflections were used in the analysis. They were converted to $|F|$ by applying Lorentz and polarization corrections. No corrections were made for absorption or extinction ($\mu r=0.2$).

The crystal data are:

$Cu(C_4H_9N_3O_2)_2(ClO_4)_2$, *F.W.* 524.72, monoclinic, $a=6.183(2)$, $b=17.617(4)$, $c=8.900(2)$ Å, $\beta=110.2(1)°$, $U=908$ Å^3, $D_m=1.94$, $D_x=1.92$ g cm^{-3}, $Z=2$.

The systematic absences are $h0l$ with l odd and $0k0$ with k odd. Hence, the space group is $P2_1/c$.

Solution and Refinement of the Structure

The copper atoms must lie on a set of twofold special positions, since there are only two formula units in a unit cell. The complex must thus have a center of symmetry. The coordinates of the chlorine atoms were determined from the prominent peaks in a Patterson map; those of all the other atoms except the hydrogens were determined by a three-dimensional electron density map calculated on the basis of the copper and chlorine atoms.

The block-diagonal least-squares refinements were carried out for the 950 reflections with equal weights. After five cycles of refinement with isotropic thermal parameters, the R-value became 0.12. Further refinements with anisotropic thermal parameters finally reduced the R-value to 0.08.

The atomic scattering factors were taken from the "International Tables for X-ray Crystallography."[15]

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Table 2. Final atomic parameters and their estimated standard deviations

Values are given $\times 10^4$. Positional parameters are expressed as fractions of the lattice parameters. The estimated standard deviations are in parentheses and refer to the last decimal positions of the respective values in this table and other subsequent tables.

Thermal parameters are in the form: $\exp[-(h^2\beta_{11}+k^2\beta_{22}+l^2\beta_{33}+hk\beta_{12}+hl\beta_{13}+kl\beta_{23})]$

Atom	x	y	z	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Cu	0	0	0	198(1)	12(1)	85(1)	16(3)	108(2)	14(4)
Cl	2123(1)	1877(1)	4403(1)	268(1)	16(1)	113(2)	−9(3)	161(2)	−11(5)
O(1)	2212(2)	−189(1)	−1078(3)	230(.2)	8(2)	119(4)	30(8)	116(5)	17(11)
O(7)	3076(3)	−88(2)	2650(4)	262(4)	17(1)	86(2)	−44(9)	93(6)	−5(13)
O(10)	2001(3)	1637(2)	2853(4)	702(11)	47(5)	120(7)	48(17)	346(7)	−44(18)
O(11)	−225(4)	2020(2)	4285(3)	365(12)	43(5)	381(11)	99(18)	425(19)	46(24)
O(12)	3075(3)	1311(2)	5622(2)	476(8)	37(6)	187(12)	112(14)	184(17)	79(19)
O(13)	3390(3)	2557(2)	4835(2)	729(19)	38(7)	386(19)	−301(19)	309(35)	−107(26)
N(4)	453(2)	−1106(2)	638(2)	199(4)	12(1)	73(2)	20(9)	54(6)	4(13)
N(8)	4578(3)	−1089(1)	−1504(2)	192(2)	19(2)	112(3)	−0(12)	226(2)	−8(15)
N(9)	2274(3)	−505(2)	4812(2)	339(10)	43(2)	94(3)	−70(16)	194(12)	−7(19)
C(2)	3130(3)	−843(2)	−846(3)	214(7)	18(1)	87(4)	−47(11)	27(11)	−7(17)
C(3)	2528(2)	−1395(4)	296(2)	231(3)	20(3)	93(5)	6(14)	186(3)	160(18)
C(5)	691(3)	−1192(1)	2347(1)	213(8)	16(1)	57(2)	−55(12)	152(10)	−3(15)
C(6)	2086(2)	−549(2)	3282(2)	205(5)	14(2)	83(4)	−9(11)	100(5)	8(16)

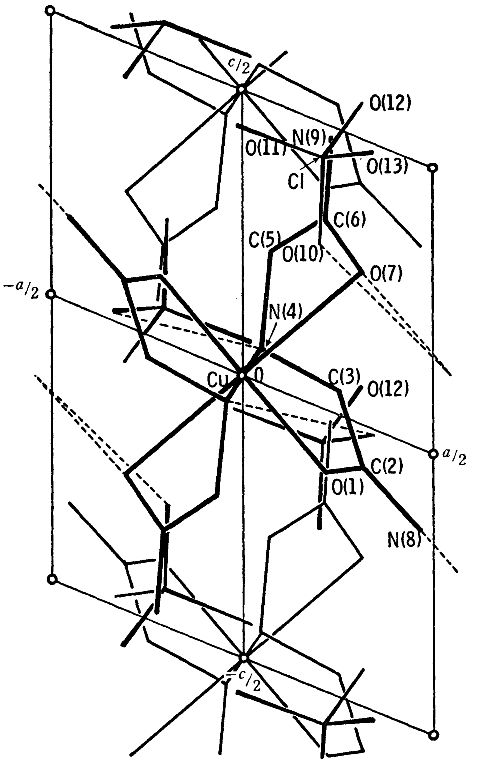

Fig. 1. Projection of the structure along the b axis. Dashed lines indicate hydrogen bonds.

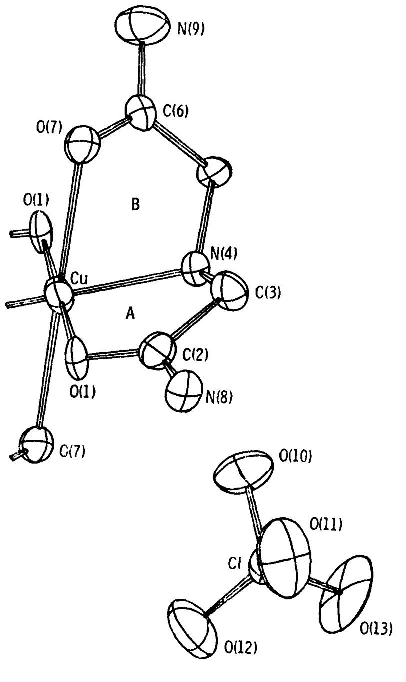

Fig. 2. Thermal ellipsoids of atoms at 50% probability level.

The calculations of the data reduction and the Fourier syntheses were carried out by means of programs written by Dr. Sasaki. The block-diagonal least-squares refinements and the calculations of the bond distances and angles were done with the HBLS-4 and DAPH programs written by Dr. Ashida. The thermal ellipsoids were drawn by means of the ORTEP program of Dr. Johnson. All the calculations were performed on a FACOM 230-60 computer at the Computation Center of Nagoya University.

The observed and calculated structure factors are listed in Table 1,** and the final atomic parameters, in Table 2.

Results and Discussion

A projection of the structure along the b axis is shown in Fig. 1. The anisotropic thermal ellipsoids of the

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** Table 1 has been deposited with the Chemical Society of Japan (Document No. 7414).

Table 3. Bond distances and angles

Cu-O (1)	1.952(2) Å	O (1)-C (2)-C (3)	118.9(3)
Cu-N (4)	2.021(2)	C (2)-C (3)-N (4)	109.6(4)
Cu-O (7)	2.471(3)	C (3)-N (4)-Cu	108.3(3)
O (1)-C (2)	1.269(3)	C (5)-N (4)-Cu	110.0(2)
C (2)-C (3)	1.543(5)	C (3)-N (4)-C (5)	112.5(3)
C (3)-N (4)	1.506(5)	N (4)-C (5)-C (6)	109.1(2)
N (4)-C (5)	1.484(3)	C (5)-C (6)-O (7)	121.1(3)
C (5)-C (6)	1.492(3)	C (6)-O (7)-Cu	97.7(3)
C (6)-O (7)	1.261(4)	O (1)-C (2)-N (8)	124.6(3)
C (2)-N (8)	1.301(3)	N (8)-C (2)-C (3)	116.6(3)
C (6)-N (9)	1.328(4)	O (7)-C (6)-N (9)	122.4(3)
Cl-O (10)	1.420(3)	N (9)-C (6)-C (5)	116.5(3)
Cl-O (11)	1.441(3)	Perchlorate ion	
Cl-O (12)	1.441(2)	O (10)-Cl-O (11)	105.5(2)
Cl-O (13)	1.409(3)	O (11)-Cl-O (12)	108.3(2)
Complex ion		O (12)-Cl-O (13)	109.8(2)
O (1)-Cu-N (4)	85.5(1)°	O (13)-Cl-O (10)	110.9(2)
O (1)-Cu-O (7)	91.1(1)	O (10)-Cl-O (12)	113.3(2)
N (4)-Cu-O (7)	71.7(1)	O (11)-Cl-O (13)	108.8(2)
Cu-O (1)-C (2)	115.2(2)		

Table 4. Intermolecular contacts less than 3.5 Å

O(13$^{\mathrm{I}}$)-O(10$^{\mathrm{II}}$)	3.401(4) Å	N(8$^{\mathrm{I}}$)-O(10$^{\mathrm{V}}$)	2.933(3)
O(11$^{\mathrm{I}}$)-C(3$^{\mathrm{III}}$)	3.214(5)	O(1$^{\mathrm{I}}$)-C(2$^{\mathrm{V}}$)	3.335(3)
O(13$^{\mathrm{I}}$)-C(5$^{\mathrm{III}}$)	3.406(3)	O(1$^{\mathrm{I}}$)-O(1$^{\mathrm{V}}$)	3.381(5)
O(11$^{\mathrm{I}}$)-C(5$^{\mathrm{III}}$)	3.439(3)	N(4$^{\mathrm{I}}$)-O(11$^{\mathrm{VI}}$)	3.307(3)
O(11$^{\mathrm{I}}$)-N(4$^{\mathrm{III}}$)	3.307(3)	N(4$^{\mathrm{I}}$)-O(13$^{\mathrm{VI}}$)	3.268(3)
O(13$^{\mathrm{I}}$)-N(4$^{\mathrm{III}}$)	3.268(3)	C(3$^{\mathrm{I}}$)-O(11$^{\mathrm{VI}}$)	3.214(5)
N(8$^{\mathrm{I}}$)-N(4$^{\mathrm{IV}}$)	3.469(3)	C(5$^{\mathrm{I}}$)-O(11$^{\mathrm{VI}}$)	3.439(3)
N(8$^{\mathrm{I}}$)-O(1$^{\mathrm{V}}$)	3.337(3)	C(5$^{\mathrm{I}}$)-O(13$^{\mathrm{VI}}$)	3.406(3)
N(8$^{\mathrm{I}}$)-O(7$^{\mathrm{V}}$)	2.910(4)		

I at	x	y	z
II	x	$1/2-y$	$1/2+z$
III	$-x$	$1/2+y$	$1/2-z$
IV	$1+x$	y	z
V	$1-x$	$-y$	$-z$
VI	$-x$	$-1/2+y$	$1/2-z$

atoms are shown in Fig. 2. The bond distances and angles are listed in Table 3, and the intermolecular contacts, in Table 4.

The complex is centrosymmetric, with two ligand molecules coordinating in *trans* positions through two imino nitrogen atoms, N(4), and two of the four amide oxygen atoms, O(1). The other two amide oxygen atoms, O(7), lie above and below the plane defined by the N(4), O(1), and Cu atoms, thus completing an *s-facial* octahedral coordination.

The bond distances and angles of the two chelate rings, Cu–O(1)–N(4) (Chelate ring A in Fig. 2) and Cu–O(7)–N(4) (Chelate ring B), are shown in Fig. 3 along with those of *cis*-bis(glycinato)copper(II) monohydrate.16) All the distances and angles except for the C(2)–O(1) double bond in the Chelate ring A agree with those of the glycinato complex. This indicates that no large influence due to terdentate coordination is introduced in the Chelate ring A.

The Cu–O(7) distance (2.47 Å) in the Chelate ring B is much longer than the Cu–O(1) distance in the ring A, indicating a weak bonding interaction, a "semi-coordination bond,"6) between Cu and O(7). The O(7)–Cu–N(4) angle (71.7°) is too small to be a normal angle between the coordination bonds. Hence, the structure of the complex is not simply elongated but is distorted octahedral.

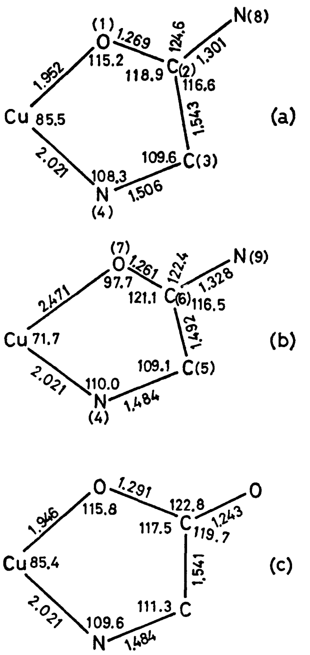

Fig. 3. Bond distances and angles of (a) Chelate ring A, (b) Chelate ring B and (c) *cis*-Cu(H_2NCH_2COO)$_2$·H_2O.16)

The equations of the planes defined by Cu and the coordinating atoms (coordination planes) are listed in Table 5. The Chelate rings, A and B, are not planar and show considerable deviations of carbon atoms from each of the coordination planes, while the chelate ring of the glycinato complex is almost coplanar.16) Judging by the model, this difference may be due to the C=O double bond in these chelate rings rather than to fused-ring formation.

Table 5. Equations for the coordination planes in the chelate rings A and B, and the deviations of the atoms therefrom

Planes are expressed in the form: $DX+EY+FZ=0$, where X, Y, and Z are coordinates in Å measured along the a, b, and c^* axes respectively

Chelate ring	A		B	
Atoms defining the plane	Cu, O(1), N(4)		Cu, O(7), N(4)	
D	0.4911		−0.8925	
E	0.2494		0.0831	
F	0.8346		0.4434	
Deviation of the atoms from the plane	C (2)	0.118 Å	C (5)	0.958 Å
	C (3)	0.316	C (6)	0.887

The complex cations are connected through hydrogen bonds between N(8^{I}) and O(7^{V}), forming infinite chains along the a axis. These chains are held with one another by perchlorate ions through hydrogen bonds of the N–H···O type between O(13^{I}) and N(4^{III}) and between O(10^{I}) and N(8^{V}) (Table 4). The crystal thus consists of three-dimensional networks of hydrogen bonds connecting the complex and perchlorate ions with one another.

The perchlorate ion is regularly tetrahedral, and the thermal motions of the four oxygen atoms are larger than those of the atoms in the complex ion.

The infrared and visible spectra of nickel(II) and cobalt(II) complexes of iminodiacetamide could be well assigned on the basis of the structural features of this complex. These results will be published elsewhere.[17]

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References

1) Spectroscopic and Crystallographic Investigations of the Metal Complexes of Iminodiacetamide. I.

2) M. Sekizaki and K. Yamasaki, *Revue de Chimie Minérale*, **6**, 255 (1969).

3) M. Mikami, I. Nakagawa, and T. Shimanouchi, *Spectrochim. Acta*, **25A**, 365 (1969).

4) D. H. Brown, D. R. MacSween, M. Mercer, and D. W. A. Sharp, *J. Chem. Soc.*, *A*, **1971**, 1574.

5) M. Sekizaki, *Acta Crystallogr.*, **B29**, 327 (1973).

6) M. Sekizaki, F. Marumo, K. Yamasaki, and Y. Saito, This Bulletin, **44**, 1731 (1971).

7) Refs. 11, 12, and 13 cited in Ref. 5.

8) F. S. Stephens, *J. Chem. Soc.*, *A*, **1969**, 883.

9) B. J. Hathaway and A. A. G. Tomlinson, *Coord. Chem. Revs.*, **5**, 1 (1970).

10) S. Laitinen and T. Nortia, *Suomen Kemistilehti*, **B43**, 61 (1970).

11) S. Chaberek, Jr. and A. E. Martell, *J. Amer. Chem. Soc.*, **74**, 5052 (1952).

12) H. B. Jonassen, R. B. LeBranc, and R. M. Rogan, *ibid.*, **72**, 4968 (1950).

13) See for example: Ref. 3; J. A. Kieft and K. Nakamoto, *Inorg. Chim. Acta*, **2**, 225 (1968); J. L. Walter, C. S. C. and R. J. Hooper, *Spectrochim. Acta*, **25A**, 647 (1969).

14) W. J. A. Jongkees, *Rec. Trav. Chim. Pays-Bas*, **27**, 300.

15) "International Tables for X-ray Crystallography," Vol. III, Kynoch Press, Birmingham (1962).

16) H. C. Freeman, M. R. Snow, I. Nitta, and K. Tomita, *Acta Crystallogr.*, **17**, 1463 (1964).

17) M. Sekizâki, Y. Yamada, and H. Takahashi, *Nippon Kagaku Kaishi*, **1974**(6), 1057.