The Crystal Structure of 1-(2-Thiazolylazo)-2-naphtholato-diaquacopper(II) Perchlorate

Masayasu KURAHASHI and Akira KAWASE*

National Research Institute for Metals, 2-3-12, Nakameguro, Meguro-ku, Tokyo 153

(Received July 22, 1975)

The crystal structure of 1-(2-thiazolylazo)-2-naphtholatodiaquacopper(II) perchlorate, $[Cu^{II}(TAN)(H_2O)_2]ClO_4$, has been determined from three-dimensional X-ray data collected by counter methods. The crystals are monoclinic, with the space group $P2_1/c$; $a=13.481(4)$, $b=8.060(4)$, $c=15.307(7)$ Å, $\beta=95.58(4)°$, and $Z=4$. The structure was refined to an R value of 0.086 for 952 non-zero reflections. The copper atom is five-coordinated and has a distorted square-pyramidal environment. The 1-(2-thiazolylazo)-2-naphtholato group (TAN) acts as a terdentate ligand, the phenolic oxygen, the azo nitrogen and the thiazole nitrogen atoms being coordinated to the copper atom to give two five-membered chelate rings. The remaining two positions are occupied by water molecules.

This work is part of a series of studies of the structures of metal chelates of 1-(2-thiazolylazo)-2-naphthol (abbr. as H-TAN). Recently, one of the present authors (M.K.) reported the structures of the Pd(II)-[1] and Ni(II)-chelates[2] and showed that the coordination configurations around the metals are square-planar and octahedral respectively (Fig. 1a and 1b). In both complexes, the 1-(2-thiazolylazo)-2-naphtholato group (abbr. as TAN) is exactly or nearly planar and acts as a terdentate ligand to form two five-membered chelate rings with the metal atom. It can easily be understood that a planar terdentate ligand like TAN can further form a five-coordinated square-pyramidal or trigonal-bipyramidal structure with a metal and two additional unidentate ligands (Fig. 1c and 1d). However, it is impossible for the TAN to give a tetrahedral coordination around the metal (Fig. 1e). In this paper, we will describe the structure of the five-coordinated Cu(II)–TAN complex, in which the copper atom has a square-pyramidal environment. A preliminary account of this work has already been given.[3]

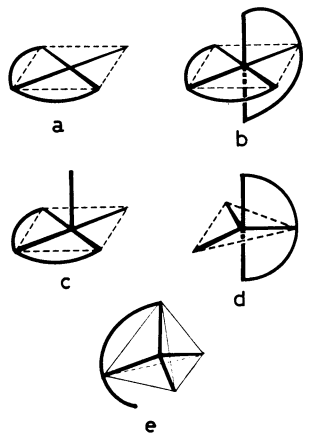

Fig. 1. Coordination of a planar terdentate ligand to the metal. The planar terdentate ligand can coordinate to the metal with (a) square-planar, (b) octahedral, (c) square-pyramidal, and (d) trigonal-bipyramidal environment; however, it is impossible to form a metal-complex with (e) tetrahedral environment.

* Present address: National Chemical Laboratory for Industry, 5-5, 1-Chome, Honmachi, Shibuya-ku, Tokyo, 151

The reaction of Cu(II) with H-TAN gives 1:1 as well as 1:2 Cu(II)–TAN chelates.[4] Furthermore, in view of the structures reported for the Cu(II)–complexes with analogous ligands,[5-7] it was thought that there probably exist various types of 1:1 Cu(II)–TAN complexes with the chemical formulae $[Cu^{II}(TAN)X]$, $[Cu^{II}(TAN)X_2]$, and $[Cu^{II}(TAN)XY]$, where X and Y are unidentate ligands. Accordingly, several attempts were made to produce the complexes using different reactants, different solvents, and different ratios of the reactants. Three crystalline forms (orthorhombic, monoclinic, and triclinic) of 1:1 Cu(II)–TAN complexes were obtained from the different solvents. The present study will deal with the structure of the monoclinic form, the crystallinity of which was comparatively better than the other two. An attempt to crystallize the complex with the composition of $[Cu^{II}Cl(TAN)]$, insoluble either in water or in most organic solvents, has been unsuccessful.

Experimental

An aqueous solution of $Cu^{II}(ClO_4)_2\cdot 6H_2O$ and a dioxane solution of H-TAN were mixed in an approximate molar ratio of 1:1. Blue needle crystals of $[Cu^{II}(TAN)(H_2O)_2]ClO_4$, elongated along the b-axis, were obtained by slow evaporation. The crystal used for the X-ray diffraction study had the dimensions of $0.1\times0.1\times0.25$ mm. The crystal data are listed in Table 1. The unit-cell dimensions were initially determined by Weissenberg photographs taken with Cu$K\alpha$ radiation; they were refined by the least-squares method, using 9 reflections

Table 1. Crystal data

$[Cu(C_{13}H_8N_3OS)(H_2O)_2]ClO_4$
F.W.=453.3
Monoclinic
$a=13.481\pm0.004$ Å
$b=8.060\pm0.004$ Å
$c=15.307\pm0.007$ Å
$\beta=95.58\pm0.04°$
$V=1655.1\pm1.2$ Å^3
$D_m=1.81$ g·cm^{-3}
$D_x=1.819$ g·cm^{-3}
$Z=4$
$\mu=17.0$ cm^{-1} (for Mo$K\alpha$)
Space group $P2_1/c$

measured by a diffractometer with Mo$K\alpha$ radiation. The density was measured by flotation in an aqueous solution of sodium iodide.

The intensity data were collected on a Rigaku automated four-circle diffractometer, using Mo$K\alpha$ radiation monochromatized with a graphite crystal. The ω-2θ scan technique was employed at a scan rate of 4°/min. The background countings were taken on both sides of each peak for 10 s. If the value of $\sigma(F)/F$ was larger than 0.03, the measurement was repeated and the average value was adopted. All unique reciprocal lattice points with $2\theta \leq 45°$ were examined; 953 reflections with $F > 3\sigma(F)$ were regarded as observed. The measured intensities were corrected for the Lorentz and polarization factors, but no corrections were made for absorption and extinction.

TABLE 2. ATOMIC PARAMETERS AND THEIR ESTIMATED STANDARD DEVIATIONS[a)]

Atom	x/a	y/b	z/c	B (Å^2)
Cu	0.7455(2)	0.4788(4)	0.4102(2)	*
S	0.7544(5)	0.4705(10)	0.6934(4)	*
Cl	0.4542(5)	0.8925(8)	0.3650(4)	*
O	0.8213(10)	0.4198(10)	0.3111(10)	3.1(3)
W(1)	0.6545(11)	0.6236(20)	0.3342(10)	4.5(4)
W(2)	0.6359(14)	0.2659(25)	0.3887(11)	6.1(5)
N(1)	0.8613(12)	0.3780(22)	0.4785(9)	2.6(4)
N(2)	0.8644(11)	0.3802(22)	0.5625(10)	2.6(4)
N(3)	0.7131(11)	0.5185(24)	0.5297(12)	3.6(4)
C(1)	0.9327(14)	0.3181(26)	0.4312(13)	2.4(5)
C(2)	0.9031(15)	0.3396(28)	0.3384(13)	2.9(5)
C(3)	0.9633(16)	0.2839(32)	0.2748(14)	3.6(5)
C(4)	1.0505(16)	0.2011(27)	0.3057(14)	3.8(5)
C(5)	1.0821(15)	0.1725(28)	0.3957(16)	4.2(6)
C(6)	1.1712(17)	0.0898(28)	0.4199(17)	4.0(6)
C(7)	1.1997(15)	0.0675(31)	0.5096(13)	4.4(6)
C(8)	1.1438(17)	0.1286(28)	0.5706(13)	3.8(5)
C(9)	1.0549(15)	0.2112(27)	0.5948(12)	3.2(5)
C(10)	1.0221(13)	0.2378(22)	0.4616(12)	2.3(4)
C(11)	0.7788(13)	0.4588(26)	0.5873(14)	2.7(4)
C(12)	0.6480(20)	0.5756(34)	0.6609(14)	5.4(7)
C(13)	0.6362(15)	0.5880(26)	0.5720(14)	3.1(5)
O(1)	0.4516(14)	0.7869(26)	0.2901(10)	6.0(5)
O(2)	0.5549(15)	0.8894(31)	0.4081(17)	9.9(7)
O(3)	0.3879(18)	0.8348(29)	0.4214(14)	9.1(7)
O(4)	0.4305(18)	1.0552(25)	0.3415(18)	9.8(7)
H(3)	0.9472	0.3100	0.2084	4.0
H(4)	1.0895	0.1587	0.2490	4.0
H(6)	1.2055	0.0357	0.3723	4.0
H(7)	1.2644	0.0016	0.5137	4.0
H(8)	1.1593	0.1224	0.6364	4.0
H(9)	1.0158	0.2460	0.5945	4.0
H(12)	0.5749	0.6104	0.7033	4.0
H(13)	0.5572	0.6532	0.5218	4.0

Anisotropic temperature factors ($\times 10^4$)[b)]

Atom	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
Cu	38(1)	112(6)	25(6)	26(6)	4(2)	9(5)
S	79(5)	227(16)	37(3)	3(16)	28(6)	−34(13)
Cl	59(4)	157(13)	53(3)	19(13)	25(6)	1(11)

a) E.s.d.'s in parentheses are in units of least significant digit. b) The anisotropic temperature factors are of the form:
$\exp\{-(B_{11}h^2+B_{22}k^2+B_{33}l^2+B_{12}hk+B_{13}hl+B_{23}kl)\}$

Structure Determination and Refinement

The structure was solved by the heavy-atom method. The positions of the copper and sulfur atoms were deduced from a three-dimensional Patterson map. From the Fourier synthesis phased on the heavy atoms only, the positions of all the non-hydrogen atoms could be found. Block-diagonal least-squares refinement using isotropic temperature factors for all the non-hydrogen atoms reduced R $(=\sum||F_o|-|F_c||/\sum|F_o|)$ to 0.105. A further three cycles of refinement with anisotropic thermal parameters for the copper, sulfur, and chlorine atoms improved R to 0.095. At this stage a difference synthesis was carried out and several hydrogen positions were revealed; however, a few ghost peaks as large as the hydrogen peaks appeared. Accordingly, the hydrogen positions of the ring systems were evaluated by assuming sp^2 hybrid bonds around the relevant carbon atoms and a C–H distance of 1.08 Å; these positions were included but not refined in the final least-squares cycles. The isotropic thermal parameter of 4.0 Å^2 was assigned to the hydrogen atoms. Convergence was reached at $R=0.086$ for all the 952 observed reflections. A unit weight was given to each reflection. The atomic scattering factors were taken from International Tables for X-ray Crystallography, Vol III.[8)] The final atomic parameters and their estimated standard deviations are listed in Table 2. The observed and calculated structure factors are given in Table 3.**

Description of the Structure and Discussion

Perspective drawings of the complex cation and perchlorate anion are shown in Fig. 2, along with the numbering of the atoms. The complex cation is composed of Cu, TAN, and $2H_2O$. The TAN, 1-(2-thiazolylazo)-2-naphtholato group, acts as a terdentate ligand; the phenolic oxygen atom, the azo nitrogen atom adjacent to the naphthol ring, and the thiazole nitrogen atom being coordinated jointly to the copper

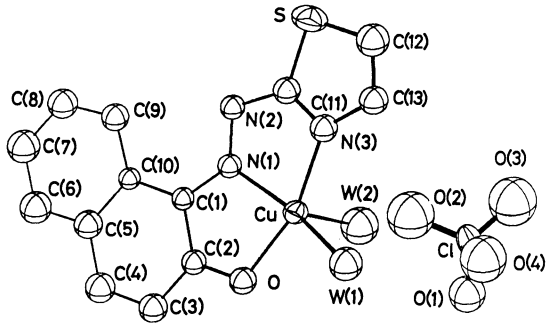

Fig. 2. Perspective drawings of $[Cu(TAN)(H_2O)_2]^+$ and ClO_4^- with numbering of atoms. The Thermal ellipsoids are drawn at 50% probability level (DEAM-4 diagram[11)]). W denotes the water oxygen atom.

** Table 3 is kept as Document No. 7605 at the Chemical Society of Japan, 1-5 Surugadai, Kanda, Chiyoda-ku, Tokyo, 101.

atom, thus giving two five-membered chelate rings. This mode of attachment of the TAN to the metal atom coincides with that observed in the crystals of Fe(II)-,[9] Co(III)-,[10] Ni(II)-,[2] and Pd(II)-chelate.[1] The thiazole sulfur atom does not coordinate to the metal in the present Cu(II)–TAN complex, either.

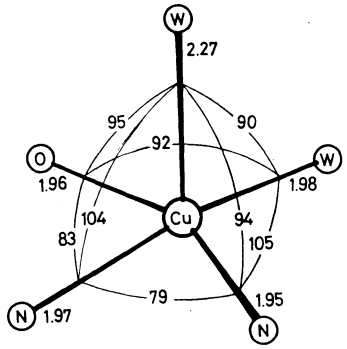

Fig. 3. Coordination geometry about the copper atom.

The coordination geometry about the copper atom is, as is shown in Fig. 3, a distorted square-pyramid whose basal plane consists of three coordinating atoms of TAN and a water-oxygen atom. The copper atom is displaced 0.18 Å from the basal plane toward an apical water oxygen atom.

It has been reported that a copper(II) complex of 1-(2-pyridylazo)-2-naphthol (abbr. as H-PAN), $[Cu^{II}(PAN)H_2O]ClO_4$, has a square-planar environment and that PAN is bonded to the copper atom through the phenolic oxygen atom, the azo nitrogen atom, and the pyridine nitrogen atom, thus giving two five-membered chelate rings.[5] Therefore, the coordination of TAN to the copper atom is similar to that of PAN. However, the coordination number and geometry around the metal are different between the $[Cu^{II}(TAN)(H_2O)_2]^+$ and $[Cu^{II}(PAN)H_2O]^+$ complexes.

The bond lengths and angles in the complex cation are shown in Figs. 4a and 4b respectively. The equatorial bond lengths, Cu–N(1), Cu–N(3), Cu–O, and Cu–W(1) (W refers to an oxygen of the water molecule), are 1.97, 1.95, 1.96, and 1.98 Å respectively, while the axial bond length, Cu–W(2), is 2.27 Å, longer by *ca.* 0.3 Å than any of the equatorial bond lengths. A similar feature has been observed in many copper complexes with a square-pyramidal coordination.[6,7,11] The bond angles around the metal, O–Cu–N(1) and N(1)–Cu–N(3), are compressed to 83 and 79° respectively. In relation to this deformation, Cu–N(3)–C(13), S–C(11)–N(2), N(2)–N(1)–C(1), and N(1)–C(1)–C(10) are enlarged to 134, 123, 127, and 127° respectively. Such deviations from the normal valence angles have been observed in all the metal-TAN complexes reported previously. The W(1)–Cu–W(2) angle is 90°. There is a close intra-ligand contact (2.3 Å) between N(2) and H(9) (hydrogen atom attached to C(9)), as is shown in Fig. 4.

The bond lengths and angles in the perchlorate anion are as follows: Cl–O(1)=1.42(2), Cl–O(2)=1.41(3), Cl–O(3)=1.39(3) and Cl–O(4)=1.41(3) Å, O(1)–Cl–O(2)=105(1), O(1)–Cl–O(3)=109(1), O(1)–Cl–O(4)=111(1), O(2)–Cl–O(3)=114(2), O(2)–Cl–O(4)=108(2),

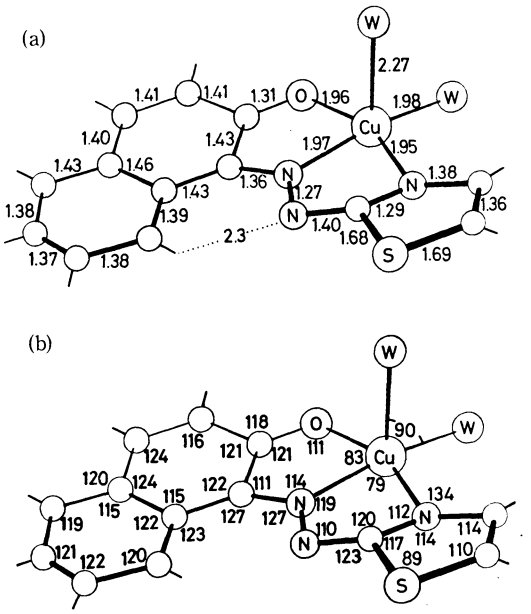

Fig. 4. Bond lengths (a) and bond angles (b) in $[Cu(TAN)(H_2O)_2]^+$. E. s. d.'s are as follows: 0.02Å for Cu–O, Cu–W, and Cu–N. 0.02—0.03 Å for S–C. 0.03 Å for C–O, N–N, and N–C. 0.03—0.04 Å for C–C. 1° for O–Cu–W, O–Cu–N, N–Cu–N, C–S–C, Cu–O–C, and Cu–N–N. 1—2° for N–N–C, C–N–C, and C–C–C.

TABLE 4. EQUATIONS OF THE LEAST-SQUARES PLANES[a] AND DEVIATIONS OF ATOMS FROM THE PLANES

Plane 1 The plane through Cu and TAN anion
$0.4790X+0.8769Y+0.0415Z=8.204$

Plane 2 The naphthalene ring plane
$0.4963X+0.8679Y+0.0207Z=8.293$

Plane 3 The basal plane of square-pyramid
$0.5559X+0.8249Y+0.1024Z=9.240$

Atoms	Plane 1	Plane 2	Plane 3
Cu	0.04*	0.13	0.18
S	0.07*	0.25	−0.04
O	−0.04*	−0.00	0.07*
W(1)	−0.42	−0.33	−0.06*
W(2)	2.25	2.33	2.42
N(1)	0.01*	0.08	−0.08*
N(2)	−0.02*	0.09	−0.18
N(3)	−0.02*	0.12	0.07*
C(1)	−0.03*	0.01*	−0.19
C(2)	0.00*	0.02*	−0.03
C(3)	−0.00*	−0.02*	−0.08
C(4)	0.03*	−0.01*	−0.21
C(5)	0.03*	0.01*	−0.33
C(6)	0.04*	0.01*	−0.47
C(7)	0.03*	0.01*	−0.60
C(8)	−0.04*	−0.01*	−0.62
C(9)	−0.06*	−0.01*	−0.49
C(10)	−0.03*	−0.01*	−0.35
C(11)	−0.02*	0.12	−0.07
C(12)	0.01*	0.21	0.09
C(13)	−0.01*	0.16	0.16

a) *X*, *Y*, *Z*, are orthogonal coordinate in Å and axes parallel a, b, c*.

b) Only the atoms marked with an asterisk are included in the calculation of each plane.

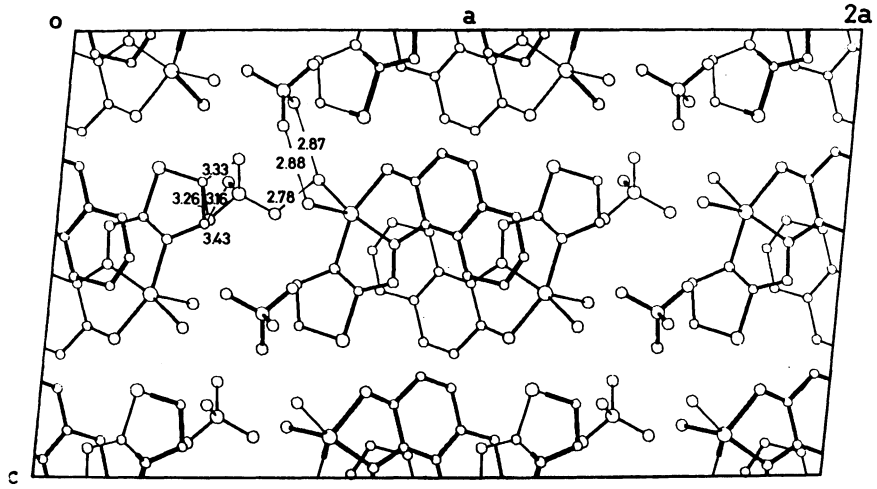

Fig. 5. Crystal structure projected along the b-axis (DEAM-4 diagram[12]).

and O(3)–Cl–O(4)=109(2)°. The perchlorate ion is slightly distorted from a regular tertrahedron. No close contact between Cu and oxygen of the perchlorate anion is observed. The isotropic temperature factors for the oxygen atoms of the perchlorate ion range from 6.0 to 9.9 Å^2, somewhat larger than those for the non-hydrogen atoms of the complex cation.

The deviations of atoms from the various planes are given in Table 4. The mean plane through the Cu and non-hydrogen atoms of the TAN ligand (plane 1) is significantly non-planar, and the S and C(9) atoms are displaced by +0.07 and −0.06 Å respectively. The distances of W(1) and W(2) from this plane are −0.42 and 2.25 Å respectively. On the other hand, the naphthalene ring (plane 2) is planar within a deviation of ±0.02 Å, and all the remaining atoms except oxygens are displaced from the naphthalene plane in the same direction; that is, the TAN ligand is slightly folded along the Cu–N(1) bond at an angle of 2.5°. The non-planarity of the TAN is probably the result of:

(1) the N(2)···H(9) intra-ligand repulsion mentioned above,
(2) the distorted square-pyramidal environment of the Cu atom, or
(3) interionic interactions; relatively short interatomic distances are found between thiazole-ring atoms and perchlorate-oxygen atoms.

The crystal structure projected along the b-axis is shown in Fig. 5. Interatomic distances less than 3.4 Å are listed in Table 5. $[Cu^{II}(TAN)(H_2O)_2]^+$ cations related by the center of symmetry at (0, 0, 0) are stacked alternately along the b-axis to form columns. The columns are held together by van der Waals forces, forming layers parallel to the (001) plane. Perchlorate anions are located around $x=1/2$ between the layers of the complex cations. There are some close approaches between the water-oxygen atoms and the perchlorate-oxygen atoms (Table 5). As can be seen in Fig. 5, the van der Waals forces are predominant around $x=0$, whereas the ionic interactions are predominant around $x=1/2$.

Calculations were carried out on a HITAC 5020F computer at the Computer Center of the National Aerospace Laboratory, using such programs of the UNICS system as PAMI, HBLS-4, and SFR-5. Figures 2 and 5 were produced by the plotter program of DEAM-4.[12]

TABLE 5. INTERATOMIC DISTANCES LESS THAN 3.4 Å

Atoms		Symmetry operation	Distance (Å)
N(3)	O(3)	3	3.27
C(11)	O(3)	3	3.26
C(12)	O(1)	3	3.33
C(12)	O(4)	4	3.16
W(1)	O(2)	1	2.78
W(1)	O(4)	5	2.87
W(2)	O(1)	6	2.88
W(2)	O(2)	2	3.24
W(2)	O(3)	3	3.07
W(2)	O(4)	2	3.27
O(1)	O(4)	5	3.27

Symmetry operations

1 (x y z) 4 ($1-x$ $2-y$ $1-z$)

2 (x $y+1$ z) 5 ($1-x$ $y-\frac{1}{2}$ $\frac{1}{2}-z$)

3 ($1-x$ $1-y$ $1-z$) 6 ($1-x$ $\frac{1}{2}+y$ $\frac{1}{2}-z$)

References

1) M. Kurahashi, This Bulletin, **47**, 2045 (1974).
2) M. Kurahashi, *ibid.*, **47**, 2067 (1974).
3) M. Kurahashi, *Chem. Lett.*, **1974**, 63.
4) A. Kawase, *Bunseki Kagaku*, **11**, 628 (1962).
5) S. Ooi, D. Carter, and Q. Fernando, *Chem. Commun.*, **1967**, 1301.
6) T. Ueki, T. Ashida, Y. Sasada, and M. Kakudo, *Acta Crystallogr.*, B**24**, 1361 (1968).
7) J. Coetzer, *ibid.*, B**26**, 1414 (1970).
8) "International Tables for X-ray Crystallography," Vol. III, Kynoch Press, Birmingham (1962).
9) M. Kurahashi, A. Kawase, K. Hirotsu, M. Fukuyo, and A. Shimada, This Bulletin, **45**, 1940 (1972).
10) M. Kurahashi, *Chem. Lett.*, **1974**, 1271.
11) T. J. Kistenmacher and D. J. Szalda, *Acta Crystallogr.*, B**31**, 1659 (1975).
12) A. Takenaka, "Schematic Drawing of Crystal and Molecular Structures Containing Atomic Thermal Motions," APPLY 270/30-503-001, Tokyo, Fujitsu Ltd.