Stereochemical Properties of Copper(II) Complexes of (*S*)-3-Aminohexahydroazepine. Crystal and Molecular Structure of Bromobis[(*S*)-3-aminohexahydroazepine]copper(II) Perchlorate [CuBr(*S*-ahaz)$_2$]ClO$_4$

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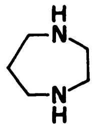
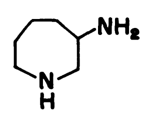
A series of copper(II) complexes of (*S*)-3-aminohexahydroazepine (abbreviated as *S*-ahaz) were prepared. The molecular structure of bromobis[(*S*)-3-aminohexahydroazepine]copper(II) perchlorate, [CuBr(*S*-ahaz)$_2$]ClO$_4$, was determined using single-crystal X-ray diffraction method. The complex crystallizes is space group $P2_12_12_1$ with a=13.449(6), b=17.411(11), c=7.937(2) Å, and Z=4. The structure was solved by the direct method and refined by the least squares to R value of 0.068 for 1853 unique reflections. The Cu^{2+} ion has the square-pyramidal five-coordination geometry with four nitrogen atoms as basal donors and a bromide as an apical donor. The structures of other copper(II) complexes of *S*-ahaz were assigned on the basis of the above X-ray analysis result, together with electronic spectral and conductivity measurements. The complexes having the formula Cu(*S*-ahaz)$_2$X(ClO$_4$) (X$^-$=Cl$^-$, I$^-$, NCS$^-$, ONO$^-$) were assigned to have square-pyramidal five-coordinated structures. The *S*-ahaz complexes Cu(*S*-ahaz)$_2$X$_2$ (X$^-$=Cl$^-$, Br$^-$, NO$_3$$^-$) were also considered to have similar five-coordination geometries, while the complexes Cu(*S*-ahaz)$_2$X$_2$ (X$^-$=ClO$_4$$^-$, BF$_4$$^-$) to be four-coordinated in the crystalline state.



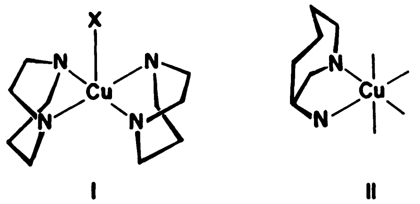
(1)



(2)

Musker and collaborators reported that 1,4-diazacycloheptane (**1**), abbreviated as dach, acts as a bidentate ligand for certain transition metal ions.[1,2] The structure of the copper(II) complex obtained from dach and Cu(NO$_3$)$_2$·6H$_2$O was determined by an X-ray crystallographic study,[3] which revealed that two Cu^{II} species, [Cu(NO$_3$)(dach)$_2$]$^+$ and [Cu(H$_2$O)(dach)$_2$]$^{2+}$, with square-pyramidal five-coordination geometries, were involved in the crystal. The molecular structure of [CuX(dach)$_2$]$^{n+}$ (X=NO$_3$$^-$ or H$_2$O), illustrated in Fig. 1 (I), indicated that the access of another monodentate ligand to the sixth coordination site is sterically blocked by the ligand methylene chains.

3-Aminohexahydroazepine (**2**), abbreviated hereafter as ahaz, is a unique chiral 1,2-diamine having C- and N-substituents which are fused into a seven-membered mono-azaheterocycle, while dach can be regarded as an *N,N'*-disubstituted 1,2-ethanediamine. If ahaz acts as a bidentate ligand for a metal ion, the ring carbon chain is required to orient nearly perpendicular to the five-membered chelate ring as in Fig. 1 (II). The ring carbon chain of ahaz should hang over the central metal ion in a similar manner as that of dach. Therefore, the coordination of a further ligand to the apical site should be significantly restricted for ahaz complexes due also to steric interactions with the ring methylenes.



I II

Fig. 1. The five-coordinated structure of [CuX(dach)$_2$]$^{n+}$ ion (I),[3] and a possible structure of ahaz coordinating to a metal ion, (II).

It seems interesting to compare the stereochemical and other properties of metal complexes of ahaz with those of dach. This paper describes the results on the preparation and stereochemical properties of copper(II) complexes of the optically active form of ahaz, i.e., (*S*)-3-aminohexahydroazepine (=S-ahaz), and, further, those of the X-ray structural analysis of a square-pyramidal copper(II) complex of *S*-ahaz, [CuBr(*S*-ahaz)$_2$]ClO$_4$.

Experimental

Measurements. Visible reflectance and absorption spectra were recorded with a Hitachi 340 spectrophotometer. Infrared spectra were obtained with a Jasco IRA-2 spectrophotometer. Electric conductivities were measured by a Toa Electronics CM-20A conductivity meter. Magnetic susceptibilities were measured at room temperature using a Shimadzu MB-100 magnetic balance (Faraday method). Optical rotations were measured with a Jasco DIP-360 polarimeter.

(*S*)-3-Aminohexahydroazepine (*S*-ahaz). To a suspension of lithium tetrahydridoaluminate (17.5 g) in dry tetrahydrofuran (THF, 400 cm^3) was added (*S*)-3-aminohexahydro-2-azepinone hydrochloride (25.0 g) in small portions with stirring. The mixture was stirred and heated under reflux for 24 h, and then cooled to room temperature. To the mixture was added water (33 cm^3) drop by drop with stirring, and the resultant slurry was heated under reflux for 1 h. The cooled slurry was filtered off, and the solid mass was washed with THF. The solid was stirred with THF (150 cm^3) under reflux for 1 h, filtered, and washed as above. All the filtrates and washings were united, neutralized with dilute hydrochloric acid, and rotary-evaporated. The oily residue was dissolved in water (100 cm^3), and solid sodium hydroxide was added in small portions to make the mixture strong alkaline. The amine which separated from the aqueous layer was extracted with diethyl ether (total 250 cm^3), and the extracts were combined and dried over solid potassium hydroxide. The solvent was removed under reduced pressure, and the residual amine was distilled under reduced pressure. Bp, 92 °C/23 mmHg (3066 Pa). Yield; 9.5 g. α_{obsd} (neat, 589.3 nm, 1 cm cell)$=-0.167° \pm 0.002°$.

In the same manner, (*S*)-3-aminohexahydro-2-azepinone prepared from L-lysine methyl ester dihydrochloride by the reported method,[4] was converted to *S*-ahaz. The product thus obtained was slightly racemized. α_{obsd} (neat, 589.3 nm, 1 cm cell)$=-0.150° \pm 0.002°$.

(*RS*)-3-Aminohexahydroazepine (*RS*-ahaz). This was obtained by the same procedure for preparing *S*-ahaz, except the use of (*RS*)-3-aminohexahydro-2-azepinone hydrochloride in place of the *S*-enantiomer.

Preparation of Cu(*S*-ahaz)$_2$X$_2$ ($X^- = ClO_4^-$, NO_3^-, Cl^-, and Br^-). $CuX_2 \cdot nH_2O$ (5 mmol) dissolved in ethanol (5—10 cm^3) was added drop by drop to an ethanol solution (5 cm^3) of *S*-ahaz (11 mmol). Diethyl ether was added to complete the precipitation of copper(II) complex. The crystals formed were collected, washed with diethyl ether, and air-dried. The crude product was recrystallized from hot methanol.

Cu(*S*-ahaz)$_2$(BF$_4$)$_2$ was obtained similarly using 45% aqueous solution of Cu(BF$_4$)$_2$. Diethyl ether (100 cm^3) was added to an aqueous ethanol solution of the crude product to induce the precipitation of the complex. The analytical data of copper(II) complexes are given in Table 1.

Preparation of Cu(*S*-ahaz)$_2$X(ClO$_4$) ($X^- = Cl^-$, Br^-, I^-, NCS^-, and ONO^-). To a methanol solution of Cu(*S*-ahaz)$_2$(ClO$_4$)$_2$ (0.93 g; 2 mmol) was added a methanol solution of LiX($X^- = Cl^-$, Br^-, or I^-) or NaX($X^- = NCS^-$ or NO_2^-) (3 mmol). The crystals which appeared were collected, and washed with methanol and diethyl ether. The product was recrystallized from methanol–water mixture (3:1 v/v). Table 1 lists the analytical data of the hetero-anion[5] complexes obtained as above.

X-Ray Diffraction Analysis. A violet needle crystal, 0.20×0.38×0.57 mm, was used for the X-ray analysis. Diffraction data were collected on a Rigaku AFC-5 four-circle diffractometer with graphite-monochromatized Mo $K\alpha$ radiation ($\lambda = 0.71073$ Å) at 296 K. Unit cell parameters were derived from a least squares fit of 16 2θ values in the range $20° < 2\theta < 30°$

Crystal Data. $C_{12}H_{28}BrClCuN_4O_4$, $M = 471.28$, Orthorhombic, $a = 13.449(6)$, $b = 17.411(11)$, $c = 7.937(2)$ Å, $U = 1859(2)$ Å^3, space group $P2_12_12_1$, $Z = 4$, $D_m = 1.66$ (298 K), $D_x = 1.684$ g cm^{-3}, $F(000) = 964$, $\mu(\text{Mo } K\alpha) = 3.47$ mm^{-1}. Data were collected by ω and $\omega - 2\theta$ ($2\theta > 30°$) scan mode and at scan rate, 4.0° min^{-1}. The three standard reflections were monitored every 150 reflections and their intensities varied by < 0.06. A total 1906 reflections obtained in the range of $2\theta < 55°$, of which 1853 independent reflections with $|F_o| > 3\sigma(|F_o|)$ were used for the structure determination. The intensities data were corrected for Lorentz and polarization factors, but not for absorption.

Solution and Refinement. The structure was solved by the direct method, and was refined by using a block diagonal least-squares procedure based on $|F_o|$. Unit weight was used for all reflections. H-Atom coordinates were generated assuming the standard bond lengths and angles. All non-hydrogen atoms are anisotropic and H atoms are isotropic (321 parameters). The final indices R $(=(|F_o|-|F_c|)/|F_o|)$ and R_w $(=[w(|F_o|-|F_c|)^2/w|F_o|^2]^{1/2})$ were 0.068 and 0.079 respectively. The largest shift to error value on the final cycle is 0.13. The maximum height in the final difference Fourier maps was 1.8 e Å^{-3} near the disordered perchlorate, O(3).

Atomic scattering factors are taken from International

Table 1. Elemental Analyses, Electric Conductivity, and Magnetic Susceptibility Data of Copper(II) Complexes

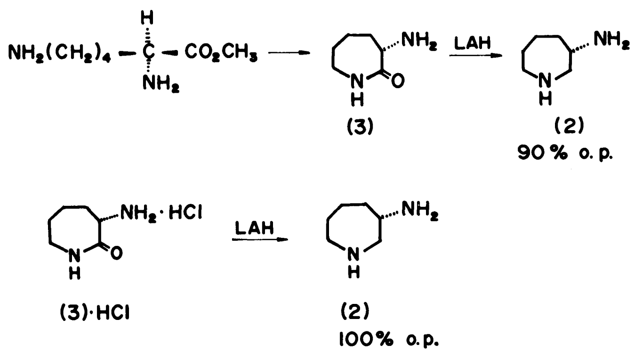
Complex	Elemental analyses[a)]			Conductivity[b)]	μ_{eff}
	C (%)	H (%)	N (%)	S 10^{-3} m^2 mol^{-1}	BM
Cu(*S*-ahaz)$_2$(ClO$_4$)$_2$	29.49 (29.36)	5.55 (5.75)	11.28 (11.42)	151	1.76
Cu(*RS*-ahaz)$_2$(ClO$_4$)$_2$[c)]	29.05 (29.36)	5.60 (5.75)	11.40 (11.42)	161	1.78
Cu(*S*-ahaz)$_2$(BF$_4$)$_2$	30.38 (30.96)	6.36 (6.06)	11.74 (12.04)	174	
Cu(*S*-ahaz)$_2$(NO$_3$)$_2$	34.76 (34.65)	6.97 (6.78)	19.96 (20.21)	84	
Cu(*S*-ahaz)$_2$Cl$_2$	39.21 (39.72)	7.85 (7.78)	15.15 (15.44)	71	1.73
Cu(*S*-ahaz)$_2$Br$_2$	31.16 (31.90)	6.55 (6.25)	12.25 (12.41)	81	
Cu(*S*-ahaz)$_2$Cl(ClO$_4$)	33.38 (33.77)	6.50 (6.61)	12.90 (13.13)	97	1.77
Cu(*S*-ahaz)$_2$Br(ClO$_4$)	30.61 (30.58)	5.84 (5.99)	12.24 (11.89)	97	1.83
Cu(*S*-ahaz)$_2$I(ClO$_4$)	27.02 (27.81)	5.67 (5.44)	10.44 (10.81)	102	1.81
Cu(*S*-ahaz)$_2$(NCS)(ClO$_4$)	34.02 (34.74)	6.65 (6.28)	15.17 (15.59)	102	
Cu(*S*-ahaz)$_2$(ONO)(ClO$_4$)	32.35 (32.95)	6.19 (6.45)	16.06 (16.02)	100	

a) The calculated values are in parentheses. b) Obtained for nitromethane solution (4×10^{-4} mol dm^{-3}) at 19 °C. c) The orange-red complex of racemic ahaz.

Tables for X-ray Crystallography.[6] The crystallographic calculations were performed on a FACOM M-380 computer of The Institute of Physical and Chemical Research using program MULTAN 78[7] and the UNICS III program system.[8] Their positional parameters for non-hydrogen atoms are listed in Table 2.[9]

Results

Isolation of Violet and Orange-Red Forms of Cu(ahaz)$_2$(ClO$_4$)$_2$. In our first examination, we prepared the ligand *S*-ahaz by lithium tetrahydridoaluminate reduction of (*S*)-3-aminohexahydro-2-azepinone (**3**), which was obtained via the cyclization of methyl L-lysinate[4] (Scheme 1). The copper(II) complex obtained from the above-mentioned ahaz (α_{obsd} (neat, 598.3 nm, 1 cm cell)$=-0.150° \pm 0.002°$) and $Cu(ClO_4)_2 \cdot 6H_2O$ consisted of two crystalline forms of different color, the dominant violet and the minor orange-red ones. Because the latter was less soluble than the former, they could be separated from each other by recrystallization from methanol.



Scheme 1.

Table 2. Positional Parameters (×10^4) and Equivalent Isotropic Temperature Factors for Non-Hydrogen Atoms in [CuBr(*S*-ahaz)$_2$]ClO$_4$

Atom	*x*	*y*	*z*	B_{eq}(Å^2)
Cu	1153(1)	4046(1)	4583(2)	2.8(0.0)
Br	2998(1)	4790(1)	4215(2)	4.1(0.0)
N(1)	548(9)	5028(7)	5535(19)	4.0(0.3)
C(2)	441(13)	5527(9)	4224(32)	5.6(0.6)
C(3)	−3(12)	5124(11)	2583(25)	4.9(0.5)
C(4)	−1098(13)	4915(13)	2732(27)	6.0(0.6)
C(5)	−1409(13)	4488(13)	4331(36)	7.1(0.7)
C(6)	−1294(14)	4930(15)	5866(32)	8.0(0.8)
C(7)	−313(14)	4986(13)	6648(27)	6.2(0.6)
N(8)	608(10)	4424(8)	2398(17)	4.0(0.4)
N(1)'	1818(10)	3076(8)	3716(19)	4.4(0.4)
C(2)'	2448(12)	2792(10)	4960(27)	5.0(0.5)
C(3)'	1898(15)	2806(10)	6706(24)	5.1(0.5)
C(4)'	1142(19)	2166(11)	7022(33)	7.0(0.7)
C(5)'	654(20)	1787(13)	5568(44)	9.2(1.0)
C(6)'	323(15)	2247(12)	4122(35)	7.0(0.7)
C(7)'	1123(16)	2490(11)	2958(25)	5.9(0.6)
N(8)'	1403(12)	3563(8)	6855(17)	4.7(0.4)
Cl	3709(4)	1961(3)	490(7)	6.2(0.1)
O(1)	4616(13)	1615(11)	467(28)	10.6(0.7)
O(2)	2919(13)	1495(11)	330(35)	12.6(0.9)
O(3)	3729(20)	2497(13)	−674(45)	17.0(1.3)
O(4)	3628(21)	2364(20)	1942(38)	19.2(1.4)

In spite of the clear difference in their color, the elemental analysis results of these two forms agreed adequately with the expected values for the formula $C_{12}H_{28}Cl_2CuN_4O_8 = Cu(C_6H_{14}N_2)_2(ClO_4)_2$. Electric conductivity measurements showed that they dissociated as bi-univalent electrolites in nitromethane. Further, magnetic susceptibility measurements suggested that both were mononuclear Cu^{II} species. The electric conductivity and magnetic susceptibility data of copper(II) complexes of ahaz are also summarized in Table 1.

A remarkable distinction between the two forms, which could be noticed finally with a surprise, was that the orange-red form was optically inactive, while the violet one optically active. Thus, the violet crystals evidently involve the optically active ahaz, the chiral carbon center of which should assume the *S*-configuration, because the starting material of the present ligand was L-lysine (Scheme 1). On the other hand, the orange-red form was thought to include the racemic ahaz. These results indicated that *S*-ahaz employed here was partially racemized.

To confirm the difference between copper(II) complexes caused by employing either the racemate or the optically-active *S*-enantiomer as the ligand, we synthesized both modifications of ahaz. The enantiomerically pure *S*-ahaz was prepared from the pure (*S*)-3-aminohexahydro-2-azepinone hydrochloride ((**3**)·HCl) (Scheme 1). The optically-pure *S*-ahaz showed an optical rotation α_{obsd} (neat, 589.3 nm, 1 cm cell)$=-0.167° \pm 0.002°$, and gave rise to only the violet form. On the other hand, the orange-red form was the sole product for the reaction of *RS*-ahaz (*RS*-ahaz=racemic ahaz) with $Cu(ClO_4)_2$. These observations confirm that the violet form involves the pure *S*-antipode of ahaz.

Preparation of Copper(II) Complexes of *S*-ahaz. It was observed that the homo-anion[10] copper(II) complexes of *S*-ahaz, Cu(*S*-ahaz)$_2$X$_2$, obtained by mixing $CuX_2 \cdot nH_2O$ and twice the molar of *S*-ahaz were violet ($X^- = ClO_4^-$, BF_4^-, NO_3^-) or blue-violet ($X^- = Br^-$, Cl^-). As these complexes gave no single crystals suitable for X-ray structural analysis, their exact structures have not been clarified yet. The circular dichroism spectral feature of the S-ahaz complex has been reported.[11]

The hetero-anion[5] copper(II) complexes of *S*-ahaz having the formula $Cu(C_6H_{13}N_2)_2X(ClO_4)$ were obtained by either of the following two methods; (i) the addition of an excess amount of LiX ($X^- = Cl^-$, Br^-, I^-)

or NaX ($X^-=NCS^-$, NO_2^-) to a methanol solution of Cu(*S*-ahaz)$_2$(ClO$_4$)$_2$ (Eq. 1), and (ii) the addition of LiClO$_4$ to a methanol solution of Cu(*S*-ahaz)$_2$X$_2$ ($X^-=Cl^-$, Br^-) (Eq. 2).

$$\mathrm{Cu}(S\text{-ahaz})_2(\mathrm{ClO_4})_2 + \mathrm{MX} \rightarrow \mathrm{Cu}(S\text{-ahaz})_2\mathrm{X}(\mathrm{ClO_4}) + \mathrm{MClO_4} \quad (1)$$

($M^+=Li^+$ or Na^+; $X^-=Cl^-$, Br^-, I^-, NCS^-, ONO^-)

$$\mathrm{Cu}(S\text{-ahaz})_2\mathrm{X}_2 + \mathrm{LiClO_4} \rightarrow \mathrm{Cu}(S\text{-ahaz})_2\mathrm{X}(\mathrm{ClO_4}) + \mathrm{LiX} \quad (2)$$

($X^-=Cl^-$, Br^-)

These hetero-anion complexes formed well-developed single crystals so that the molecular structure of the bromo complex, Cu(*S*-ahaz)$_2$Br(ClO$_4$), was determined using the single-crystal X-ray diffraction method.

The Molecular Structure of Bromobis[(*S*)-3-aminohexahydroazepine]copper(II) Ion. Figure 2 shows the perspective views of the complex cation, [CuBr(*S*-ahaz)$_2$]$^+$. The selected bond parameters are listed in Table 3. The absolute configuration of the complex were assigned from the known absolute configuration of the ligand as an internal reference. The complex ion has a square-pyramidal structure with the bromide at the apex. Two *S*-ahaz ligands coordinate to Cu^{2+} ion in the trans fashion, and, expectedly, the seven-membered rings orient perpendicular to the CuN$_4$ basal plane. The seven-membered rings extend toward the same side of the basal plane, and disturb obviously the access of additional ligand to the sixth coordination site.

It is noticeable that the seven-membered ring of *S*-ahaz depicted on the left side of the structure in Fig.2 with the non-primed atoms N(1), C(2), ···N(8) has a different conformation from that of the right side *S*-ahaz with the primed atoms N(1)′, C(2)′, ···N(8)′. In spite that the seven-membered rings of both *S*-ahaz adopt the preferred twist-chair conformation,[12] the cyclic sequence of dihedral angles in the non-primed *S*-ahaz is different from that of the primed one as shown in Fig. 3. This is the reason for that the complex ion lacks the true C_2 symmetry. Both five-membered chelate rings take the λ conformation, though the chelate of the primed ligand is deformed to an envelope. The coordinating secondary asymmetric nitrogen center adopts the *R*-configuration.

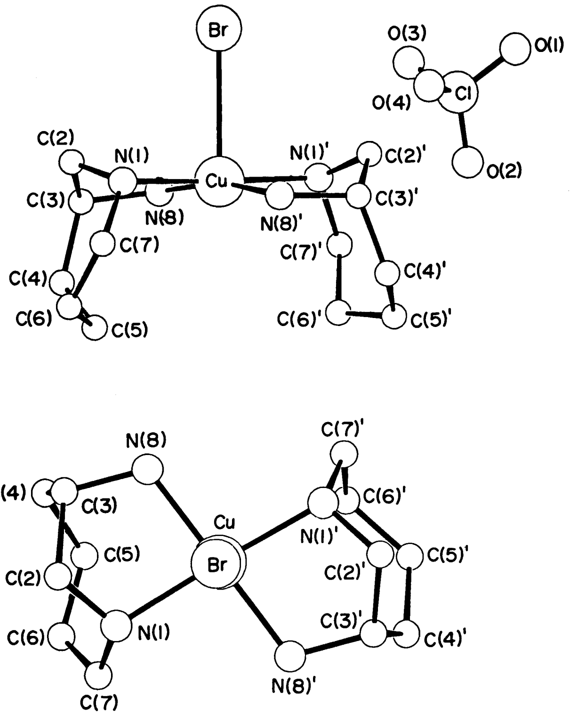


Fig. 2. Perspective views of [CuBr(*S*-ahaz)$_2$]$^+$ ion.

Table 3. Bond Lengths (l/Å) and Angles (ϕ/°)

Cu-Br	2.813(2)		
N(8)-Cu	2.00(1)	N(8)'-Cu	2.02(1)
Cu-N(1)	2.04(1)	Cu-N(1)'	2.03(1)
N(1)-C(2)	1.36(3)	N(1)'-C(2)'	1.39(2)
C(2)-C(3)	1.60(3)	C(2)'-C(3)'	1.57(3)
C(3)-N(8)	1.48(2)	C(3)'-N(8)'	1.48(2)
C(3)-C(4)	1.52(2)	C(3)'-C(4)'	1.53(3)
C(4)-C(5)	1.53(3)	C(4)'-C(5)'	1.48(4)
C(5)-C(6)	1.45(4)	C(5)'-C(6)'	1.47(4)
C(6)-C(7)	1.46(3)	C(6)'-C(7)'	1.48(3)
C(7)-N(1)	1.46(2)	C(7)'-N(1)'	1.51(2)
Cl-O(1)	1.36(2)		
Cl-O(2)	1.34(2)		
Cl-O(3)	1.31(3)		
Cl-O(4)	1.35(3)		
N(8)-Cu-Br	94.7(4)	N(8)'-Cu-Br	98.0(5)
N(1)-Cu-Br	90.3(3)	N(1)'-Cu-Br	87.7(4)
N(8)-Cu-N(1)	84.2(6)	N(8)'-Cu-N(1)'	83.3(6)
Cu-N(1)-C(2)	107(1)	Cu-N(1)'-C(2)'	109(1)
Cu-N(1)-C(7)	120(1)	Cu-N(1)'-C(7)'	115(1)
N(1)-C(2)-C(3)	112(1)	N(1)'-C(2)'-C(3)'	110(1)
C(2)-C(3)-N(8)	104(1)	C(2)'-C(3)'-N(8)'	107(1)
C(4)-C(3)-N(8)	110(2)	C(4)'-C(3)'-N(8)'	110(2)
C(3)-N(8)-Cu	113(1)	C(3)'-N(8)'-Cu	112(1)
C(7)-N(1)-C(2)	114(1)	C(7)'-N(1)'-C(2)'	115(1)
N(1)-C(2)-C(3)	112(1)	N(1)'-C(2)'-C(3)'	110(1)
C(2)-C(3)-C(4)	114(2)	C(2)'-C(3)'-C(4)'	116(2)
C(3)-C(4)-C(5)	116(1)	C(3)'-C(4)'-C(5)'	119(2)
C(4)-C(5)-C(6)	114(2)	C(4)'-C(5)'-C(6)'	120(2)
C(5)-C(6)-C(7)	119(2)	C(5)'-C(6)'-C(7)'	115(2)
C(6)-C(7)-N(1)	118(2)	C(6)'-C(7)'-N(1)'	113(2)
O(1)-Cl-O(2)	116(1)		
O(1)-Cl-O(3)	107(2)		
O(1)-Cl-O(4)	108(2)		
O(2)-Cl-O(3)	112(2)		
O(2)-Cl-O(4)	109(2)		
O(3)-Cl-O(4)	103(2)		

The three possible N-O hydrogen-bond distances are 3.20 [N(8)—O(1^{i})], 3.07 [N(1)—O(4^{ii})], and 3.22 Å [N—O(1^{iii})]. The symmetry codes are (i) $x-1/2$, $-y+1/2$, $-z$, (ii) x, y, z, and (iii) $x-1/2$, $-y+1/2$, $-z+1$. There are no particularly short intermolecular distances.

Discussion

Square-Pyramidal Geometry of [CuBr(*S*-ahaz)$_2$]$^{2+}$ Ion. As has been described, one of the apical coordination site of Cu^{2+} ion in the title complex is effectively shielded from the coordination of a ligand by the seven-membered ring of *S*-ahaz. Similar five-coordination geometries of copper(II) complexes containing diamine ligands were established for [CuX(dach)$_2$]$^{n+}$ (X=NO$_3^-$ or H$_2$O)[3] and [CuCl(1,3-dach)$_2$]$^+$ (1,3-dach=*cis*-1,3-cyclohexanediamine).[13] In the case of 1,3-dach complex, the methylene chains of the ligands shield one of the apical coordination sites in a closely similar manner to that of *S*-ahaz or dach.[13]

It was indicated for a number of copper(II) complexes with square-pyramidal coordination that the ratio of the apical Cu-X distance to the mean value of in-plane bond lengths (ca. 2.0 Å), i.e., (Cu-N/Cu-X), is 0.83 on an average, which is correlated to the geometry and/or electronic energy level.[14,15] The value of the present complex is 0.72, indicating that the Cu-Br distance is fairly longer than the average value for typical square-pyramidal configuration, and that the bromide ion binds to Cu^{2+} rather weakly. Concomitantly, the deviation of Cu^{2+} from the basal plane is very small (0.0097 Å).

Stereochemistries of Hetero-Anion Copper(II) Complexes of *S*-ahaz. Figure 4 shows the possible geometries of *S*-ahaz complex in which four amino nitrogen atoms occupy the basal coordination plane. The secondary (or primary) amino groups of the diamines are located in the cis relationship for (III) and in the trans fashion for (IV). The seven-membered rings are depicted in a twist-chair conformation, though certain other conformations will be plausible as well. The methylene chain of the ligand should strictly prevent the anion coordination at the apical site close to it, so that the cis isomer is necessary to take the four-coordination geometry (III), while the trans isomer may adopt either four- or five-coordination depending on the coordinating abilities of the anion present, since one of the apical sites in (IV) is not blocked by the ring methylenes. When the fifth coordination site of (IV) is occupied by a monodentate ligand, a square pyramidal five-coordination geometry (V) is effected. The X-ray diffraction study on [CuBr(*S*-ahaz)$_2$]ClO$_4$ clearly indicates the presence of such geometry as (V).

The hetero-anion complexes of *S*-ahaz other than [CuBr(*S*-ahaz)$_2$]ClO$_4$ were blue-violet, and their

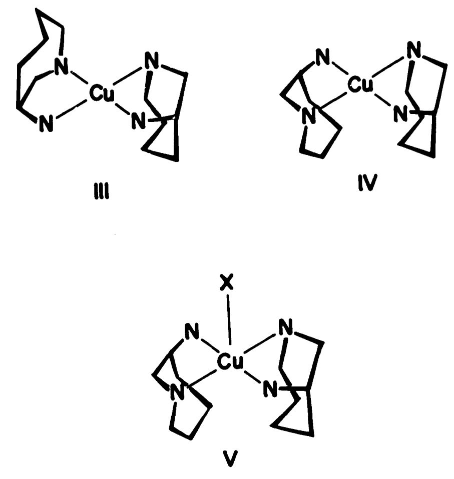


Fig. 4. Possible geometries of *S*-ahaz complexes. The four-coordinated cis form, (III); the four-coordinated trans form, (IV); the five-coordinated trans form (V). (X represents a coordinating anion).

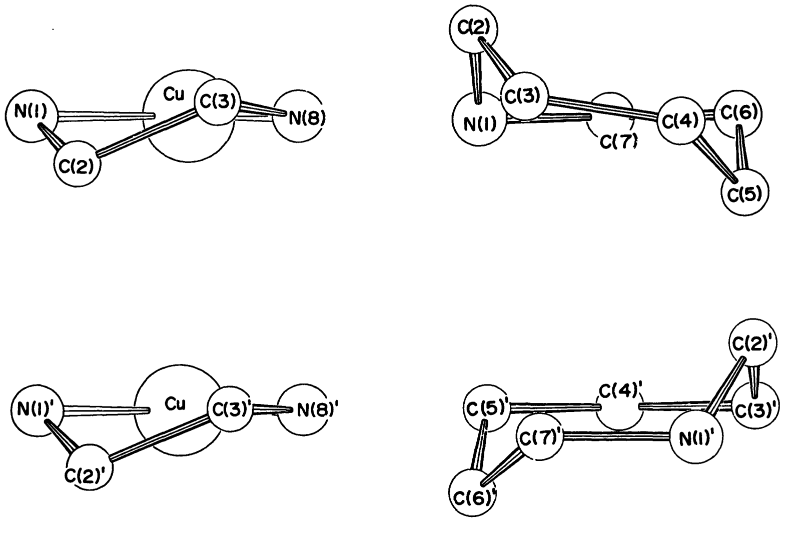


Fig. 3. Structures of five-membered chelate rings and seven-membered rings of *S*-ahaz.

reflectance spectra resembled one another as shown in Fig. 5 (see also Table 4). Further, all these complexes were found to dissociate uni-univalently in nitromethane (Table 1). This indicates that the halides or pseudohalides (NCS^-, ONO^-) with relatively high coordinating ability enter into the fifth coordination site to give rise to the complexes having the five-coordination structure (V) in a way similar to the $[CuBr(S\text{-ahaz})_2]^+$ ion. We concluded, therefore, that the hetero-anion complexes are thoroughly five-coordinated, and can be formulated as $[CuX(S\text{-ahaz})_2]ClO_4$ (X^-=Cl^- etc.).

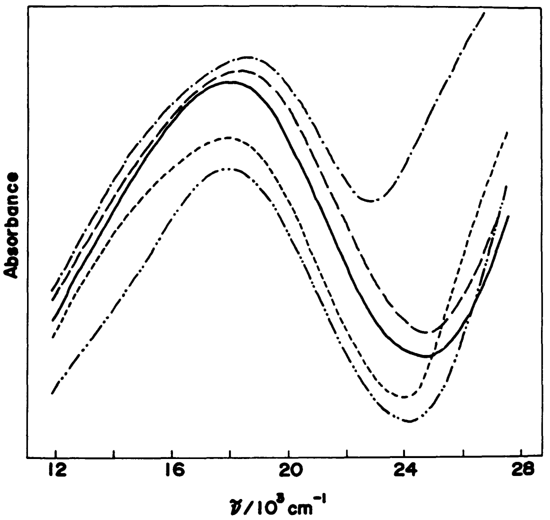


Fig. 5. Reflectance spectra of $[CuX(S\text{-ahaz})_2]ClO_4$: X^-=Cl^- (——), X^-=Br^- (— —), X^-=I^- (—·—), X^-=NCS^- (—··—), X^-=ONO^- (----).

Table 4. Electronic Spectral Data of Copper(II) Complexes

Complex	Solvent[a]	$\tilde{\nu}_{max}$/cm^{-1}	ε_{max}
$Cu(S\text{-ahaz})_2(ClO_4)_2$	R	18950	
	A	19420	97
	B	19050	84
$Cu(RS\text{-ahaz})_2(ClO_4)_2$	R	21100	
$Cu(S\text{-ahaz})_2(BF_4)_2$	R	19200	
	A	19530	103
	B	19050	84
$Cu(S\text{-ahaz})_2(NO_3)_2$	R	18950	
$Cu(S\text{-ahaz})_2Cl_2$	R	18590	
	A	17040	118
$Cu(S\text{-ahaz})_2Br_2$	R	18700	
	A	17210	117
$Cu(S\text{-ahaz})_2Cl(ClO_4)$	R	18200	
	A	17210	107
$Cu(S\text{-ahaz})_2Br(ClO_4)$	R	18300	
	A	17210	113
	B	18520	91
$Cu(S\text{-ahaz})_2I(ClO_4)$	R	18500	
	A	17860	108
$Cu(S\text{-ahaz})_2(NCS)(ClO_4)$	R	17850	
$Cu(S\text{-ahaz})_2(ONO)(ClO_4)$	R	17900	

a) R; reflectance spectra. A; obtained for nitromethane solution using 5 cm cells. B; obtained for methanol solution using 5 cm cells.

The infrared spectra of $[CuX(S\text{-ahaz})_2]ClO_4$ (X^-= NCS^- and NO_2^-) were examined to clarify the coordination mode of these ambidentate anions. The complex with NCS^- showed bands at 2070 cm^{-1} for ν(CN) and at 856 cm^{-1} for ν(CS), and no band around 720—690 cm^{-1}. These are characteristic for the N-coordination of NCS^- ion.[16] The NO_2^- complex has bands at 1464 and 1452 cm^{-1} for ν(N=O) and at 1058 cm^{-1} for ν(N–O), indicative of the O-coordination of the NO_2^- group.[16]

Musker and Hussain described the preparation of hetero-anion complexes $[CuX(dach)_2]ClO_4$ (X^-=Cl^-, Br^-, NCS^-), and postulated their structures to be five-coordinated on the basis of electronic spectral and conductivity data.[1] The evidence of the square-pyramidal five-coordination geometry (Fig. 1 (I)) was provided by the X-ray analysis study on $[Cu(dach)_2(NO_3)]NO_3$,[3] which suggested that the other hetero-anion complexes of dach also took square pyramidal structures.

Stereochemistries of Homo-Anion Copper(II) Complexes of *S*-ahaz. The above-mentioned structure determination of $[CuBr(S\text{-ahaz})_2]ClO_4$ could imply the possible stereochemistries of the complex ions in $Cu(S\text{-ahaz})_2X_2$. Since the reflectance spectra of these complexes (Fig. 6 and Table 4) showed no significant change from those of the hetero-anion complexes, it seems likely that all the complexes adopt five-coordinated structures such as (V). However, these complexes were found to be classified into two groups on the basis of their conductivity behaviors.

The first group, which involves $Cu(S\text{-ahaz})_2X_2$ (X^-=Cl^-, Br^-, and NO_3^-), are uni-univalent electrolites in nitromethane, indicating that the complex ions have five-coordinated structures $[CuX(S\text{-ahaz})_2]^+$ in

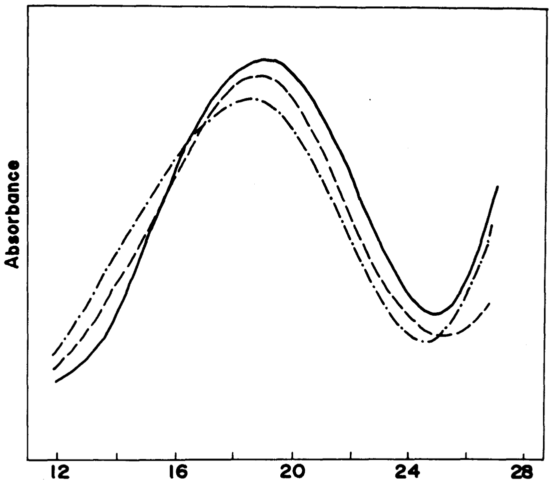


Fig. 6. Reflectance spectra of $Cu(S\text{-ahaz})_2X_2$: X^-= ClO_4^- (——), X^-=Cl^- (— —), X^-=Br^- (—·—).

nitromethane solution. Because the rapid rearrangement and exchange of ligands are generally effected for labile copper(II) complexes in solution, it is difficult on the basis of conductivity and spectral data alone to determine unambiguously whether the crystalline state structures of these *S*-ahaz complexes are five-coordinated square-pyramidal as (V) or four-coordinated as (IV). Nevertheless we consider it to be more likely that these complexes adopt the structures (V) in a similar manner as $[CuBr(S\text{-ahaz})_2]ClO_4$ and can be formulated as $[CuX(S\text{-ahaz})_2]X$, because of that for most metal complexes such anions as halides tend to coordinate to the central metal ion in the crystalline state.

The second group, which involves the complexes with relatively weak coordinating anions as ClO_4^- and BF_4^-, were found to dissociate uni-bivalently in nitromethane. This indicates no coordination of the anion to Cu^{2+} in solution, and suggests that the interaction between the anions and Cu^{2+} for these complexes is negligible, or, if any, very weak even in the crystalline state. We supposed, therefore, that these two may adopt four-coordination structures, either (III) or (IV), and the complexes be formulated as $[Cu(S\text{-ahaz})_2]X_2$ ($X^-=ClO_4^-$, BF_4^-). We have not obtained any direct evidence of the above presumption yet, but a helpful information for considering the stereochemistry of above complexes is provided by the structural determination study of $[Cu(deen)_2](ClO_4)_2$ (deen=*N*,*N*-diethyl-1,2-ethanediamine).[17]

It is well-known that $[Cu(deen)_2]X_2$ exhibits reversible thermochromism between the red lower temperature form and the blue higher temperature form, when X^- is of low coordinating ability as ClO_4^- and BF_4^-.[17–22] The structural change which may accompany with the color change had been studied from various aspects,[17,19–22] and conclusively demonstrated was that the most apparent stereochemical change in the course of the transformation from the red to blue form is the coformational inversion of one of the deen chelates.[17]

The red form has a strictly four-coordinated structure illustrated as (VI) in Fig. 7, in which the chelates assume the opposite conformation with each other.[17] On the other hand, the structure of the complex ion in the blue form can be depicted by (VII) in Fig. 7 or its antipode, where the chiralities of both chelate conformations are the same and the complex ion has a two-fold rotation axis perpendicular to the CuN_4 plane.[17] The coordination of perchlorate group to Cu^{2+} ion was indicated not to take place in the blue form, since the interatomic distance of Cu–O is not shorter than 4 Å.[17] This means that the color change mentioned above does not necessary mean the transformation from four to five coordination around Cu^{2+}. It is interesting to note that the stereochemical features of (VII), the presence of a two-fold rotation axis perpendicular to the CuN_4 plane and the identical chiralities of the conformation of both chelates, are same as those of (IV), one of the possible structures for $[Cu(S\text{-ahaz})_2]X_2$ ($X^-=ClO_4^-$, BF_4^-). We consider, therefore, that the S-ahaz complexes of perchlorate series ($X^-=ClO_4^-$, BF_4^-) has the four-coordination geometry (IV), and can be formulated as $[Cu(S\text{-ahaz})_2]X_2$.

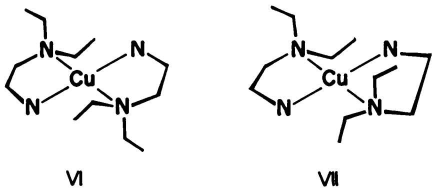

VI VII

Fig. 7. Structures of $[Cu(deen)_2]^{2+}$ ion in the red form, (IV), and in the blue form, (VII).[16]

The structure of the orange-red complex containing *RS*-ahaz is remained unsolved in the present paper. The structure determination of this and related complexes will be presented in a following paper.

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9) Tables of the coordinates of hydrogen atoms, the anisotropic thermal parameters of the non-hydrogen atoms, selected torsional angles, and observed and calculated structure factors are kept as Document No. 8707 at the Chemical Society of Japan.

10) The term "homo-anion" indicates that the complexes contain only one kind of the anion, so that the complexes

are represented in the form Cu(diamine)$_2$X$_2$ (X$^-$=Cl$^-$, ClO$_4^-$ etc.).

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