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Stereochemical Properties of Copper(II) Complexes of (*RS*)-3-Aminohexahydroazepine: Crystal and Molecular Structures of [(*R*)-3-Aminohexahydroazepine][(*S*)-3-aminohexahydroazepine]copper(II) Diperchlorate, [Cu(*R*-ahaz)(*S*-ahaz)]$(ClO_4)_2$ and Related Complexes

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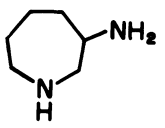
Orange-red copper(II) complexes of (*RS*)-3-aminohexahydroazepine (=*RS*-ahaz), Cu(*RS*-ahaz)$_2$X$_2$·nH$_2$O (X$^-$=ClO_4^-, BF_4^-, NO_3^-, Br$^-$, I$^-$) were prepared, and the molecular structures of complex **1** (X$^-$=ClO_4^-; n=0) and complex **2** (X$^-$=Br$^-$; n=2) were determined by the single-crystal X-ray diffraction method. The complex **1** has centrosymmetry, and the complex cation in **1** involves a pair of *R*- and *S*-ahaz (*R*- and *S*-ahaz refer to (*R*)- and (*S*)-3-aminohexahydroazepine) and takes a strict four-coordination geometry, so that **1** is formulated as [Cu(*R*-ahaz)(*S*-ahaz)]$(ClO_4)_2$. The complex cation in **2** resembles closely that of **1**, and **2** can be represented as [Cu(*R*-ahaz)(*S*-ahaz)]Br$_2$·2H$_2$O. The other orange-red complexes of *RS*-ahaz (X$^-$=BF_4^-, NO_3^-, I$^-$) were concluded to take similar strict four-coordinated structures. Blue-violet hetero-anion complexes Cu(*RS*-ahaz)$_2$X(ClO_4) were obtained from complex **1** and LiX (X$^-$=Cl$^-$, Br$^-$). The crystal structure determination of Cu(*RS*-ahaz)$_2$Br(ClO_4) (=complex **3**) revealed that **3** involves a pair of enantiomeric five-coordinated cations, [CuBr(*R*-ahaz)$_2$]$^+$ and [CuBr(*S*-ahaz)$_2$]$^+$, in the single crystal, whereby the ligand exchange which proceeds during the transformation from **1** to **3** is indicated.

3-Aminohexahydroazepine abbreviated as ahaz is a unique chiral 1,2-diamine having C- and N-substituents which are connected to form a seven-membered monoazaheterocycle. The R- and S-enantiomers and racemic form will be indicated hereafter by *R*-ahaz, *S*-ahaz, and *RS*-ahaz, respectively.



ahaz

In a previous paper we demonstrated through the X-ray crystallographic structure determination of a copper(II) complex of *S*-ahaz, [CuBr(*S*-ahaz)$_2$]ClO_4, that ahaz functions as a bidentate ligand, and that its ring carbon chain directs nearly perpendicular to the five-membered chelate ring as illustrated in Fig. 1 (I) (X$^-$=Br$^-$).[1] Evidently, the ring carbon chain of S-ahaz hangs over the central metal ion and blocks effectively the sixth coordination site from the access of a further ligand to maintain the square-pyramidal geometry of (I).

We noticed, further, that the copper(II) complex prepared from $Cu(ClO_4)_2$ and *RS*-ahaz was orange-red, while the corresponding complex with the single enantiomer (*S*-ahaz) was violet.[1] The latter was supposed to take a four-coordinated geometry such as

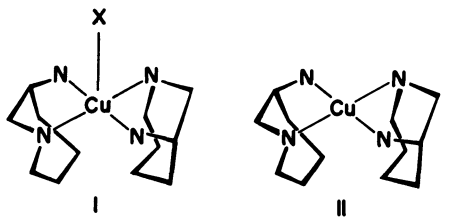


Fig. 1. Stereochemistries of copper(II) complexes of *S*-ahaz; five-coordinated [CuX(*S*-ahaz)$_2$]$^+$ ion, (I) and four-coordinated [Cu(*S*-ahaz)$_2$]$^{2+}$ ion, (II).

Fig. 1 (II),[1] but the structure of the former remained unsolved. To our surprise, the copper(II) complexes of *RS*-ahaz with certain anions other than perchlorate are thoroughly orange-red, which is rather exceptional color for bis(diamine)copper(II) complexes.[2] The coexistence of both *R*- and *S*-ahaz seems to be necessary to give these orange-red complexes, because no copper(II) complex of *S*-ahaz exhibits reddish color.[1] With a view to elucidate the common structural features of orange-red *RS*-ahaz copper(II) complexes, the crystal structures of Cu(*RS*-ahaz)$_2$-$(ClO_4)_2$[3] (**1**) and Cu(*RS*-ahaz)$_2$Br$_2$·2H$_2$O (**2**) were determined by the X-ray diffraction method. This paper describes the structural characteristics of complexes **1** and **2** and other *RS*-ahaz complexes, Cu(*RS*-ahaz)$_2$X$_2$.

In addition we isolated the hetero-anion complexes[4] of *RS*-ahaz having the formula Cu(*RS*-ahaz)$_2$X(ClO$_4$)[3] (X$^-$=Cl$^-$, Br$^-$) from complex **1** and LiX. The crystal structure determination of Cu(*RS*-ahaz)$_2$Br(ClO$_4$) (complex **3**) revealed that a pair of enantiomeric five-coordinated cations, [CuBr(*R*-ahaz)$_2$]$^+$ and [CuBr(*S*-ahaz)$_2$]$^+$, are involved in the single crystal and suggested a possibility of interesting ligand exchange during the conversion of **1** into **3**. Besides the stereochmical features of complex **3**, the pathway for formation of five-coordinated **3** from four-coordinated **1** in solution will be discussed in the present paper.

Experimental

Measurements. Spectroscopic and electric conductivity data were obtained in the same way as in the previous paper.[1]

(*RS*)-3-Aminohexahydroazepine (*RS*-ahaz). This was obtained by the same procedure for preparing *S*-ahaz,[1] except the use of (*RS*)-3-aminohexahydro-2-azepinone hydrochloride in place of the *S*-enantiomer. The product was purified by distillation. Bp, 92—94 °C 27 mmHg (1 mmHg=133.322 Pa).

Preparation of Cu(*RS*-ahaz)$_2$X$_2$·*n*H$_2$O (*n*=0 for X$^-$=ClO$_4^-$, NO$_3^-$, BF$_4^-$, and I$^-$; *n*=2 for X$^-$=Br$^-$). The complexes (X$^-$=ClO$_4^-$, NO$_3^-$, or Br$^-$) were obtained from CuX$_2$·*n*H$_2$O and *RS*-ahaz in the same way for preparing the corresponding *S*-ahaz complexes.[1] Cu(*RS*-ahaz)$_2$(BF$_4$)$_2$ was prepared by using 45% aqueous solution of Cu(BF$_4$)$_2$ in a similar method of obtaining Cu(*S*-ahaz)$_2$(BF$_4$)$_2$.[1] Cu(*RS*-ahaz)$_2$I$_2$ was obtained by adding a methanol solution of LiI to an aqueous methanol solution of Cu(*RS*-ahaz)$_2$(ClO$_4$)$_2$. Found (complex **1**; X$^-$=ClO$_4^-$): C, 29.05; H, 5.60; N, 11.40. Calcd for $C_{12}H_{28}Cl_2CuN_4O_8$: C, 29.36; H, 5.75, N, 11.42%. Found (complex **2**; X$^-$=Br$^-$): C, 29.68; H, 6.56; N, 11.55. Calcd for $C_{12}H_{32}Br_2CuN_4O_2$: C, 29.54; H, 6.63; N, 11.49%. Found (X$^-$=NO$_3^-$): C, 34.59; H, 6.74; N, 20.16. Calcd for $C_{12}H_{28}CuN_6O_6$: C, 34.65; H, 6.78, N, 20.21%. Found (X$^-$=BF$_4^-$): C, 31.21; H, 6.04; N, 11.69. Calcd for $C_{12}H_{28}B_2CuF_8N_4$: C, 30.96; H, 6.06; N, 12.04%. Found (X$^-$=I$^-$): C, 26.22; H, 5.22; N, 10.47. Calcd for $C_{12}H_{28}CuI_2N_4$: C, 26.28; H, 5.14; N, 10.24%.

Table 1 summarizes the spectral and conductivity data of copper(II) complexes prepared in this study.

Preparation of Cu(*RS*-ahaz)$_2$X(ClO$_4$) (X$^-$=Cl$^-$, Br$^-$). Complex **1** (0.93 g, 2 mmol) was dissolved in hot aqueous methanol (methanol–water=4:1) and mixed with a methanol solution of LiX (3 mmol). The crystals which appeared were collected, washed with ethanol and diethyl ether, and air-dried. The crude product was recrystallized from aqueous methanol containing LiX. The bromo complex **3** (X$^-$=Br$^-$) was also obtained by adding a slight excess of LiClO$_4$ to a solution of complex **2**. Found (X$^-$=Cl$^-$): C, 33.44; H, 6.60; N, 12.77%. Calcd for $C_{12}H_{28}Cl_2CuN_4O_4$: C, 33.77; H, 6.61, N, 13.13%. Found (X$^-$=Br$^-$): C, 30.49; H, 5.85; N, 11.77%. Calcd for $C_{12}H_{28}BrClCuN_4O_4$: C, 30.58; H, 5.99; N, 11.89%.

X-Ray Diffraction. Diffraction data for the orange-red complexes **1** and **2** and blue-violet complex **3** were collected on a Rigaku AFC-5 four-circle diffractometer with graphite-monochromatized Mo *Kα* radiation (λ=0.71073 Å) at 296 K. Details of crystal data and experimental conditions are listed in Table 2. Intensity data were collected by ω and ω—2θ (2θ>30°) scan mode and at scan rate, 4.0° min^{-1}. For each of the complexes, the intensities of three standard reflections

Table 1. Electronic Spectral and Electric Conductivity Data of Copper(II) Complexes of *RS*- and *S*-ahaz

Complex	Reflectance ν_{max} / cm^{-1}	Absorption[a] $\nu_{max}(\varepsilon_{max})$[c] / cm^{-1}	Conductivity[b] / 10^{-3} S m^2 mol^{-1}
Cu(*RS*-ahaz)$_2$(ClO$_4$)$_2$	21100	19340 (96)	161
		19230 (84)[d]	
Cu(*S*-ahaz)$_2$(ClO$_4$)$_2$	18950	19420 (97)	152
		19050 (86)[d]	
Cu(*RS*-ahaz)$_2$Br$_2$·2H$_2$O	20900	17300	75
Cu(*S*-ahaz)$_2$Br$_2$	18700	17120 (117)	81
Cu(*RS*-ahaz)$_2$(BF$_4$)$_2$	21100	19490 (96)	179
Cu(*S*-ahaz)$_2$(BF$_4$)$_2$	19200	19530 (103)	174
Cu(*RS*-ahaz)$_2$(NO$_3$)$_2$	21550	e)	71
Cu(*S*-ahaz)$_2$(NO$_3$)$_2$	18950	e)	88
Cu(*RS*-ahaz)$_2$I$_2$	21280	e)	96
Cu(*RS*-ahaz)$_2$Br(ClO$_4$)	18300	17270 (115)	97
		18660 (90)[d]	
Cu(*S*-ahaz)$_2$Br(ClO$_4$)	18300	17210 (113)	97
		18520 (91)[d]	
Cu(*RS*-ahaz)$_2$Cl(ClO$_4$)	17900	17060 (107)	97
Cu(*S*-ahaz)$_2$Cl(ClO$_4$)	18200	17120 (107)	97

a) Obtained for nitromethane solution using 5 cm cells unless otherwise noted. b) Obtained for nitromethane solution (4×10^{-4} mol dm^{-3}) at 19 °C. c) Given in mol^{-1} dm^3 cm^{-1} unit. d) Obtained for methanol solution using 5 cm cells. e) Unmeasurable due to insufficient solubility of the complex in the solvent.

Table 2. Crystallographic Parameters and Experimental Conditions

Compound	1	2	3	4[a]
Color	Orange-red	Orange-red	Blue-violet	Blue-violet
Formula	$C_{12}H_{28}Cl_2CuN_4O_8$	$C_{12}H_{32}Br_2CuN_4O_2$	$C_{12}H_{28}BrClCuN_4O_4$	$C_{12}H_{28}BrClCuN_4O_42$
M	490.83	487.77	471.28	471.28
Crystal system	Monoclinic	Orthorhombic	Orthorhombic	Orthorhombic
Space group	$P2_1/a$	$Iba2$	$Pna2_1$	$P2_12_12_1$
a/Å	8.849(3)	11.087(5)	13.655(4)	13.449(6)
b/Å	16.869(5)	23.64(3)	17.480(9)	17.411(11)
c/Å	6.649(3)	14.67(1)	7.863(3)	7.937(2)
β/°	99.36(3)			
U/Å^3	979.3(6)	3848(6)	1877(1)	1859(2)
Z	2	8	4	4
D_m/g cm^{-3} [b]	1.66	1.69	1.67	1.66
D_c/g cm^{-3}	1.665	1.684	1.671	1.684
F(000)	510	1976	964	964
μ(Mo $K\alpha$)/cm^{-1}	14.4	52.6	34.5	34.7
Crystal size(mm)	0.30×0.30×0.50	0.20×0.40×0.60	0.20×0.20×0.40	0.20×0.38×0.57
No. of reflections obsd[c]	3973	1563	1188	1906
No. of unique reflections	1874	1437	1137	1853
R[d]	0.054	0.100	0.151	0.068
Rw[e]	0.056	0.107	0.140	0.079
Largest shift/error value on final cycle	0.14	0.35	0.21	0.13

a) Ref. 1. b) Obtained at 293 K by the floating method in CBr_4-CCl_4 mixture. c) Critetion: $|F_o|>3\sigma(|F_o|)$. d) $R=\Sigma(||F_o|-|F_c||)/\Sigma|F_o|$. e) $Rw=[\Sigma w(|F_o|-|F_c|)^2/\Sigma w|F_o|^2]^{1/2}$.

Table 3. Positional Parameters (×10^4) and Equivalent Isotropic Temperature Factors for Complex 1

Atom	x	y	z	B_{eq}/Å^2
Cu	0	0	0	2.6(0.03)
N(1)	690(5)	968(3)	1739(7)	4.1(0.1)
C(2)	2332(7)	917(3)	2452(8)	4.3(0.1)
C(3)	3138(6)	496(3)	835(8)	3.7(0.1)
C(4)	3241(6)	1008(3)	−1020(8)	4.1(0.1)
C(5)	1764(7)	1392(3)	−2057(8)	4.3(0.1)
C(6)	1131(7)	2020(3)	−787(9)	4.4(0.2)
C(7)	212(7)	1730(3)	783(9)	4.3(0.1)
N(8)	2218(5)	−228(2)	267(7)	4.1(0.1)
Cl	−2724(2)	1330(1)	−5340(2)	4.0(0.05)
O(1)	−1605(5)	704(3)	−5292(7)	5.9(0.1)
O(2)	−3566(7)	1376(3)	−7296(7)	8.0(0.2)
O(3)	−3621(9)	1217(5)	−3889(11)	13.3(0.3)
O(4)	−1892(8)	2052(4)	−5051(13)	12.0(0.3)

Table 4. Positional Parameters (×10^4) and Equivalent Isotropic Temperature Factors for Complex 2

Atom	x	y	z	B_{eq}/Å^2
Cu	2420(3)	1290(1)	1434(3)	2.6(0.1)
Br(1)	287(3)	2806(2)	2587(3)	5.1(0.1)
Br(2)A	0	0	0	4.5(0.1)
Br(2)B	0	5000	740(5)	6.5(0.2)
N(1)	3447(28)	1858(13)	814(25)	6.1(1.0)
C(2)	3953(30)	1572(18)	0(26)	5.2(1.1)
C(3)	3024(35)	1193(17)	−448(23)	5.4(1.1)
C(4)	1949(35)	1481(17)	−908(23)	5.6(1.1)
C(5)	1250(42)	1913(22)	−336(40)	8.8(1.9)
C(6)	1992(53)	2451(23)	−176(33)	10.2(2.0)
C(7)	2967(33)	2451(23)	585(24)	5.6(1.1)
N(8)	2644(36)	824(11)	306(21)	5.6(0.9)
N(1)′	1338(25)	696(12)	1992(23)	5.3(0.9)
C(2)′	926(32)	959(17)	2858(22)	4.9(1.0)
C(3)′	1894(35)	1350(18)	3266(24)	5.8(1.2)
C(4)′	2963(32)	1047(15)	3727(23)	4.4(0.9)
C(5)′	3660(31)	633(15)	3118(26)	4.6(1.0)
C(6)′	2916(37)	108(20)	2876(25)	6.8(1.4)
C(7)′	2064(42)	170(23)	2058(37)	9.4(1.9)
N(8)′	2278(26)	1746(10)	2533(23)	4.9(0.8)
O(W)1	1705(27)	3843(15)	1462(35)	9.4(1.1)
O(W)2	4094(30)	3843(16)	1033(20)	9.0(1.2)

were measured after every 150 reflections, but they showed no appreciable changes. The intensities were corrected for Lorentz and polarization factors, but not for absorption.

Structure Analysis. Atomic scattering factors are taken from International Table for X-ray Crystallography.[5] All structures were refined by a block diagonal least-squares procedure based on $|F_o|$ including H atoms. Unit weight was used for all reflections. H atom coordinates were obtained by calculation. All non-hydrogen atoms are anisotropic and H atoms isotropic. The crystallographic calculations were performed on a FACOM M-380 computer of The Institute of Physical and Chemical Research using UNICS III program system.[6] The maximum heights in the final difference Fourier maps were 1.2, 1.5, and 0.9 e/Å^3 near

Table 5. Positional Parameters ($\times 10^4$) and Equivalent Isotropic Temperature Factors for Complex **3**

Atom	x	y	z	B_{eq}/Å^2
Cu	1383(3)	859(2)	0	4.6(0.1)
Br	−392(3)	−39(3)	3(18)	7.6(0.1)
N(1)	2014(28)	−40(27)	1322(52)	8.0(1.4)
C(2)	2174(36)	−657(25)	206(139)	7.9(1.7)
C(3)	2576(38)	−331(27)	−1537(72)	7.5(1.8)
C(4)	3704(38)	−111(33)	−1299(75)	8.9(2.0)
C(5)	3958(32)	489(26)	137(130)	8.1(1.6)
C(6)	3833(38)	143(34)	1895(78)	9.1(2.1)
C(7)	2828(41)	159(38)	2525(69)	8.7(2.0)
N(8)	1985(21)	350(18)	−1927(35)	4.0(0.8)
N(1)′	659(30)	1643(25)	−1239(60)	8.0(1.5)
C(2)′	17(24)	2076(21)	−182(77)	4.5(1.1)
C(3)′	597(44)	2247(38)	1522(81)	10.4(2.4)
C(4)′	1362(41)	2859(32)	1330(82)	9.6(2.1)
C(5)′	2096(42)	2745(34)	−294(151)	11.0(2.8)
C(6)′	1629(44)	2831(33)	−1866(79)	9.2(2.1)
C(7)′	1146(45)	2166(36)	−2490(74)	9.5(2.2)
N(8)′	969(27)	1483(21)	2075(44)	6.0(1.1)
Cl	3647(11)	1988(9)	5115(48)	11.6(0.6)
O(1)	3462(37)	2719(28)	4690(117)	15.7(2.5)
O(2)	2785(38)	1542(30)	5280(161)	17.5(2.7)
O(3)	4115(93)	1949(69)	6425(169)	43.2(9.7)
O(4)	4160(59)	1635(47)	3875(109)	25.6(4.4)

the heavy atoms for **1**, **2**, and **3**, respectively. The atomic coordinates for complexes **1**, **2**, and **3** are listed in Tables 3, 4, and 5.[7]

Complex **1**: Since Z is 2 in space group $P2_1/a$, Cu atom is at the origin. Thus, the structure was solved by the heavy atom method. The R index gave 0.054.

Complex **2**: Two space groups *Iba*2 and *Ibam* are possible from the systematic extinction. Independent structure analyses were attempted for both space groups using MULTAN 78 program.[8] The satisfactory solution was obtained only for *Iba*2. During the refinement, however, Br(2) was found to be disordered in two positions with equal population. Then, a half atomic multiplicity was given to these positions. The final R index gave 0.10.

Complex **3**: Two space groups $Pna2_1$ and *Pnam* are possible from the systematic extinction. Independent structure analyses were attempted for both space groups using MULTAN 78. It was found that all three heavy atoms, Cu, Br, and Cl, are happened to be on the ab plane, and the mirror symmetry appeared in both cases. However, the structure could not be refined for space group *Pnam*. After several trials, the structure was solved by assuming the space group $Pna2_1$ and carefully eliminating the ghost atoms due to the pseudo mirror operation.[6] The structure was refined to R=0.11. However, oxygen atoms of perchlorate and some of the carbon atoms in the ligands were disordered. Therefore, at the last stage the ligand was refined by using the molecular mechanical calculation (MM2 program described by Allinger[10]). The final R factor constrained by MM2 was 0.151.

Results

Preparation of Orange-Red Homo-Anion Copper(II) Complexes of *RS*-ahaz. The copper(II) complexes obtained by adding $CuX_2 \cdot nH_2O$ (X^-=ClO_4^-, NO_3^-, Br^-, BF_4^-) to twice the molar of *RS*-ahaz were found to be orange-red without exception. The diiodide prepared by mixing $[Cu(RS\text{-ahaz})_2](ClO_4)_2$ and LiI in methanol solution was also orange-red. It was found, however, that the product with $CuCl_2 \cdot 2H_2O$ was a mixture of red and blue complexes. We did not examine the dichloride further.

These orange-red homo-anion complexes had the general composition $Cu(C_6H_{14}N_2)_2X_2 \cdot nH_2O$ (n=0 for X^-=ClO_4^-, NO_3^-, BF_4^-, and I^-; n=2 for X^-=Br^-). Although the complex **2**, prepared from *RS*-ahaz and $CuBr_2$, was found to contain two water molecules per one complex molecule, it exhibited the visible reflectance spectrum closely similar to those of the others. The spectral data are summarized in Table 1.

As described in introduction, it is rather unusual[2] that a series of copper(II) complexes of bis(diamine) type is thoroughly orange-red and shows the reflectance spectral maximum around 21000 cm^{-1} regardless of the sort of counter ion. Hence, the crystal structures of complexes **1** and **2** were examined by the X-ray diffraction method.

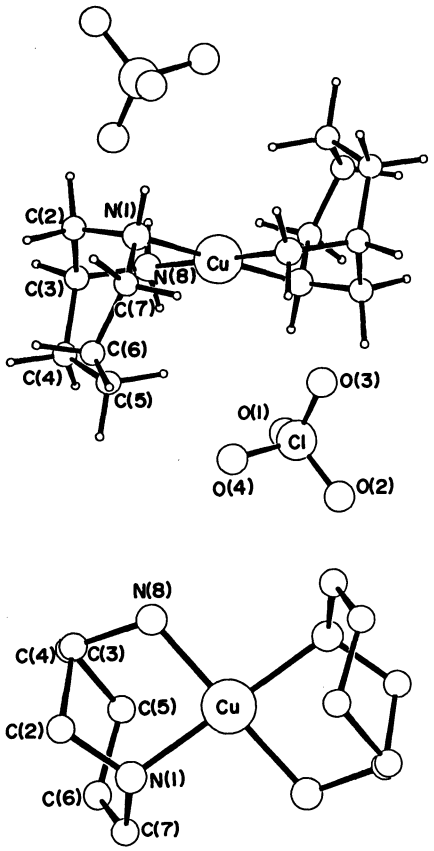


Fig. 2. Perspective views of complex **1**.

Molecular Structure of Complex 1. As is indicated by the crystal parameters, the molecular structure of the complex **1** has the strict C_i symmetry, where the Cu^{2+} ion occupies the center of inversion. The perspective views of **1** are shown in Fig. 2. The selected bond parameters are listed in Table 6. The bond distances and angles are in the normal range. It is noticed that one of two ahaz ligands has the R- and the other has the S-configuration.

Obviously the seven-membered rings of both ahaz stand perpendicular to the respective five-membered chelate rings. The primary and secondary amino groups of both diamines are located at the trans positions around the Cu^{2+} ion, and the seven-membered rings extend towards the opposite sides of the CuN_4 plane. Thus, the C(5) methylene group of *S*-ahaz and C(5)′ methylene of *R*-ahaz prevent completely the approach of the perchlorate, respectively, to the top and bottom apical sites of the central metal ion. The interatomic distance Cu–O(1), the shortest distance between Cu atom and the perchlorate group, is 3.77 Å and the Cu–O(1) vector intersects the CuN_4 plane at 62.8°, indicating no appreciable coordination of the anion to the Cu^{2+}. It is apparent, therefore, that the complex cation of **1** takes the strict four-coordination geometry with C_i symmetry, and that the cation can be expressed by the formula $[Cu(R\text{-ahaz})(S\text{-ahaz})]^{2+}$.

The five-membered chelate and the seven-membered ring of *S*-ahaz in **1** is depicted in Fig. 3 (i) and (ii). The chelate ring adopts a λ conformation, and the seven-membered ring takes a twist-chair conformation. The coordinating secondary N center has the S-configuration. The structural characteristics for *R*-ahaz are exactly antipodal to those for *S*-ahaz, reflecting the C_i symmetry of **1**.

The hydrogen bonding modes and intermolecular short contacts in complex **1** are summarized in Table 7. The nitrogen atoms of the ligands of **1** are hydrogen-bonded to the oxygen atoms of the perchlorate ions. Therefore, the shape of perchlorate is fairly normal in **1**.

Molecular Structure of Complex 2. The perspective views of complex **2** are shown in Fig. 4, and the selected bond parameters are given in Table 6. Each complex cation contains an *R*-ahaz and an *S*-ahaz as the ligands, in the same manner as **1**, but **2** no longer has the true centrosymmetry. The distances between Cu^{2+} and Br^- or O of water molecules, Cu–Br(1), Cu–Br(2)A, Cu–O(2)B, Cu–O(1), and Cu–O(2) are respectively, 4.6, 4.6, >7.0, 6.1, and 6.3 Å. Thus, neither the bromides nor the water molecules coordinate to

Table 6. Bond Lengths (l/Å) and Bond Angles (ϕ/°) for Complexes **1**, **2**, and **3**

	1	**2**	**3**		**1**	**2**	**3**
N(8)-Cu	1.979(5)	2.00(3)	1.94(3)	Cu-N(1)-C(2)	109.2(3)	106(2)	109(4)
N(8)′-Cu		1.95(3)	2.04(4)	Cu-N(1)′-C(2)′		104(2)	113(3)
Cu-N(1)	2.036(4)	1.98(3)	2.07(4)	N(1)-C(2)-C(3)	110.3(4)	111(3)	109(4)
Cu-N(1)′		2.02(3)	1.95(4)	N(1)′-C(2)′-C(3)′		112(3)	107(4)
N(1)-C(2)	1.456(7)	1.48(5)	1.41(9)	C(2)-C(3)-N(8)	104.9(4)	103(3)	106(4)
N(1)′-C(2)′		1.49(5)	1.43(6)	C(2)′-C(3)′-N(8)′		107(3)	104(4)
C(2)-C(3)	1.555(8)	1.52(5)	1.6(1)	C(3)-N(8)-Cu	111.0(3)	109(2)	116(3)
C(2)′-C(3)′		1.54(5)	1.59(8)	C(3)′-N(8)′-Cu		106(2)	110(3)
C(3)-N(8)	1.482(6)	1.47(5)	1.47(6)	C(7)-N(1)-C(2)	113.3(4)	111(3)	117(4)
C(3)′-N(8)′		1.49(5)	1.49(7)	C(7)′-N(1)′-C(2)′		117(3)	109(4)
C(3)-C(4)	1.521(8)	1.53(5)	1.60(7)	C(2)-C(3)-C(4)	113.3(4)	117(3)	109(4)
C(3)′-C(4)′		1.54(5)	1.50(8)	C(2)′-C(3)′-C(4)′		115(3)	113(5)
C(4)-C(5)	1.519(8)	1.53(7)	1.58(9)	C(3)-C(4)-C(5)	116.7(5)	117(3)	117(4)
C(4)′-C(5)′		1.54(5)	1.6(1)	C(3)′-C(4)′-C(5)′		115(3)	115(5)
C(5)-C(6)	1.517(8)	1.53(8)	1.5(1)	C(4)-C(5)-C(6)	114.4(4)	111(4)	111(4)
C(5)′-C(6)′		1.53(6)	1.4(1)	C(4)′-C(5)′-C(6)′		112(3)	113(5)
C(6)-C(7)	1.505(9)	1.56(6)	1.46(8)	C(5)-C(6)-C(7)	116.7(4)	116(4)	114(5)
C(6)′-C(7)′		1.53(6)	1.42(9)	C(5)′-C(6)′-C(7)′		116(4)	115(4)
C(7)-N(1)	1.465(7)	1.46(5)	1.50(7)	C(6)-C(7)-N(1)	115.8(5)	118(3)	119(5)
C(7)′-N(1)′		1.49(6)	1.50(7)	C(6)′-C(7)′-N(1)′		118(4)	119(5)
Cl-O(1)	1.445(5)		1.34(6)	O(1)-Cl-O(2)	108.8(3)		113(3)
Cl-O(2)	1.392(5)		1.42(6)	O(1)-Cl-O(3)	111.1(4)		111(7)
Cl-O(3)	1.358(8)		1.2(1)	O(1)-Cl-O(4)	106.6(4)		111(6)
Cl-O(4)	1.421(7)		1.35(9)	O(2)-Cl-O(3)	112.7(4)		109(8)
Cu-Br			2.888(9)	O(2)-Cl-O(4)	105.3(4)		104(5)
N(8)-Cu-N(1)	84.5(2)	86(1)	82(1)	O(3)-Cl-O(4)	111.9(5)		108(7)
N(8)′-Cu-N(1)′		90(1)	83(2)				

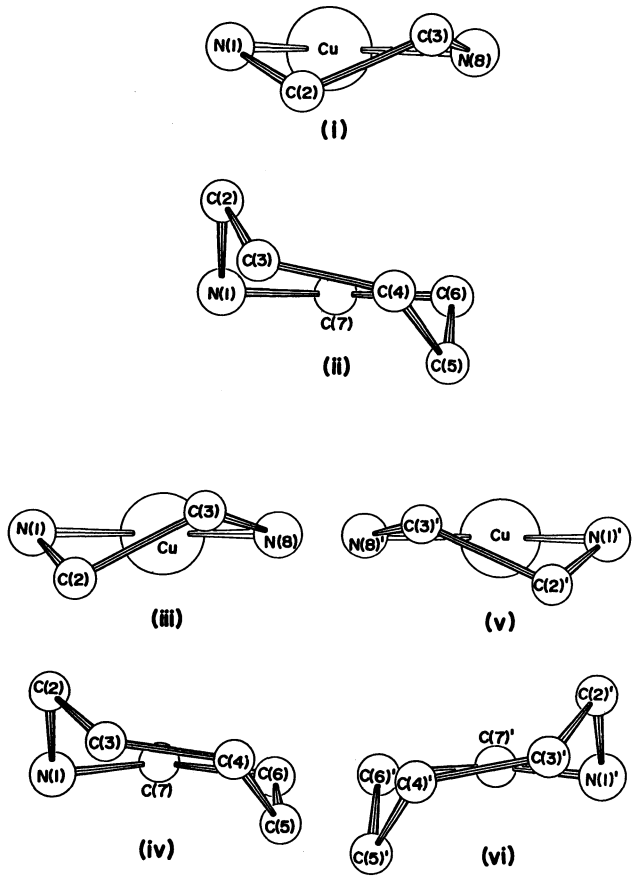


Fig. 3. Fiv-membered chelate rings (i), (iii), (v), and seven-membered rings (ii), (iv), (vi) in **1** and **2**. (i) and (ii) for *S*-ahaz in **1**; (iii) and (iv) for *s*-ahaz in **2**; (v) and (vi) for *R*-ahaz in **2**.

Table 7. Hydrogen Bond Distances and Intermolecular Contacts (Å)

Atom 1 Atom2	Distance	Symmetry[a]
	Complex **1**	
Hydrogen bond		
N(1)-O(1)	3.086(7)	I
N(8)-O(1)	3.361(6)	II
N(8)-O(2)	3.138(7)	II
N(8)-O(3)	3.025(8)	III
Intermolecular contact (<3.5 Å)		
C(3)-O(2)	3.329(7)	IV
	Complex **2**	
Hydrogen bond		
Br(1)-N(1)	3.40(3)	V
Br(2)A-O(2)	3.29(4)	V
Br(2)B-N(8)	3.32(4)	V
N(1)'-O(2)	3.06(4)	V
Intermolecular contact (<3.5 Å)		
C(2)'-O(2)	3.39(5)	V
	Complex **3**	
Hydrogen bond		
Br-N(8)	3.30(3)	VI

a) Symmetry of atom 2,
I: $x, y, z+1$, II: $-x, 1-y, -1-z$, III: $-x, 1-y, -z$, IV: $x+1, y, z+1$, V: $x-1/2, -y+1/2, z$, VI: $1-x, 1-y, z+1/2$.

the central Cu^{2+} ion, showing that the complex cation also holds the strict four-coordination geometry as found in complex **1**, and that **2** can be represented with the formula $[Cu(R\text{-ahaz})(S\text{-ahaz})]Br_2 \cdot 2H_2O$.

The conformations of five-membered chelates and those of seven-membered rings of *S*-ahaz and *R*-ahaz in **2** are shown in Fig. 3 (iii)—(vi). The chelate rings of *S*-ahaz and *R*-ahaz take a λ and a δ gauche conformation respectively, and the seven-membered rings of these ligands adopt twist-chair conformations. Because of lacking the exact C_i symmetry, the conformation of *S*-ahaz is not the exact antipode of that of *R*-ahaz in **2** as indicated in Fig. 3, in contrast to the case of complex **1**. Despite of this fact, the conformation of *S*-ahaz (or *R*-ahaz) in **1** is quite similar to that of *S*-ahaz (or *R*-ahaz) in **2**, though slight deformations are recognized between them (Fig. 3).

The hydrogen bonding modes and intermolecular short contacts in **2** are also listed in Table 7. For complex **2**, the bromide ions are situated on the two fold axis and form rectangular parallelepiped with one-eighth of the unit cell as shown in Fig. 5. The Br(1) atom is near the center of bc plane of the

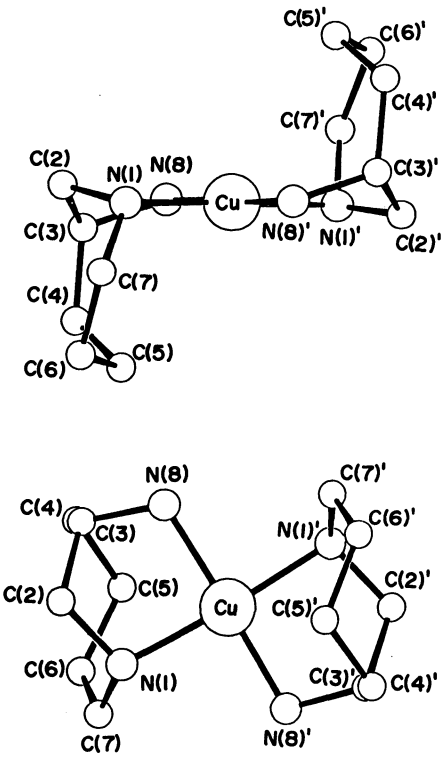


Fig. 4. Perspective views of complex **2**.

parallelepiped. The complex cation is surrounded by Br^- ions. Although the Cu^{2+} ion is situated at a

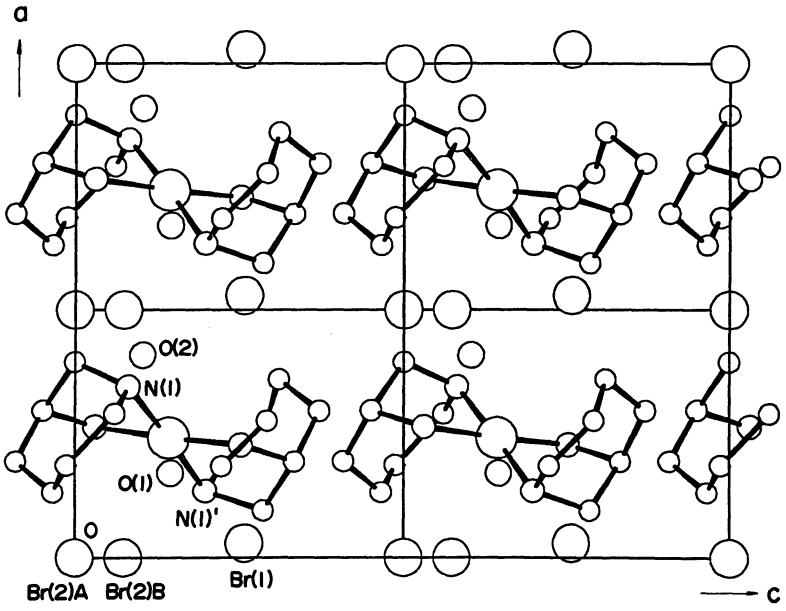


Fig. 5. Crystal packing of complex **2**.

general position, the complex has an approximate centrosymmetry similar to the complex **1**.

Preparation of Hetero-Anion Copper(II) Complexes of *RS*-ahaz. It was found that the orange-red complexes of *RS*-ahaz are classified into two categories based on their electric conductivity behaviors. The complexes with X^-=ClO_4^- and BF_4^- were bi-univalent electrolytes in nitromethane solution, while those of X^-=Br^-, I^-, and NO_3^- dissociated uni-univalently in the same solvent (Table 1). With regard to the latter family, the coordination of an X^- to the central Cu^{2+} seems to take place in the solution, generating new mono-positively charged five-coordinated Cu^{II} species. In spite of the clear difference in the conductivity behaviors, these two families showed no significant differences in their solution spectra (Table 1). Further, it was noticed that the visible absorption spectra of Cu(*RS*-ahaz)$_2$X$_2$ resemble closely those of Cu(*S*-ahaz)$_2$X$_2$ taken in the same solvent (Table 1). For example, the absorption curve of complex **2** is similar to that of Cu(*S*-ahaz)$_2$Br$_2$ and, further, to that of five-coordinated [CuBr(*S*-ahaz)$_2$]-ClO_4 (Fig. 6).

It was demonstrated previously[1] that a series of hetero-anion complexes of *S*-ahaz, Cu(*S*-ahaz)$_2$X-(ClO_4) were obtained by adding LiX or NaX to a solution of Cu(*S*-ahaz)$_2$(ClO_4)$_2$ or, alternatively, adding $LiClO_4$ to Cu(*S*-ahaz)$_2$X$_2$. Similarly the addition of $LiClO_4$ to a methanol solution of complex **2** resulted in the formation of blue-violet crystals having the composition Cu($C_6H_{14}N_4$)$_2$Br(ClO_4). The addition of LiX to a solution of Complex **1** afforded hetero-anion complexes more generally, but in a slightly limited manner compared with the case of *S*-ahaz complexes. The hetero-anion complexes

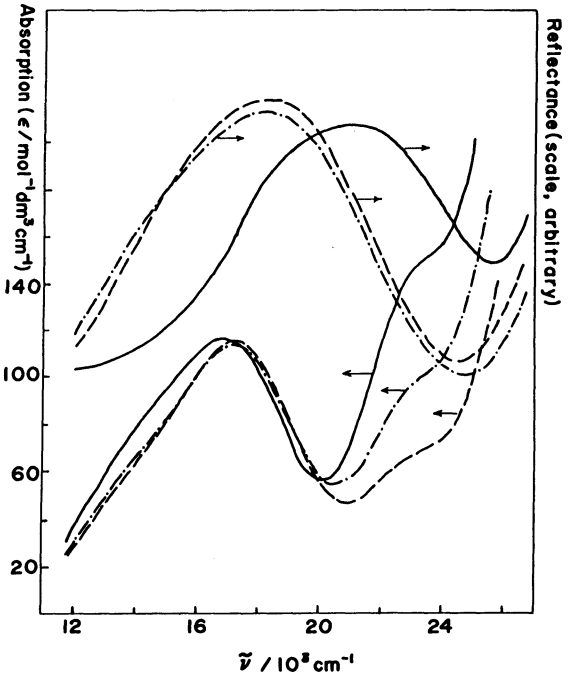


Fig. 6. Reflectance and absorption spectra in nitromethane solution for complexes **2**: (——), **3**: (------), and **4**; (-·-·-).

Cu(*RS*-ahaz)X(ClO_4) were obtained only for X^-=Cl^- and Br^-, while the addition of LiI resulted in the precipitation of orange-red [Cu(*R*-ahaz)(*S*-ahaz)]I_2 as described previously.

The reflectance and absorption spectral as well as electronic conductivity features of the hetero-anion complexes of *RS*-ahaz resembled indistinguishably those of the corresponding *S*-ahaz complexes (Table 1

and Fig. 6). This implies that both *RS*- and *S*-ahaz complexes of the hetero-anion type took stereochemistries closely similar to one another. Since the structure of $[CuBr(S\text{-ahaz})_2]ClO_4$, referred hereafter as to complex **4**, has already been clarified crystallographically,[1] the structure determination of the corresponding *RS*-ahaz complex **3** was performed by the X-ray diffraction method with a view to compare the stereochemical characteristics of **3** and **4** and to examine the ligand exchange mode for the formation of **3** from **1** or **2**.

Molecular and Crystal Structure of Complex 3. Although complex **3** has been represented as $Cu(RS\text{-ahaz})_2Br(ClO_4)$ for simplicity, the X-ray analysis result demonstrated that a racemic pair of five-coordinated complex ions, $[CuBr(R\text{-ahaz})_2]^+$ and $[CuBr(S\text{-ahaz})_2]^+$, exists in the single crystal, and so **3** is represented with the formula $[CuBr(R\text{-ahaz})_2]$-$[CuBr(S\text{-ahaz})_2](ClO_4)_2$. The perspective views shown in Fig. 7 are those for the complex cation comprised with *S*-ahaz, which is exactly antipodal to the counterpart involving *R*-ahaz. We will consider the stereochemical characteristics of the cation with *S*-ahaz as the representative, in relation to that of complex **4**. The selected bond parameters of **3** are listed in Table 6.

The $[CuBr(S\text{-ahaz})_2]^+$ ion in **3** (Fig. 7) is similar to that in **4**[1]. Both complex ions adopt typical square-pyramidal geometries, in which four amino nitrogens of ahaz ligands occupy the basal plane and a bromide at the apex, and the five-membered chelate rings take λ conformations. Seven-membered rings thoroughly assume preferable twist-chair conformations. A noticeable difference between **3** and **4** is found with regard to the cyclic sequences of dihedral angles of both seven-membered rings; i.e. those are nearly identical for **3**, but evidently different for **4**.[1] Thus, the complex ion of **3** appears to have a pseudo C_2 axis perpendicular to CuN_4 plane (Fig. 7), though that of **4** seems not to have such symmetry axis at all.[1]

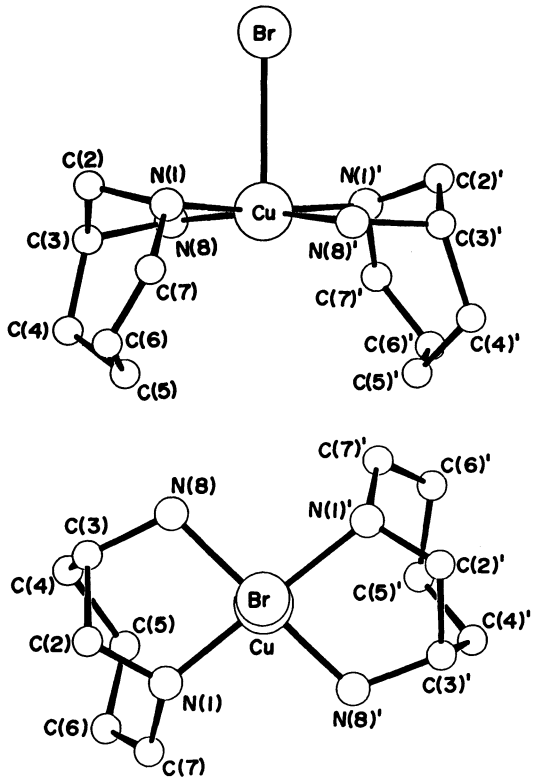


Fig. 7. Perspective views of complex **3**.

The crystal packings and lattice constants of complexes **3** and **4**, as well as their molecular structures, are fairly similar to each other, as shown in Fig. 8 and Table 2. Each complex forms zigzag chains consisting of the complex of the same chirality along c axis through two fold screw operation. Each chain is surrounded by four similar chains as in polyethylene packing.[11] For complex **3**, the neighboring chains, indicated by the broken line rectangles, have the chirality opposite to the chain shown with the solid line rectangle as indicated in Fig. 8 (a). On the other hand, all the chains for complex **4** in Fig. 8 (b) have the same chirality.

Discussion

Structural Characteristics of Reddish Bis(diamine)-copper(II) Complexes. The X-ray diffraction study revealed that $[Cu(R\text{-ahaz})(S\text{-ahaz})]^{2+}$ ion in **1** adopts the strictly rhombic-coplanar CuN_4 stereochemistry, and that the complex cation in **2** is intrinsically identical with that in **1**, though slight deformations from the centrosymmetric geometry take place. The fact that the reflectance spectra of other orange-red homo-anion complexes of *RS*-ahaz resemble those of **1** and **2** strongly suggests that these complexes also assume similar coplanar configurations represented as the structure (III) in Fig. 9 and can be formulated as $[Cu(R\text{-ahaz})(S\text{-ahaz})]X_2$ (X^-=BF_4^-, NO_3^-, I^-).

However, the existence of rhombic- or square-coplanar CuN_4 chromophore in copper(II) complexes has been considered to be unusual.[2] One of the rare examples of such chromophore has been established for $[Cu(deen)_2]^{2+}$ ion (deen=*N*,*N*-diethyl-1,2-ethanediamine) in the diperchlorate[12] or dinitrate.[2] In these deen complexes the coordination of the anions (ClO_4^- or NO_3^-) is disturbed by the *N*-ethyl groups, which orient axially with regard to the respective chelate rings as indicated by Fig. 9 (IV). It is noticeable that $[Cu(deen)_2]X_2$ (X^-=ClO_4^-, NO_3^-) are also reddish-colored and have centrosymmetric rhombic-coplanar structures in a similar manner as **1**.

In addition, it was demonstrated that the wine-red complexes $[Cu(1,3\text{-chxn})_2]X_2$ (1,3-chxn=*cis*-1,3-cyclohexanediamine; X^-=NO_3^-, Br^-) also took square-coplanar stereochemistries.[13,14] The established

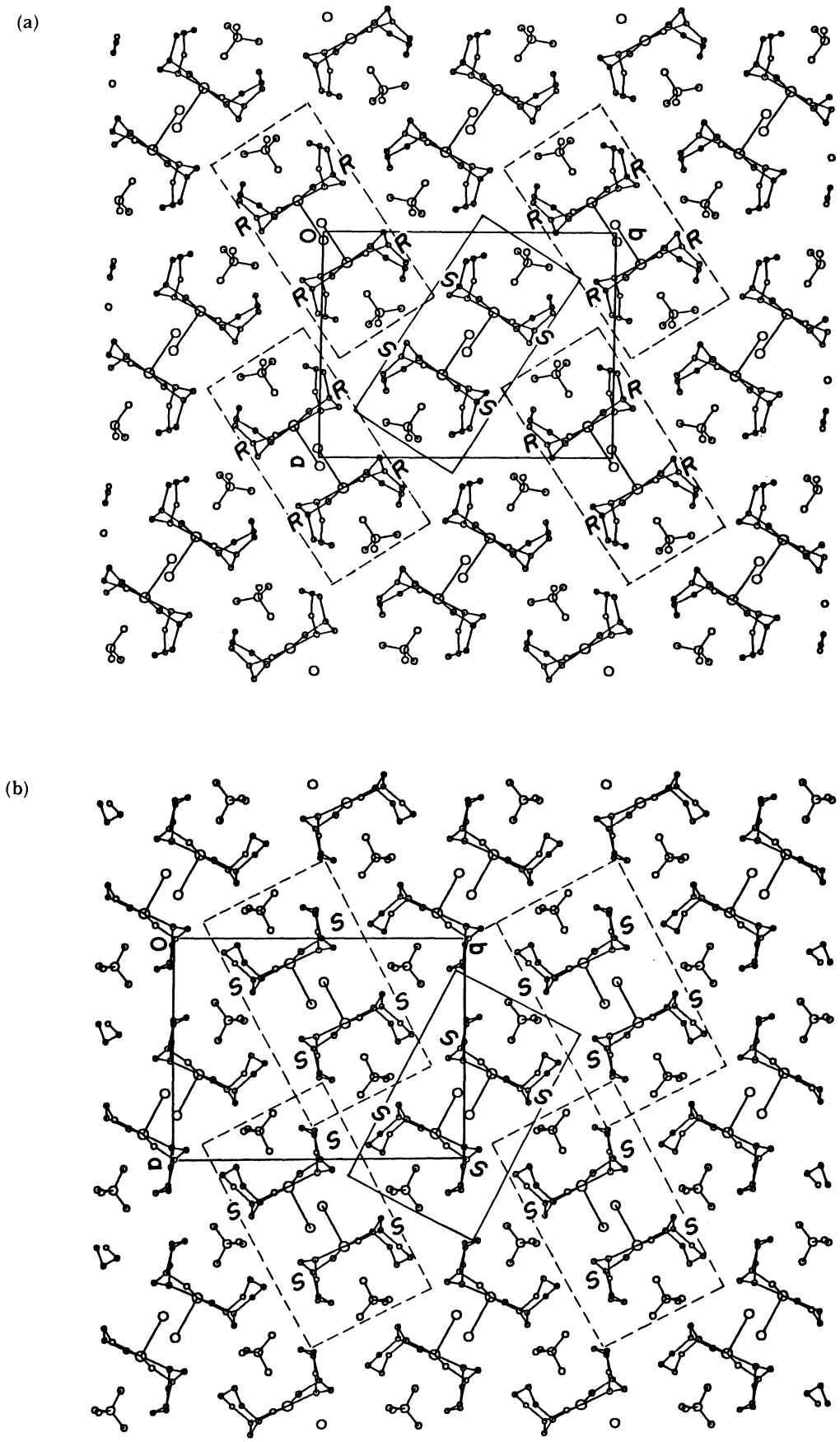


Fig. 8. Comparative views of the crystal structures (projection along c axis); (a) for complex **3** and (b) for complex **4**.

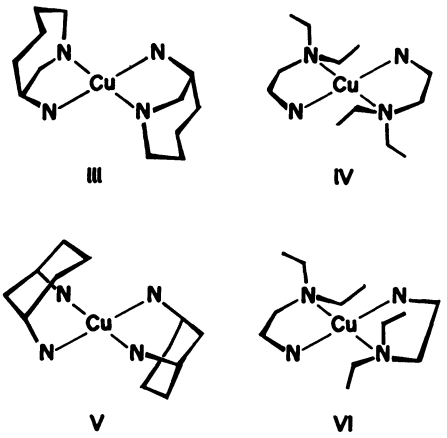


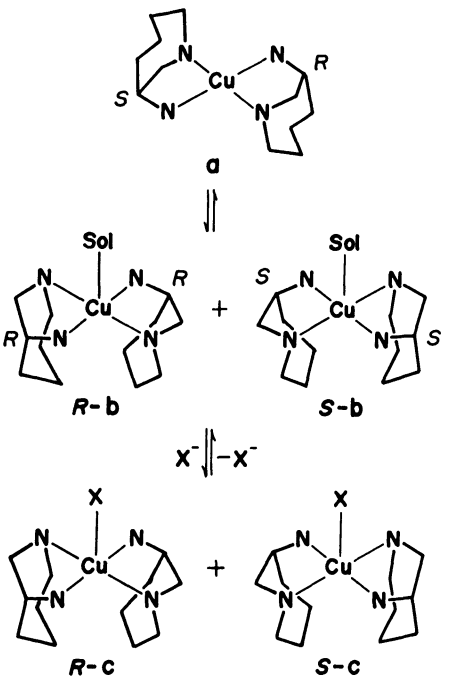
Fig. 9. Stereochemistries of copper(II) complexes having the CuN_4 chromophore. $[Cu(R\text{-ahaz})(S\text{-ahaz})]^{2+}$ ion, (III); $[Cu(deen)_2]^{2+}$ ion (red-form), (IV)[2,12]; $[Cu(1,3\text{-chxn})_2]^{2+}$ ion, (V)[14]; $[Cu(deen)_2]^{2+}$ ion (blue-form), (VI).[12]

structure of $[Cu(1,3\text{-chxn})_2]^{2+}$ ion in these wine-red complexes is illustrated in Fig. 9 (V), where the contact of anions to the apical coordination sites is completely prevented by the ring methylene chains of the ligands in quite a similar manner as that in (III). It can be concluded, therefore, that the common structural features of reddish-colored copper(II) complexes with diamine ligands are the strict four-coordination geometries with C_i or closely similar molecular symmetry and the absence of the coordination of anions to the central ion.

It is noteworthy that the production of reddish-colored bis(diamine)copper(II) complex with the square- or rhombic-coplanar stereochemistry is rather delicate phenomena, being influenced with some complicated factors. For example, $Cu(1,3\text{-chxn})_2Br_2$ was found to form violet crystals from ethanol, in spite that it afforded wine-red crystals from methanol.[13] In the case of *RS*-ahaz complexes, the dibromide gave only orange-red crystals, but the dichloride was a mixture of orange-red and blue-violet forms. For deen complex, the dibromide was no longer reddish-colored, but blue-violet.[15] For the violet or blue-violet modifications of these diamine complexes, some intrinsic changes from the strictly four-coordinated centrosymmetric structure should be effected within the complex ion, though the details of such structural changes are uncertain.

Pathway for Formation of $[CuBr(R\text{-ahaz})_2]^+$ and $[CuBr(S\text{-ahaz})_2]^+$ Ions from $[Cu(R\text{-ahaz})(S\text{-ahaz})]^{2+}$ Ion. The X-ray diffraction study of complex **3** clarified the formation of the five-coordinated $[CuBr(S\text{-ahaz})_2]^+$ and its antipode from $[Cu(R\text{-ahaz})(S\text{-ahaz})]^{2+}$ ion, indicating that not only the coordination of Br^- but certain ligand exchanges of ahaz take place during such transformation in solution. Moreover, the pair of **1** and **3** exemplifies two typical coordination modes possible for metal complexes containing the racemic modification of a chiral bidentate ligands; the first involves both of the R- and S-enantiomers in each complex ion, giving a meso type compound as **1**, while in the second case each complex ion comprises two molecules of the single enantiomer and becomes chiral as in **3**. The formation of **3** can therefore be regarded as a process of chiral discrimination; that is, the first *R*-ahaz (or *S*-ahaz) coordinated to Cu^{2+} ion chooses the same enantiomer as the second ligand to form the chiral five-coordinated complex.

The ligand exchange which occurs upon the dissolution of ahaz complexes is presumed by comparing the electronic spectral data of a series of copper(II) complexes of *RS*- and *S*-ahaz. Thus, the absorption spectrum of complex **1** obtained in nitromethane solution was found to be markedly different from its reflectance spectrum, while it closely resembles the solution spectrum of $Cu(S\text{-ahaz})_2(ClO_4)_2$ (Table 1). Taking into consideration that these complexes dissociate uni-bivalently, it is supposed that such ligand exchanges as those shown in Scheme 1 occur in nitromethane solution, at least in part, to generate a racemic pair of $[Cu(R\text{-ahaz})_2(Sol)]^{2+}$ and $[Cu(S\text{-ahaz})_2(Sol)]^{2+}$ ((Sol) denotes the coordinating solvent molecule). When all the complexes take exclusively the square-pyramidal structures in solution, the spectra for the *RS*-ahaz complex should



Scheme 1. Equilibria for copper(II) complexes of *RS*-ahaz in the presence of X^-: **a**, $[Cu(R\text{-ahaz})(S\text{-ahaz})]^{2+}$; *R*-**b**, $[Cu(R\text{-ahaz})_2(Sol)]^{2+}$; *S*-**b**, $[Cu(S\text{-ahaz})_2(Sol)]^{2+}$; *R*-**c**, $[Cu(R\text{-ahaz})_2X]^+$; *S*-**c**, $[Cu(S\text{-ahaz})_2X]^+$.

coincide with that for the *S*-ahaz complex. In methanol, the absorption spectra of the above complexes of racemic and optically active ahaz actually become almost identical with each other, probably due to that most part of the racemic complex takes the solvent-coordinated square-pyramidal structures.

In the presence of anions such as Cl^-, Br^-, or I^-, the solvent-coordinated species tend to be converted into the five-coordinated $[CuX(S\text{-ahaz})_2]^+$ and its enantiomer as shown in Scheme 1. It is interesting to note that $[Cu(R\text{-ahaz})(S\text{-ahaz})]X_2$ (X^-=Br^-, I^-) dissociates uni-univalently in nitromethane, in contrast to that $[Cu(R\text{-ahaz})(S\text{-ahaz})]X_2$ (X^-=ClO_4^-, BF_4^-) behaves as uni-bivalent electrolytes in the same solvent. These facts suggest that the halide complexes transform almost completely into $[CuX(R\text{-ahaz})_2]^+$ and $[CuX(S\text{-ahaz})_2]^+$ in nitromethane.

Alternatively, when halides or pseudohalides (NCS^- or ONO^-) were added in excess to a solution of **1**, most part of the complex species would adopt the five-coordinated structures with a coordinating X^-. In the case where ClO_4^- and X^- coexist, the product that crystallized from an equilibrated mixture in Scheme 1 is likely to depend on the relative concentrations of ClO_4^- and X^- and the solubilities of individual species as the perchlorate or halide.

Thus, under the conditions where X^- is Cl^- or Br^- and sufficient amounts of both X^- and ClO_4^- coexist in aqueous methanol solution, the hetero-anion complex $Cu(RS\text{-ahaz})_2X(ClO_4)$ is the least soluble species and crystallizes out as the sole product. But in the case where X^- is I^-, $[Cu(R\text{-ahaz})(S\text{-ahaz})]I_2$ is the least soluble one in methanol, so that the addition of NaI to a solution of **1** results in the precipitation of $[Cu(R\text{-ahaz})(S\text{-ahaz})]I_2$. When X^- is ONO^-, a mixture of blue-violet crystals, probably the hetero-anion complex $Cu(RS\text{-ahaz})_2(ONO)(ClO_4)$, and orange-red **1** precipitated out of a solution of **1** containing $NaNO_2$. When X^- is NCS^-, the precipitation of blue-violet crystals no longer resulted, but complex **1** recovered.

It was found, further, that complex **1** crystallized out of an aqueous methanol solution of complex **3**. It was necessary for the recrystallization of the hetero-anion complex to add a small amount of LiBr to the solution. But the addition of a large excess of bromide to a solution of **3** resulted in the precipitation of complex **2**. We observed actually that the lattice constants of an orange-red crystal obtained from **3** by the treatment with excess KBr solution were the same as those of complex **2**. These facts demonstrate that the coordinating bromide is easily replaced with a solvent molecule in aqueous methanol solution, and that the equilibrium shown in Scheme 1 actually exists.

Stereochromism: Dichromism Due to Enantiomeric Composition of Chiral Ligand. Since the structural characteristics of orange-red homo-anion complexes of *RS*-ahaz has been clarified as mentioned above, it becomes possible to consider the interesting phenomenon caused by employing either the racemate or the pure single enantiomer of ahaz; i.e. $Cu(RS\text{-ahaz})_2X_2\cdot nH_2O$ are thoroughly orange-red, while the corresponding *S*-ahaz complexes $Cu(S\text{-ahaz})_2X_2$ are violet or blue-violet.[1] Although no exact structures of *S*-ahaz complexes have been established by the crystallographic method owing to poor quality of crystals, we have postulated them to be (I) or (II).[1] Whichever structures the *S*-ahaz complexes assume, they are intrinsically chiral, so that it is impossible for them to adopt any meso type structures such as centrosymmetric (III). Therefore, it is reasonable that no orange-red form was found for *S*-ahaz complexes, because it is concluded necessary for reddish bis(diamine)copper(II) complexes to adopt the centrosymmetric strict coplanar geometry.

Such color change depending on the enantiomeric composition of a chiral ligand, the racemate or the pure single enantiomer, may be termed "stereochromism" in analogy with thermochromism[16] or other dichromic phenomena. As far as bis(diamine)copper(II) complexes concern, the thermochromism exhibited by deen complexes is one of the most well known and thoroughly examined cases, i.e., $Cu(deen)_2X_2$ interconverts reversibly between the red lower temperature form and the blue higher temperature form, when X^- is of low coordinating ability as ClO_4^- or BF_4^-.[12,15,17-21] The structural change which may accompany with the color change has been studied from various aspects.[12,15,18-21] The hexagonal distortion involving the Cu–N bond lengthening and the synchronous access of anions to the apical sites of Cu^{2+} had been suggested to be responsible for the color change.[15,18-20] However, it was conclusively demonstrated for the diperchlorate[12] that in the course of the transformation from red to blue form no obvious Cu–N bond lengthening took place, and that the most apparent stereochemical change was the conformation inversion of one of the deen chelates. The structures of the red and blue forms thus determined[12] are illustrated in Fig. 9 (IV) and (VI), respectively. It should be pointed out that both chelate rings in (VI) adopt λ conformations (or δ conformations for the antipode of (VI)), so that the complex cation of the blue form (VI) is chiral, even though it has a C_2 axis perpendicular to the CuN_4 plane. As previously noted, (IV) in the red form is strictly centrosymmetric.[2,12] Thus, we can deduce common stereochemical features between the stereochromism of ahaz complexes and the thermochromism of deen complexes; the complex ions in the red forms has the C_i molecular symmetry and are strictly four-coordinated, and in the blue or violet forms they assume certain kind of chiral structures, irrespective of its coordination number being four or

five.

It is apparent that the interconversion between (II) and (III) requires the configurational inversion at the asymmetric carbon center of ahaz. Such conversion is difficult under ordinary condition, so that it is reasonable that orange-red Cu(*RS*-ahaz)$_2$X$_2$ does not show any sign of thermochromism. Alternatively, stereochromism can be realized by using *S*-ahaz in place of *RS*-ahaz as the ligand. More examples of stereochromism will probably be observed among copper(II) complexes by employing both racemic and optically pure forms of certain N-substituted diamines, an example of which will be presented in a following paper.[22]

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3) For simplicity, copper(II) complexes of *RS*-ahaz are indicated with the formula such as Cu(*RS*-ahaz)$_2$X$_2$ or CuX(*RS*-ahaz)$_2$ClO$_4$ throughout the text regardless of the actual formulae which will be clarified in the following part.

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