Preparation, Molecular Structure,† and Stereochemical Properties of Copper(II) Complexes Co-ordinated to (3*S*)- and (*RS*)-3-Aminopiperidine: Effect of Ring Size on Stereochromism

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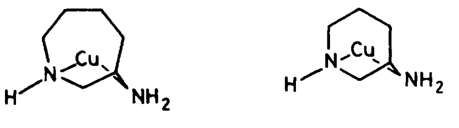
A series of copper(II) complexes co-ordinated to a chiral heterocyclic diamine 3-aminopiperidine (apip) has been prepared. The complexes obtained from the racemic and optically active forms of apip with BF_4^- or ClO_4^- as the counter anions differ significantly in their spectroscopic properties. Such differences are discussed in comparison with those observed in the related copper(II) complexes of 3-aminohexahydroazepine. Mixed-anion complexes $Cu(apip)_2X(ClO_4)$ have been prepared, and the *X*-ray crystallographic analysis of $[Cu(NCS)(S\text{-apip})_2][ClO_4]$ revealed that the thiocyanate occupies the fifth co-ordination site yielding a complex having square-pyramidal geometry. The anion dependency of the reflectance spectra revealed that the spectral change in the apip complexes is caused by steric rather than electronic effects of the anion.

In previous papers [1,2] we reported that the heterocyclic diamine 3-aminohexahydroazepine (ahaz), which can be regarded as a chiral 1,2-diamine having both C- and N-substituents, acts as a bidentate ligand. A typical structure involving chelating *S*-ahaz (abbreviation for *S* isomer of ahaz), (**I**), established by *X*-ray diffraction, is shown in Figure 1. The seven-membered ring of ahaz is perpendicular to the five-membered chelate ring, and the apical co-ordination site of the central metal ion is blocked efficiently by the methylene chain. These characteristics of the ligand are reflected in the interesting stereochemical properties exhibited by several copper(II) complexes of ahaz.[1,2]



(**I**) (**II**)

Figure 1. The co-ordination of the diamines (3*S*)-3-aminohexahydroazepine (**I**) and (3*S*)-3-aminopiperidine (**II**)

When *RS*-ahaz (refers to the racemic mixture of ahaz) is employed as a ligand, copper(II) complexes with a single type of counter anion (homo-anion type)‡ are orange-red and adopt strictly four-co-ordinated structures, (**IIIa**) (Figure 2), which are represented by the general formula $[Cu(R\text{-ahaz})(S\text{-ahaz})]X_2$ ($X = ClO_4$, BF_4, NO_3, Br, or I).[2] On the other hand, *S*-ahaz gives rise to violet or blue-violet complexes, $Cu(S\text{-ahaz})_2X_2$, which are considered to adopt either four- or five-co-ordinated structures (**IVa**) or (**Va**) (Figure 2), depending on the co-ordinating ability of X^-.[1] These structures are inferred from the *X*-ray crystallographic analyses of $[Cu(R\text{-ahaz})(S\text{-ahaz})][ClO_4]_2$ and $[Cu(S\text{-ahaz})_2Br]Br$, and from spectroscopic analysis.[1,2] The remarkable colour change caused by the racemate was called 'stereochromism', in the case of ahaz complexes.[2]

Another interesting feature is that several hetero-anion complexes, $Cu(S\text{-ahaz})_2X(ClO_4)$ and $Cu(RS\text{-ahaz})_2X_2$ ($X =$ Cl, Br, I, NCS, or ONO), are readily obtained. From the *X*-ray crystallographic analysis of $[CuBr(S\text{-ahaz})_2][ClO_4]$ and $[CuBr(R\text{-ahaz})_2][CuBr(S\text{-ahaz})_2][ClO_4]_2$, the hetero-anion complexes are considered to adopt square-pyramidal five co-ordinated structures (**Va**), in which X^- occupies the apical co-ordination site of Cu^{2+}.[1,2] This is caused by the steric effect of the heterocyclic ring as is observed in some copper(II) complexes of 1,4-diazacycloheptane (dach).[3,4]

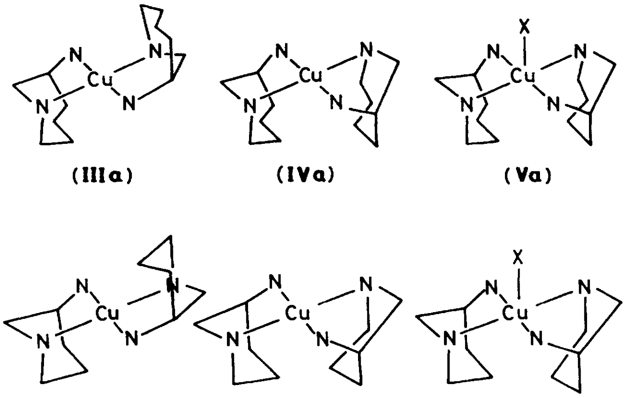


Figure 2. Possible molecular structures for bis(3-aminohexahydroazepine)copper(II) and bis(3-aminopiperidine)copper(II) complexes

3-Aminopiperidine (apip) is the six-membered homologue of ahaz, and also has a chiral carbon centre at C(3). This chiral heterocyclic 1,2-diamine with C- and N-substituents is expected to co-ordinate to a metal ion, as shown in Figure 1, (**II**), with a close similarity to the case of ahaz [Figure 1, (**I**)]. The methylene chain of apip, as well as that of ahaz, needs to be perpendicular to the five-membered chelate ring. Molecular models of co-ordinated apip and ahaz, however, reveal that apip is less

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† *Supplementary data available:* see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1988, Issue 1, pp. xvii—xx.

‡ The terms 'homo-anion' and 'hetero-anion' are used in the same manner as in ref. 1 for a complex with only a single type of anion and for a complex with two different anions.

effective in sterically influencing the apical site because the increase of ring size from six (apip) to seven (ahaz) seems to enlarge the occupied spaces and diminish the room around the apical site. Therefore, we considered it of interest to compare the stereochemical and other properties of copper(II) complexes of *S*-apip or *RS*-apip with those of ahaz, *i.e.* to compare the steric effects of the six- and seven-membered heterocyclic rings on the structure and properties of copper(II) complexes. This paper describes the preparation and stereochemical characteristics, as well as the 'stereochromism', of copper(II) complexes of both optically active (*S*-) and racemic (*RS*-) apip. The *X*-ray structure determination of $[Cu(NCS)(S\text{-apip})_2][ClO_4]$ is also presented.

Experimental

Measurements.—Visible reflectance and absorption spectra were recorded with a Hitachi 340 spectrophotometer, i.r. spectra with a Jasco IRA-2 spectrophotometer. Electric conductivities were measured with a Toa Electronics CM-20A conductivity meter.

(3*S*)-3-Aminopiperidine was prepared from L-ornithine methyl ester dihydrochloride by the procedures described elsewhere.[5] (*RS*)-3-Aminopiperidine was obtained by the same procedures as that for the (*S*) isomer, using DL-ornithine methyl ester dihydrochloride instead of the L isomer as the starting compound.

Preparations.—$Cu(S\text{-apip})_2X_2{\cdot}nH_2O$ (X = ClO_4, Cl, Br, *or* NO_3). The salt $CuX_2{\cdot}nH_2O$ (X = ClO_4, Cl, Br, or NO_3; 5 mmol) dissolved in ethanol (5—10 cm^3) was added dropwise to an ethanol solution of *S*-apip (11 mmol). Diethyl ether (10 cm^3) was then added to facilitate precipitation of the complex. The crystals were collected, washed with diethyl ether, and air-dried. The crude products were recrystallized from hot methanol {Found for $[Cu(S\text{-apip})_2][ClO_4]_2$: C, 26.35; H, 5.35; N, 12.25. Calc. for $C_{10}H_{24}Cl_2CuN_4O_8$: C, 25.95; H, 5.25; N, 12.10. Found for $[CuCl(S\text{-apip})_2]Cl{\cdot}H_2O$: C, 34.00; H, 7.15; N, 15.95. Calc. for $C_{10}H_{26}Cl_2CuN_4O$: C, 34.05; H, 6.85; N, 15.85. Found for $[CuBr(S\text{-apip})_2]Br{\cdot}H_2O$: C, 26.95; H, 5.65; N, 12.60. Calc. for $C_{10}H_{26}Br_2CuN_4O$: C, 27.20; H, 5.95; N, 12.70. Found for $[Cu(S\text{-apip})_2][NO_3]_2{\cdot}H_2O$: C, 30.30; H, 6.45; N, 20.70. Calc. for $C_{10}H_{26}CuN_6O_7$: C, 29.60; H, 6.45; N, 20.70%}.

$[Cu(S\text{-apip})_2][BF_4]_2$. The procedure was same as that for the other homo-anion complexes except for the use of a 45% aqueous solution of $Cu(BF_4)_2$ instead of the copper(II) salts. A larger amount of diethyl ether (100 cm^3) was added to induce precipitation of the product {Found for $[Cu(S\text{-apip})_2][BF_4]_2$: C, 27.25; H, 6.05; N, 12.80. Calc. for $C_{10}H_{24}B_2CuF_8N_4$: C, 27.45; H, 5.55; N, 12.80%}.

$[CuX(S\text{-apip})_2][ClO_4]$ (X = Cl, Br, I, NCS, *or* ONO). To a methanol solution of $[Cu(S\text{-apip})_2][ClO_4]_2$ (0.926 g, 2 mmol) was added an equimolar methanol solution of LiX (X = Cl, Br, or I) or NaX (X = NCS or NO_2). The crystals which formed were collected and washed with methanol and diethyl ether. The crude products were recrystallized using methanol–water (5 : 1 v/v) {Found for $[CuCl(S\text{-apip})_2][ClO_4]$: C, 29.85; H, 6.00; N, 13.85. Calc. for $C_{10}H_{24}Cl_2CuN_4O_4$: C, 30.10; H, 6.05; N, 14.05. Found for $[CuBr(S\text{-apip})_2][ClO_4]$: C, 26.80; H, 5.35; N, 12.35. Calc. for $C_{10}H_{24}BrClCuN_4O_4$: C, 27.10; H, 5.45; N, 12.65. Found for $[CuI(S\text{-apip})_2][ClO_4]$: C, 24.15; H, 4.75; N, 11.15. Calc. for $C_{10}H_{24}ClCuIN_4O_4$: C, 24.50; H, 4.95; N, 11.45. Found for $[Cu(NCS)(S\text{-apip})_2][ClO_4]$: C, 31.50; H, 5.85; N, 16.60. Calc. for $C_{11}H_{24}ClCuN_5O_4S$: C, 31.35; H, 5.75; N, 16.60. Found for $[Cu(ONO)(S\text{-apip})_2][ClO_4]$: C, 29.35; H, 6.10; N, 16.90. Calc. for $C_{10}H_{24}ClCuN_5O_6$: C, 29.35; H, 5.90; N, 17.10%}.

Table 1. Fractional atomic co-ordinates ($\times 10^4$) for $[Cu(NCS)(S\text{-apip})_2][ClO_4]$

Atom	*x*	*y*	*z*
Cu	2 085(1)	2 577(1)	1 570(1)
N(1)	2 003(4)	1 287(3)	1 684(9)
C(2)	2 967(5)	998(4)	1 660(12)
C(3)	3 421(5)	1 461(4)	3 117(11)
C(4)	3 004(6)	1 202(4)	4 833(10)
C(5)	1 983(6)	1 340(5)	4 848(11)
C(6)	1 554(5)	972(4)	3 270(14)
N(7)	3 285(4)	2 392(4)	2 810(7)
N(1′)	2 098(4)	3 876(3)	1 773(9)
C(2′)	1 443(6)	4 149(5)	439(13)
C(3′)	565(5)	3 686(5)	839(14)
C(4′)	221(6)	3 937(6)	2 591(17)
C(5′)	925(7)	3 810(6)	4 006(14)
C(6′)	1 829(6)	4 190(5)	3 495(14)
N(7′)	780(4)	2 750(4)	769(8)
N″	2 749(5)	2 606(5)	−1 023(8)
C″	3 252(5)	2 917(5)	−1 982(9)
S	3 965(1)	3 337(1)	−3 333(2)
Cl	−24(1)	817(1)	−1 980(2)
O(1)	−937(4)	693(5)	−1 477(12)
O(2)	124(5)	1 686(4)	−2 353(10)
O(3)	164(5)	319(4)	−3 446(10)
O(4)	570(5)	547(4)	−645(10)

$[Cu(RS\text{-apip})_2][ClO_4]_2$. Two crystalline forms were obtained for this complex. The orange-red form was obtained according to the same procedure as that for $[Cu(S\text{-apip})_2][ClO_4]_2$ using *RS*-apip instead of *S*-apip as the ligand. However, the complex recrystallized from aqueous solution was purple. This form was also obtained by using methanol in place of ethanol in the ordinary procedure {Found for orange-red $[Cu(RS\text{-apip})_2][ClO_4]_2$: C, 25.80; H, 5.25; N, 12.15. Found for purple $[Cu(RS\text{-apip})_2][ClO_4]_2$: C, 26.00; H, 5.20; N, 12.10. Calc. for $C_{10}H_{24}Cl_2CuN_4O_8$: C, 25.95; H, 5.25; N, 12.10%}.

$Cu(RS\text{-apip})_2X_2$ (X = Br, NO_3, *or* BF_4) *and* $[CuX(RS\text{-apip})_2][ClO_4]$ (X = Cl *or* Br). The procedure was exactly the same as that for the corresponding optically active complexes, but using *RS*-apip instead of *S*-apip as the ligand {Found for $[CuBr(RS\text{-apip})_2]Br{\cdot}H_2O$: C, 27.80; H, 6.15; N, 12.40. Calc. for $C_{10}H_{26}Br_2CuN_4O$: C, 27.20; H, 5.95; N, 12.70. Found for $[Cu(RS\text{-apip})_2][NO_3]_2$: C, 31.40; H, 6.40; N, 21.15. Calc. for $C_{10}H_{24}CuN_6O_6$: C, 30.95; H, 6.25; N, 21.70. Found for $[Cu(RS\text{-apip})_2][BF_4]_2$: C, 26.75; H, 5.80; N, 12.90. Calc. for $C_{10}H_{24}B_2CuF_8N_4$: C, 27.45; H, 5.55; N, 12.80. Found for $[CuCl(RS\text{-apip})_2][ClO_4]$: C, 30.70; H, 6.20; N, 13.60. Calc. for $C_{10}H_{24}Cl_2CuN_4O_4$: C, 30.10; H, 6.05; N, 14.05. Found for $[CuBr(RS\text{-apip})_2][ClO_4]$: C, 27.15; H, 5.80; N, 12.45. Calc. for $C_{10}H_{24}BrClCuN_4O_4$: C, 27.10; H, 5.45; N, 12.65%}.

X-*Ray Structure Analysis of Bis*[(S)-3-*aminopiperidine*] *isothiocyanatocopper*(II) *Perchlorate.*—Unit-cell parameters were derived from a least-squares fit of 18 2θ values in the range 20 < 2θ < 30°. In Table 1 are given the atomic co-ordinates for non-hydrogen atoms.

Crystal data. $C_{11}H_{24}ClCuN_5O_4S$, $M = 421.41$, orthorhombic, $a = 14.721(2)$, $b = 15.652(2)$, $c = 7.754(1)$ Å, $U = 1\,787.6(4)$ Å^3, space group $P2_12_12_1$, $D_m = 1.560$ (296 K), $Z = 4$, $D_c = 1.567$ g cm^{-3}, $F(000) = 876$. Blue prismatic crystal, dimensions 0.40 × 0.48 × 0.51 mm, $\mu(\text{Mo-}K_\alpha) = 1.51$ mm^{-1}.

Data collection and processing. Rigaku AFC-5 automated four-circle diffractometer, ω and ω—2θ (2θ > 30°) scan mode at a scan rate of 4.0° min^{-1}, graphite-monochromated Mo-K_α radiation. Four standard reflections monitored every 150 reflections, the fluctuations of their F_o values being within experimental error throughout the measurement. 1 605 Reflections measured (2θ < 55°), 1 561 unique $[|F_o| > 3\sigma(|F_o|)]$, 788

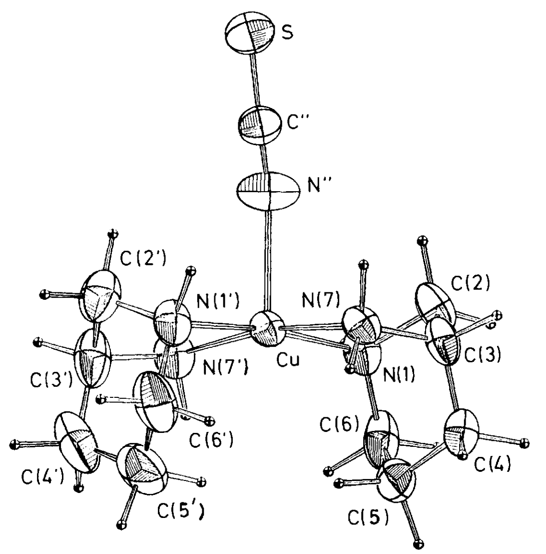

Figure 3. Perspective view of bis[(3*S*)-3-aminopiperidine]isothiocyanatocopper(II) cation

unobserved reflections. Intensities corrected for Lorentz and polarization factors, but not for absorption.

Structure analysis and refinement. Direct method. Refined by block-diagonal least-squares procedure based on $|F_o|$. Unit weights for all reflections. All non-hydrogen atoms were treated anisotropically and H atoms isotropically. Final R and R' $\{= [\Sigma w(|F_o| - |F_c|)^2/\Sigma w|F_o|^2]^{\frac{1}{2}}\}$ values were 0.039 and 0.040 respectively. The largest shift-to-error value in the final cycle was 0.38 [x co-ordinate of O(4)]. Atomic scattering factors were taken from ref. 6. The crystallographic calculations were performed on a FACOM M-780 computer using the program MULTAN 78[7] and the UNICS III program system.[8] The absolute configuration was determined using *S*-apip derived from L-ornithine as an internal reference.

Additional material available from the Cambridge Crystallographic Data Centre comprises H-atom co-ordinates, thermal parameters, and remaining bond lengths and angles.

Results and Discussion

Both the single enantiomer (*S*) and the racemate (*RS*) of apip form copper(II) complexes involving two molecules of the ligand, indicative of its co-ordination as a bidentate ligand. The striking features of the apip complexes are the 'stereochromism' and the formation of hetero-anion complexes, which will be discussed later in the text. These features are quite similar to those of ahaz complexes.[1,2] The number of carbon atoms in the heterocyclic ring is the difference between the two diamines. However, this slight difference causes notable changes in the anion dependency of the reflectance spectra between series of complexes of apip and ahaz.

Molecular Structure of Bis[(S)-3-*aminopiperidine*]*isothiocyanatocopper*(II) *Perchlorate.*—A perspective view of the complex is given in Figure 3, and selected bond parameters in Table 2.

Figure 3 shows that the complex adopts a typical square-pyramidal co-ordination [Figure 2, (**Vb**)], in which two molecules of *S*-apip are chelated to the Cu^{2+} to give a N_4 basal plane and the thiocyanate ion occupies one of the apical co-ordination sites. The Cu^{2+} is displaced 0.16 Å towards the NCS^- from the N_4 plane due to the coulombic attraction of NCS^-.

Table 2. Selected bond parameters (distances in Å, angles in °) for [Cu(NCS)(*S*-apip)$_2$][ClO$_4$]

Cu–N(1)	2.033(6)	Cu–N(1′)	2.043(6)
Cu–N(7)	2.033(7)	Cu–N(7′)	2.036(8)
N(1)–C(2)	1.491(12)	N(1′)–C(2′)	1.471(14)
C(2)–C(3)	1.512(14)	C(2)–C(3′)	1.519(14)
C(3)–N(7)	1.510(11)	C(3′)–N(7′)	1.516(12)
C(3)–C(4)	1.507(14)	C(3′)–C(4′)	1.498(19)
C(4)–C(5)	1.542(15)	C(4′)–C(5′)	1.545(18)
C(5)–C(6)	1.501(16)	C(5′)–C(6′)	1.494(16)
C(6)–N(1)	1.484(15)	C(6′)–N(1′)	1.497(15)
Cu–N″	2.239(8)	N″–C″	1.162(13)
C″–S	1.617(10)	Cl–O(2)	1.404(8)
Cl–O(1)	1.426(8)	Cl–O(4)	1.428(9)
Cl–O(3)	1.412(9)		
N(1)–Cu–N(7)	84.4(3)	N(7)–Cu–N″	92.8(3)
N(1′)–Cu–N(7′)	84.7(3)	N(1′)–Cu–N″	92.6(3)
N(1)–Cu–N(7′)	94.5(3)	N(7′)–Cu–N″	97.8(3)
N(1′)–Cu–N(7)	95.1(3)	Cu–N″–C″	150.0(7)
N(1)–Cu–N″	94.9(3)		

The thiocyanate is N-co-ordinated, as predicted from the i.r. spectrum[9] which showed bands at 2 070 cm^{-1} for ν(CN) and at 856 cm^{-1} for ν(CS), and no bands around 720—690 cm^{-1}. The NCS^- is linear but not perpendicular to the N_4 plane, and is inclined at 150°, which effects a change in symmetry from C_2 to C_1. The Cu–N(NCS) distance is 2.24 Å, which is about 0.2 Å longer than the other four Cu–N bonds in the basal plane.

Two *S*-apip ligands are located *trans* to each other with regard to the primary or secondary amino groups. The six-membered heterocyclic rings adopt chair conformations, and are perpendicular to the respective five-membered chelate rings. Both *S*-apip ligands lie on the same side of the N_4 plane, with their methylene chains hanging over the central Cu^{2+}. The closest distance between two methylene groups [hydrogens of C(5) and C(5′)] is 2.19 Å, which indicates that the vacant apical site is too narrow to permit entry of another anion.

This complex, as a whole, is quite similar to that of [CuBr(*S*-ahaz)$_2$][ClO$_4$], the structure of which is given in Figure 2, (**Va**).[1] However, the distance between the nearest two methylene groups at the fifth-co-ordinating site occupied by the anion is small in the apip complex compared with that in the ahaz complex. The shortest distances between the opposing methylene hydrogens of two diamines at the anion co-ordination site are 5.36 and 5.02 Å, respectively, in [CuBr(*S*-ahaz)$_2$][ClO$_4$] and [Cu(NCS)(*S*-apip)$_2$][ClO$_4$], and those at the vacant apical site are 2.25 and 2.19 Å. Although the co-ordinated anions differ between the apip and ahaz complexes (NCS^- for apip and Br^- for ahaz), the above facts suggest that the room available at the two apical sites of square-pyramidal apip complexes is generally less than that in ahaz complexes, and that stronger steric repulsions around the apical co-ordination sites could exist in apip complexes. This observation is in complete contrast to the assumption made on the basis of the molecular model mentioned earlier.

This difference is caused by the difference in rigidity between the heterocyclic rings of apip and ahaz. The seven-membered rings of the two ahaz in [CuBr(*S*-ahaz)$_2$][ClO$_4$] adopt different conformations from each other, so as to maintain an appropriate distance and reduce steric repulsions between the ligands. In other words, in the ahaz complex the bond strain is relaxed by the flexibility of the seven-membered rings. On the other hand, the six-membered ring of apip strictly adopts the chair conformation and there is no way to avoid steric repulsions in the complex.

Table 3. Electric conductivity, visible absorption, and reflectance spectral data for apip complexes

Complex	Absorption[a] $\tilde{\nu}_{max.}$/cm^{-1}	$\varepsilon_{max.}$/dm^3 mol^{-1} cm^{-1}	Reflectance $\tilde{\nu}_{max.}$/cm^{-1}	Conductivity[a] Λ/mS m^2 mol^{-1}
Homo-anion complexes				
$[Cu(S\text{-apip})_2][ClO_4]_2$	18 980	99	18 320	151
$[Cu(RS\text{-apip})_2][ClO_4]_2$	19 080	105		152
orange-red			20 880	
purple			19 310	
$[Cu(S\text{-apip})_2][BF_4]_2$	18 730	100	18 830	176
$[Cu(RS\text{-apip})_2][BF_4]_2$	19 010	102	21 010	182
$[Cu(S\text{-apip})_2][NO_3]_2 \cdot H_2O$	18 180	100	18 380	78
$[Cu(RS\text{-apip})_2][NO_3]_2$	18 180	110	19 420	84
$[CuCl(S\text{-apip})_2]Cl \cdot H_2O$	17 010	121	17 390	57
$[CuBr(S\text{-apip})_2]Br \cdot H_2O$	16 470	131	16 920	66
$[CuBr(RS\text{-apip})_2]Br \cdot H_2O$	16 670	125	17 790	74
Hetero-anion complexes				
$[CuCl(S\text{-apip})_2][ClO_4]$	16 530	133	16 530	92
$[CuCl(RS\text{-apip})_2][ClO_4]$	16 530	117	17 300	99
$[CuBr(S\text{-apip})_2][ClO_4]$	16 950	130	16 080	104
$[CuBr(RS\text{-apip})_2][ClO_4]$	16 950	128	16 670	103
$[CuI(S\text{-apip})_2][ClO_4]$	16 640	130	15 150	110
$[Cu(NCS)(S\text{-apip})_2][ClO_4]$	16 840	118	17 540	106
$[Cu(ONO)(S\text{-apip})_2][ClO_4]$	17 420	106	16 750	99
Ahaz complexes[b]				
$[CuCl(S\text{-ahaz})_2][ClO_4]$	17 210	107	18 200	97
$[CuBr(S\text{-ahaz})_2][ClO_4]$	17 210	113	18 300	97
$[CuI(S\text{-ahaz})_2][ClO_4]$	17 860	108	18 500	102
$[Cu(NCS)(S\text{-ahaz})_2][ClO_4]$			17 850	102
$[Cu(ONO)(S\text{-ahaz})_2][ClO_4]$			17 900	100

[a] 5 × 10^{-4} mol dm^{-3} in nitromethane, 19 °C. [b] Ref. 1.

Homo-anion Copper(II) *Complexes.*—The homo-anion complexes are obtained by mixing $CuX_2 \cdot nH_2O$ and twice the molar equivalent of apip. The elemental analysis data are in good agreement with the general composition $Cu(apip)_2X_2 \cdot nH_2O$. The complexes of *S*-apip are violet or blue-violet, and their conductivity and reflectance spectra (Table 3) resemble those of *S*-ahaz complexes.[1] This suggests that the structures of *S*-apip complexes are closely similar to those of the corresponding *S*-ahaz complexes. Thus, it is supposed that $Cu(S\text{-apip})_2X_2$ assumes the structure (**IVb**) for X = ClO_4 and BF_4, and (**Vb**) for X = Cl, Br, and NO_3 in Figure 2, though the exact structures have not been clarified by *X*-ray determination.

We have demonstrated that $Cu(RS\text{-ahaz})_2X_2$ * is orange-red and adopts the strictly four-co-ordinate structure (**IIIa**), irrespective of the type of anion.[2] However, the homo-anion complexes of *RS*-apip, $Cu(RS\text{-apip})_2X_2$, can be classified into two groups based on their colour. When X = BF_4, orange-red crystals are the sole product, which probably have the centrosymmetric four-co-ordinate geometry (**IIIb**) in Figure 2, represented as $[Cu(R\text{-apip})(S\text{-apip})]^{2+}$. On the other hand, the complexes with X = Cl, Br, and NO_3 gave rise to purple or violet crystals. The possible structures of these will be discussed later.

In the case of $Cu(RS\text{-apip})_2(ClO_4)_2$,* however, two types of crystals with the same composition but different colour were obtained. That obtained from hot ethanol is orange-red, and that obtained from methanol or aqueous solution is pale purple. The former is thought to have the structure (**IIIb**) as for the tetrafluoroborate. The purple form is transformed into the orange-red form upon prolonged heating in ethanol suspension, while the former transforms into the latter upon recrystallization from aqueous solution. Further, these two forms are different only in the crystalline state, and give exactly the same solution spectra. Thus it seems that these two crystal forms are interconvertible, and differentiation between them depends considerably on subtle crystallization conditions.

The colour of some copper(II) complexes of *S*-apip differs significantly from those of *RS*-apip, as is indicated by the reflectance spectral data (Table 3). For example, the maxima for tetrafluoroborate complexes of *RS*-apip and *S*-apip differ by 2 180 cm^{-1}. This phenomenon, termed stereochromism in our previous report,[2] has been recognized for copper(II) complexes of ahaz and is attributed to the change in co-ordination geometry. The structure of the orange-red *RS*-ahaz complexes is (**IIIa**) which is centrosymmetric and can be expressed as $[Cu(R\text{-ahaz})(S\text{-ahaz})]^{2+}$, while that of the violet *S*-ahaz complexes is (**IVa**), which has apparent C_2 symmetry. This structural change causes a shift as large as 1 900 cm^{-1} (for tetrafluoroborates)[2] in the reflectance spectra. Taking account of the similarities in the spectral change and in the structure of the apip and ahaz complexes, the stereochromism observed for BF_4^- salts of apip complexes can also be attributed to the formation of centrosymmetric $[Cu(R\text{-apip})(S\text{-apip})]^{2+}$, (**IIIb**), for *RS*-apip and non-centrosymmetric $[Cu(S\text{-apip})_2]^{2+}$, (**IVb**), for *S*-apip, respectively. The spectral difference between the orange-red form of $Cu(RS\text{-apip})_2(ClO_4)_2$ and $Cu(S\text{-apip})_2(ClO_4)_2$ is apparently similar to that of the BF_4^- salts, and can be ascribed to the same structural change as described above.

The reflectance spectral maxima of $Cu(RS\text{-apip})_2X_2$ [X =

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* For simplicity, the complexes prepared from *RS*-apip are expressed hereafter as $[Cu(RS\text{-apip})_2]^{2+}$ regardless of their exact structure, unless otherwise noted.

ClO_4^- (purple form), NO_3, or Br], which are purple or violet, differ only by 890—1 040 cm^{-1} from those of the corresponding Cu(*S*-apip)$_2$X$_2$. One possibility is that these complexes adopt a *cis*-[Cu(*R*-apip)(*S*-apip)]$^{2+}$ or *cis*-[CuX(*R*-apip)(*S*-apip)]$^+$ structure, but this can be dismissed by taking into consideration that *N*-substituted diamine complexes tend to assume a *trans* configuration with regard to the primary or secondary amino groups, probably due to the steric repulsions between two neighbouring secondary amino groups co-ordinated to Cu^{2+}, and also that close approach of the methylene chains of *R*- and *S*-apip will be present in these isomers, even closer than that in (**IVb**) or (**Vb**). Thus, either of the following two structures is most probable for purple or violet *RS*-apip complexes, because the structure (**IIIb**), which will give an orange-red complex, is considered unlikely. The first is a racemate of the structure (**IVb**) and its enantiomer, giving rise to a complex of formula [Cu(*R*-apip)$_2$][Cu(*S*-apip)$_2$]X$_4$. This may be adopted with weakly co-ordinating anions such as ClO_4^-. The second is a racemate of (**Vb**) and its enantiomer, represented by formula [CuX(*R*-apip)$_2$][CuX(*S*-apip)$_2$]X$_2$. The bromide and, presumably, the nitrate salt are thought to adopt this structure.

It should be noted that, in the crystalline state, these racemates are intrinsically different from the corresponding optically active forms such as [Cu(*S*-apip)$_2$]X$_2$ and [CuX(*S*-apip)$_2$]X. A [CuX(*S*-apip)$_2$]$^+$ ion in the racemate, for example, should interact with neighbouring [CuX(*R*-apip)$_2$]$^+$ ions in the crystal, while a [CuX(*S*-apip)$_2$]$^+$ ion in the optically active form is surrounded only by *S*-apip complexes. The difference in the environments around the complex ions and interactions with neighbouring ions could result in the small differences in the reflectance spectral maxima of 890—1 040 cm^{-1} (Table 3) between *RS*-apip and *S*-apip complexes. Thus there are two modes of stereochromism in the case of apip complexes. The first, which is observed also for the ahaz complexes previously reported,[2] is caused by the change in the molecular structure, and the second is caused by that in the crystal structure. The second mode of stereochromism is also found for hetero-anion complexes, as will be described later.

It should be noted that the phenomena of stereochromism becomes apparent only in the crystalline form. The complexes of *RS*- and *S*-apip exhibit similar absorption spectra when dissolved in nitromethane (Table 3). This indicates that the major copper(II) species in such solutions adopt similar structures for *RS*- and *S*-apip complexes. A comparison of the reflectance and absorption spectra suggests that the major species present in nitromethane solution adopt the structure (**IVb**) or (**Vb**) depending on the co-ordinating ability of the anions present, and only a small amount of other complexes is present. Therefore the crystallization of orange-red [Cu(*R*-apip)(*S*-apip)]X$_2$, a minority constituent in solution, indicates that their solubility is significantly lower than the salts of (**IVb**) or (**Vb**) and their enantiomers, *i.e.* [Cu(*R*-apip)$_2$][Cu(*S*-apip)$_2$]X$_4$ or [CuX(*R*-apip)$_2$][CuX(*S*-apip)$_2$]X$_2$. In other words, the phenomena of stereochromism is caused by the significantly low solubility of [Cu(*R*-apip)(*S*-apip)]X$_2$.

Hetero-anion Copper(II) *Complex of apip.*—The hetero-anion complexes [CuX(*S*-apip)$_2$][ClO$_4$] or [CuX(*RS*-apip)$_2$][ClO$_4$] are obtained by adding the alkali-metal salt of the corresponding anion X$^-$ (Cl$^-$, Br$^-$, I$^-$, NCS$^-$, or NO_2^-) to [Cu(*S*-apip)$_2$][ClO$_4$]$_2$ or [Cu(*RS*-apip)$_2$][ClO$_4$]$_2$. This is due to the reduced solubility of the hetero-anion compared to the homo-anion complexes. The *X*-ray crystallographic structure analysis performed on [Cu(NCS)(*S*-apip)$_2$][ClO$_4$] revealed that this complex adopts the square-pyramidal five-co-ordinated structure (**Vb**) in Figure 2. This implies that the formation of five-co-ordinate species is responsible for the formation of hetero-anion complexes.

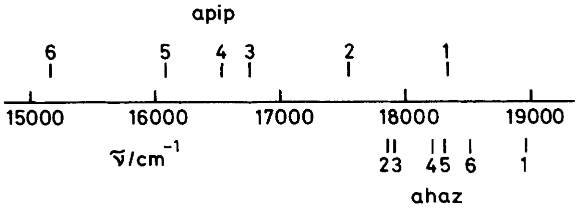

Figure 4. Reflectance spectral peak positions of Cu(*S*-apip)$_2$X(ClO$_4$) and Cu(*S*-ahaz)$_2$X(ClO$_4$)[1]: X = ClO$_4$ (1), NCS (2), ONO (3), Cl (4), Br (5), or I (6)

The reflectance spectra of the starting diperchlorate and the hetero-anion complexes (Table 3) show that a clear red shift, indicative of the co-ordination of anion species, is accompanied by the formation of hetero-anion species. Further, the electrical conductivity data in Table 3 also indicate anion co-ordination in the solution. The conductivities of the hetero-anion complexes are in the range of 92—110 mS m^2 mol^{-1}, as expected for 1:1 electrolytes. Since [Cu(*S*-apip)$_2$][ClO$_4$]$_2$ behaves as a 2:1 electrolyte it is obvious that the halides or pseudohalides (NCS$^-$ or ONO$^-$) in hetero-anion complexes bind tightly to Cu^{2+}. Thus, it can be concluded that all the hetero-anion complexes adopt the square-pyramidal five-co-ordinate structure (**Vb**).

Similar observations were also reported for copper(II) complexes of ahaz.[1] The reflectance spectra for a series of hetero-anion complexes could be dependent on the anion species at the apical co-ordination site. Interestingly, a notable difference was found between the anion dependencies of the reflectance spectra of apip and ahaz complexes (Figure 4). The shifts from the diperchlorate are clearly in the opposite order for apip and ahaz complexes. This means that the effect of the apical ligand on the ligand-field splitting follows opposite orders for these two series.

The spectrochemical series for the ligands employed is NCS$^-$ > ONO$^-$ > Cl$^-$ > Br$^-$ > I$^-$ > vacant site (vac). The four-co-ordinate complex [Cu(*S*-apip)$_2$]$^{2+}$ (**IVb**) is regarded as a five-co-ordinate complex (**Vb**) with a vacant ligand (vac). In square-pyramidal copper(II) complexes the destabilization of *d* orbitals oriented in the *z*-direction leads to a decrease in ligand-field splitting, which consequently gives a red shift in the electronic spectra.[10—12] Thus, the reflectance spectra of five-co-ordinate complexes should shift to longer wavelengths in the order of the spectrochemical series, in accord with the anion dependency observed for ahaz complexes.

In the case of apip complexes, however, the steric effect seems to play an important role, because the order of the spectral maxima (vac > NCS$^-$ > ONO$^-$ > Cl$^-$ > Br$^-$ > I$^-$) seems to be in the order of ligand size. From the *X*-ray structure analysis of apip and ahaz complexes, the room for the available apical ligand has been shown to be greater for ahaz than for apip. The approach of the ring methylene chains to the vacant apical site is eased by the conformational change of the seven-membered ring of ahaz, while the conformation of the six-membered ring of apip is too rigid for this to occur. Thus it is highly probable that the co-ordination of apip itself is affected more significantly by the access of an anion to the apical co-ordination site, as the anion size increases. In other words, some distortions or lengthening of Cu–N bonds may be caused by the co-ordination of an anion, resulting in a weakening of the ligand field due to apip and a shift of the reflectance spectral maxima to lower energy.

Another difference between apip and ahaz complexes is in the stereochromism of hetero-anion complexes. As seen in Table 3, the reflectance spectral maxima for [CuX(*RS*-apip)$_2$]$^+$ (X = Cl or Br) are shifted 590—770 cm^{-1} towards higher energy compared to those of *S*-apip, although both complexes should adopt the same molecular structure (**Vb**) (and its enantiomeric form in the case of *RS*-apip complexes). This shift is comparable to that observed for the purple homo-anion complexes of *RS*-apip and the corresponding complexes of *S*-apip (second mode of stereochromism), but such a shift is not observed for ahaz complexes.[2] This shift is ascribed to the difference in the crystal packing between the optically active form consisting only of $[\mathrm{CuX}(S\text{-apip})_2]^+$ and the racemic form involving $[\mathrm{CuX}(R\text{-apip})_2]^+$ as well as $[\mathrm{CuX}(S\text{-apip})_2]^+$ because there seems no other possible difference between the two. Such a change in the crystal structure is observed in the case of $[\mathrm{CuBr}(S\text{-ahaz})_2]\mathrm{ClO}_4$ and $[\mathrm{CuBr}(R\text{-ahaz})_2][\mathrm{CuBr}(S\text{-ahaz})_2][\mathrm{ClO}_4]_2$.[2] Taking into account the rigidity of apip and the flexibility of ahaz as a ligand, it is highly probable that the molecular structure is affected by the change in the crystal structure resulting in a spectral change in apip complexes but not in ahaz complexes. Thus the second mode of stereochromism, characteristic of apip complexes, ought to be due to the distortion in the molecular structure (**Vb**) caused by the change in the crystal structure from the optically active to the racemic form.

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