X-Ray Structures of Cu(II) Chelates of *cis*-1,3-Cyclohexanediamine

Keiko KAMISAWA, Keiji MATSUMOTO, Shun'ichiro OOI,* Reiko SAITO,** and Yoshinori KIDANI***

Department of Chemistry, Faculty of Science, Osaka City University, Sumiyoshi-ku, Osaka 558

***Aichi Junior College of Nursing, Kamishidanmi, Moriyama-ku, Nagoya 463*

****Faculty of Pharmaceutical Science, Nagoya City University, Tanabe-dori, Mizuho-ku, Nagoya 467*

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The crystal structures of wine-red $[Cu(1,3\text{-chxn})_2]Br_2$ (**1**), $[Cu(1,3\text{-chxn})_2](NO_3)_2$ (**2**), and blue-violet $[CuCl(1,3\text{-chxn})_2]ClO_4$ (**3**) (1,3-chxn=*cis*-1,3-cyclohexanediamine) have been determined from the diffractometer data measured by the use of Mo $K\alpha$ radiation. The structures were solved by the Patterson–Fourier method and refined by the least-squares method to $R=0.042$ (**1**), 0.033 (**2**), and 0.057 (**3**) for 1309, 1210, and 776 nonzero reflections respectively. The Cu atoms in **1** and **2** have a square-planar coordination by 4 N atoms, while the complex ion in **3** has a 5-coordinate square-pyramidal geometry, with the Cl atom at the apical position. The 6-membered chelate rings in **1**, **2**, and **3** are of the chair, flattened-chair, and envelope conformations respectively. The complex ions in **1** and **2** have virtually a C_{2h} symmetry, the two-fold axis of which lies on the CuN_4 plane. The virtual symmetry for $[CuCl(1,3\text{-chxn})_2]^+$ is C_{2v}, the approximate two-fold axis being coincident with the Cu–Cl bond. The cyclohexane rings (chair conformation) in **2** and **3** are roughly perpendicular to the coordination plane, but that in **1** leans toward the central Cu(II) atom. The formation of such coordinatively unsaturated Cu(II) complexes as **1**—**3** is attributable to the steric hindrance of the bulky cyclohexane ring to the axial coordination site.

Although *cis*-1,3-cyclohexanediamine (1,3-chxn) is capable of chelating to a metal ion, as has been demonstrated by X-ray structure analyses of Pd(II) and Pt(II) chelates,[1,2] it has received much less attention in coordination chemistry than the *trans*-1,2-isomer, which is chiral and stereoselective for complex formation. Recently, however, the bis 1,3-chxn chelates of several metal ions have been prepared and characterized by means of the spectral method.[3] Of these chelates, $Cu(1,3\text{-chxn})_2X_2$-type compounds show various colors depending on the course of the preparation; *e.g.*, the recrystallization of the violet bromide from methanol yields wine-red crystals, whose color is unusual for the CuN_4X_2 chromophore, while the color of the bromide is unchanged by recrystallization from ethanol. The crystal structures of wine-red $Cu(1,3\text{-chxn})_2Br_2$ (**1**), $Cu(1,3\text{-chxn})_2(NO_3)_2$ (**2**), and blue-violet $Cu(1,3\text{-chxn})_2ClClO_4$ (**3**) have been investigated in order to reveal the stereochemical features of the 1,3-chxn as a ligand.

Experimental

The preparations of **1**, **2**, and **3** were described elsewhere.[3] The unit-cell dimensions of **1**, **2**, and **3** were determined from the least-squares analyses of 18, 16, and 12 θ values of the high-angle reflections measured on an automated diffractometer. Table 1 lists the crystal data and experimental details. The intensities were measured on the diffractometer using graphite-monochromated Mo $K\alpha$ radiation, and corrected for the Lp factor, but not for absorption. For each of the three compounds, the intensities of three standard reflections were monitored every 4 h, but they showed no ap-

TABLE 1. SUMMARY OF CRYSTAL DATA AND EXPERIMENTAL DETAILS

Compound	**1**	**2**	**3**
Color	Wine-red	Wine-red	Blue-violet
Crystal system	Monoclinic	Monoclinic	Orthorhombic
Space group	$P2_1/n$	C_m	Pbnm
a/Å	7.394(2)	10.059(3)	18.206(8)
b/Å	16.893(2)	9.278(3)	13.501(5)
c/Å	6.544(2)	10.428(3)	7.552(2)
β/°	90.34(6)	117.12(4)	
D_m/g cm^{-3}	1.83	1.59	1.51
D_c/g cm^{-3}	1.84	1.59	1.53
Z	2	2	4
μ(Mo $K\alpha$)/cm^{-1}	66.9	13.4	15.2
Crystal size/mm^3	0.09×0.15×0.24	0.25×0.12×0.30	0.06×0.24×0.18
Scan type	ω	ω	ω-2θ
Scan speed/° s^{-1}	0.017	0.025	0.008
Scan range/°	1.0+0.2 tan θ	0.8+0.2 tan θ	0.9
$2\theta_{max}$/°	60	60	46
Background estimation/s^{-1} (at each side of scan range)	20	15	Half of scan time
No. of unique reflections with $F_o^2 > 3\sigma(F_o^2)$	1309	1210	776
R	0.042	0.033	0.053
R_w	0.047	0.044	0.057

preciable decay.

The crystal structures were solved by the Patterson-Fourier method. The positional and thermal parameters were refined by the block-diagonal-matrix least-squares method. The minimized functions were $\sum w(F_o-|F_c|)^2$, where $w=1/\sigma^2(F_o)$. The systematic extinctions for **2** were indicative of three possible space groups: C2/m, C2, and Cm. Refinements for nonhydrogen atoms on the assumptions of the former two gave no further improvements over $R=0.098$ and 0.118, but R was reduced to 0.051 by the refinement based on the Cm space group. The systematic extinctions for **3**, $h+l=2n+1$ for $h0l$ and $k=2n+1$ for $0kl$, indicated two possible space groups, Pbnm and $Pbn2_1$; the former was confirmed by the successful refinement of the structure.

For **1**—**3**, peaks due to all H atoms were found from the difference syntheses after anisotropic refinement for nonhydrogen atoms. The positions of these H atoms were almost entirely in agreement with those calculated on the assumption that the C–H and N–H distances are 1.00 Å. The H atoms were included in the least-squares calculations, but their parameters were not refined. The isotropic temperature factors assigned to the H atoms were as follows:

	1	**2**	**3**
B_H/Å^2	4.5	$B_P+1.0$	$B_P+1.0$,

where B_p is the isotropic temperature factor of the nonhydrogen atom to which the H atom is bonded (the temperature factor obtained at the final cycle of isotropic refinement was used as the B_p).

The atomic scattering factors, with corrections for dispersion effects for Cu^0, Br^-, Cl^-, and Cl, were taken from Ref. 4. The atomic coordinates are listed in Table 2. The corodinates of the H atoms, the anisotropic thermal parameters, and the F_o-F_c tables for the three compounds are preserved by the Chemical Society of Japan (Document No. 8120). All the computations were performed by a FACOM 230-60 computer at Osaka City University using programs in the UNICS.[5]

Table 2. Positional and thermal parameters ($\times 10^4$)

Atom	x	y	z	B_{eq}[a]/Å^2
(1) $[Cu(1,3\text{-chxn})_2]Br_2$				
Cu	0	0	0	1.85
Br	2867.8(9)	991.7(4)	−4520.8(10)	2.62
N(1)	1139(6)	1076(3)	508(7)	2.2
N′(1)	−1393(7)	500(3)	−2316(7)	2.5
C(1)	−1019(8)	1908(3)	−1485(9)	2.3
C(2)	−43(8)	1787(3)	564(9)	2.4
C(3)	−1426(9)	1727(4)	2279(10)	3.2
C(4)	−2828(9)	1081(4)	1893(10)	3.3
C′(2)	−2377(8)	1260(3)	−1931(9)	2.6
C′(3)	−3718(9)	1162(4)	−200(11)	3.4
(2) $[Cu(1,3\text{-chxn})_2](NO_3)_2$				
Cu	0	0	0	2.29
N(1)	342(4)	1574(4)	1456(3)	3.29
N(2)	−343(4)	1569(4)	−1433(3)	3.34
C(1)	834(7)	0	3536(6)	4.4
C(2)	1266(5)	1359(5)	3046(4)	3.8
C(3)	2936(5)	1331(6)	3414(5)	4.2
C(4)	3366(7)	0	2895(7)	4.1
C(5)	−791(8)	0	−3534(7)	4.7
C(6)	−1260(5)	1364(5)	−3018(4)	3.8
C(7)	−2893(5)	1353(6)	−3402(5)	4.1
C(8)	−3344(7)	0	−2870(7)	4.2
N(3)	1838(5)	5000	1100(6)	4.0
O(1)	1360(8)	5000	1954(9)	8.3
O(2)	2075(4)	3829(4)	629(4)	5.5
N(4)	−1818(6)	5000	−1046(6)	3.9
O(3)	−1350(8)	5000	−1971(8)	8.0
O(4)	−2065(4)	3833(4)	−600(4)	5.0
(3) $[CuCl(1,3\text{-chxn})_2]ClO_4$				
Cu	752.9(9)	139.3(1)	2500	2.69
Cl(1)	−137(2)	−216(3)	2500	3.70
N(1)	1389(4)	844(5)	4468(10)	3.5
N(2)	145(4)	1999(5)	4450(10)	3.8
C(1)	1961(8)	−394(10)	2500	5.8
C(2)	2043(5)	197(7)	4158(15)	4.7
C(3)	2741(5)	838(9)	4133(17)	6.4
C(4)	2780(8)	1462(13)	2500	5.9
C(5)	−894(8)	2476(10)	2500	5.4
C(6)	−484(6)	2713(7)	4146(14)	4.8
C(7)	−176(6)	3765(7)	4141(16)	5.3
C(8)	267(10)	3962(10)	2500	6.2
Cl(2)	1729(2)	3288(3)	7500	5.7
O(1)	1188(11)	2584(13)	7500	13.2
O(2)	2100(11)	3135(9)	5999(27)	23.3
O(3)	1479(10)	4225(11)	7500	12.9

a) Equivalent isotropic temperature factor (W.C. Hamilton, *Acta Crystallogr.*, **12**, 609 (1959)).

Results and Discussion

Figure 1 shows a part of the crystal structure for each of the three compounds. The interatomic distances and bond angles are given in Table 3. In **1** the Br and its symmetry-related ions lying above and below the coordination plane participate in hydrogen bonding with the axial H atoms of NH_2 groups, but not in coordination with the Cu atom ($Cu\cdots Br^-=4.015(1)$ Å). The NO_3^- ions around the complex ion in **2** are distant from the Cu atom and take part in the hydrogen bonds with NH_2 groups. The complex ions in **1** and **2** thus have the 4-coordinate square-planar coordination. The Cl^- ion in **3** is bonded to the Cu atom, thus completing a 5-coordinate square-pyramidal configuration. Although the IR spectrum of **3** at the 1000—1200 cm^{-1} region is indicative of the participation of the ClO_4^- ion in the coordination sphere,[3] the structure analysis

Table 3. Interatomic distances and bond angles

Bond lengths (l/Å)	**1**	**2**	**3**
Cu–N	2.029(5)	2.020(4)	2.025(8)
Cu–N′(1)	2.013(5)		
Cu–N(2)		2.000(4)	2.015(8)
Cu–Cl(1)			2.710(4)
N(1)–C(2)	1.487(8)	1.499(6)	1.49(1)
N′(1)–C′(2)	1.498(8)		
N(2)–C(6)		1.494(6)	1.51(1)
C(1)–C(2)	1.533(8)	1.497(9)	1.49(2)
C(1)–C′(2)	1.513(8)		
C(2)–C(3)	1.526(9)	1.543(7)	1.54(2)
C′(2)–C′(3)	1.518(10)		
C(3)–C(4)	1.525(10)	1.489(9)	1.50(2)
C′(3)–C(4)	1.523(10)		
C(5)–C(6)		1.532(9)	1.48(2)
C(6)–C(7)		1.503(8)	1.53(2)
C(7)–C(8)		1.522(9)	1.50(2)

Selected intramolecular nonbonded distances (l/Å) [a]

	1	2	3
Cu···H_{ax}[C(4)]	2.28	2.61	
Cu···H_{ax}[C(8)]		2.61	
N(1)···N′(1)	2.798(7)	2.921(6)	2.97(1)
N(2)···N′(2)		2.912(6)	2.95(1)
C(2)···C′(2)	2.531(9)	2.521(7)	2.50(2)
C(6)···C′(6)		2.532(7)	2.49(2)
Cl(1)···C(1)			3.83(2)
Cl(1)···C(5)			3.89(2)
C(4)···C(8)			5.75(3)

The H···X distances (l/Å) in N–H···X hydrogen bonds[b]

N–H···X		1	2	3
N(1)	Br	2.64		
N(1)	Br^{I}	2.51		
N′(1)	Br	2.68		
N′(1)	Br^{I}	2.57		
N(1)	O(2)		2.08	
N(1)	$O(2)^{II}$		2.16	
N(2)	O(4)		2.10	
N(2)	$O(4)^{III}$		2.15	
N(2)	O(1)			2.13
N(1)	$Cl(1)^{IV}$			2.39
N(2)	$Cl(1)^{IV}$			2.45

Bond angles (ϕ/°)

	1	2	3
N(1)–Cu–N′(1)	87.6(2)	92.6(2)	94.4(3)
N(2)–Cu–N′(2)		93.4(2)	93.9(3)
Cl(1)–Cu–N(1)			92.7(2)
Cl(1)–Cu–N(2)			89.8(2)
Cu–N(1)–C(2)	119.0(4)	122.8(3)	123.7(6)
Cu–N′(1)–C′(2)	118.7(4)		
Cu–N(2)–C(6)		122.9(3)	124.3(6)
N(1)–C(2)–C(1)	111.1(5)	111.1(5)	111.4(10)
N′(1)–C′(2)–C(1)	109.3(5)		
N(2)–C(6)–C(5)		111.1(5)	111.7(9)
N(1)–C(2)–C(3)	111.2(5)	109.5(4)	109.4(9)
N′(1)–C′(2)–C′(3)	110.6(5)		
N(2)–C(6)–C(7)		110.1(4)	108.3(8)
C(1)–C(2)–C(3)	109.8(5)	110.7(5)	111.9(11)
C(2)–C(3)–C(4)	112.5(5)	112.7(5)	111.5(11)
C(3)–C(4)–C′(3)	112.0(6)	112.1(8)	111.2(17)
C(4)–C′(3)–C′(2)	113.6(6)		
C′(3)–C′(2)–C(1)	111.7(5)		
C′(2)–C(1)–C(2)	112.4(5)	114.7(8)	114.0(16)
C′(6)–C(5)–C(6)		111.5(6)	113.8(14)
C(5)–C(6)–C(7)		112.1(5)	112.5(10)
C(6)–C(7)–C(8)		112.3(5)	111.4(11)
C(7)–C(8)–C′(7)		111.1(8)	111.2(17)

Interplanar angles (Ψ/°)[c]

		1	2	3
[Cu,N(1),N′(1)]	[N(1),C(2),C′(2),N′(1)]	139.2	158.8	183.6
[Cu,N(2),N′(2)]	[N(2),C(6),C′(6),N′(2)]		159.3	176.4

a) The subscript ax indicates the axial H atom with respect to the cyclohexane ring. b) Roman-numeral superscripts refer to the following equivalent positions: I $x, y, 1+z$; II $-1/2+x, 1/2-y, z$; III $1/2+x, 1/2-y, z$; IV $-x, -y, 1-z$. c) The atom disposition in each [N,C,C′,N′] plane is completely planar in **2** and **3**; it is also planar in **1** within the limits of experimental error.

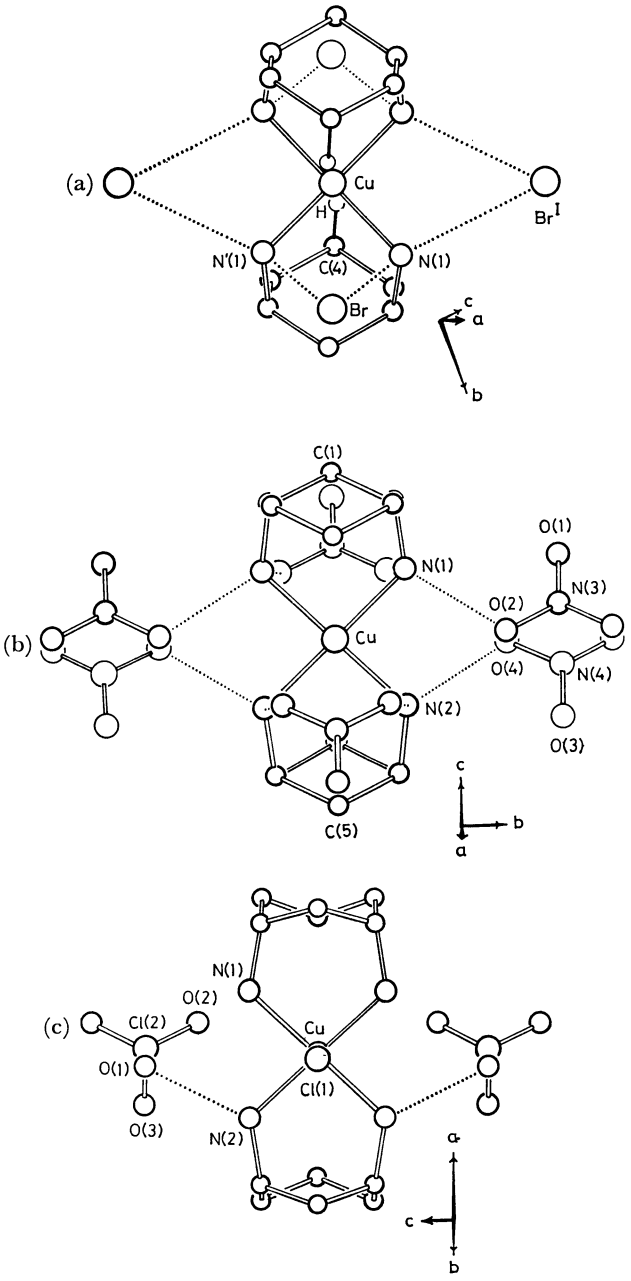

Fig. 1. Environments of the complex cations: (a) $[Cu(1,3\text{-chxn})_2]Br_2$, (b) $[Cu(1,3\text{-chxn})_2](NO_3)_2$, and (c) $[CuCl(1,3\text{-chxn})_2]ClO_4$. Each figure is the projection of a part of the crystal structure on the coordination plane defined by the 4 N atoms. The dotted lines indicate hydrogen bonds.

disclosed that one of the O atom [O(1)] of the ClO_4^- is linked to the H atom of the $N(2)H_2$ group. The ClO_4^- ion has no higher symmetry than the crystallographically imposed C_s symmetry, as was indicated by the examination of O–Cl–O bond angles,[6] and this low symmetry is responsible for the splitting of the IR band in that region.

The complex ions in **1** and **2** have strict C_i and C_s symmetries respectively, but both also have a virtual C_{2h} symmetry in which the two-fold axis bisects the N(1)–Cu–N(2) bond angle (for **1** N(2) stands for the

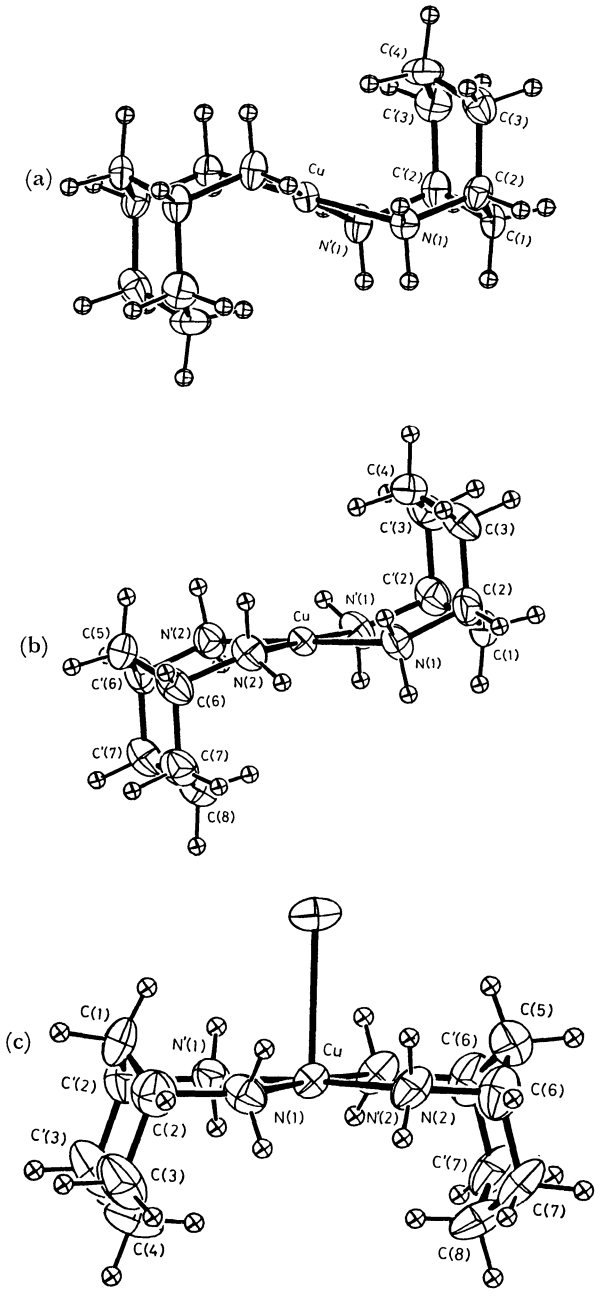

Fig. 2. Perspective views of (a) $[Cu(1,3\text{-chxn})_2]^{2+}$ in **1**, (b) $[Cu(1,3\text{-chxn})_2]^{2+}$ in **2**, and (c) $[CuCl(1,3\text{-chxn})_2]^{+}$ in **3**. Thermal ellipsoids are drawn at 50% probability level. Hydrogen atom is shown by a sphere with arbitrary radius.

equivalent of N'(1) at the $-x$, $-y$, $-z$ position). Above and below the coordination plane the most proximate atoms to the Cu are the axial H atom of $C(4)H_2$ and its symmetry-related (C_{2h}) atom [Fig. 2(a) and (b)], the Cu···H distances in **1** and **2** being 2.28 and 2.61 Å. The Cu···H vector in **1** intersects the CuN_4 plane at 79.1°, while those in 2 intersect it at 64.6° and 64.9°. The Cu–N bond lengths in **2** are slightly shorter than those in **1** and are comparable to the Cu–N (primary amine) length in the red form of bis(*N*,*N*-diethylethylenediamine)copper(II) perchlorate, in which the Cu atom has a square-planar coordination.[7] In general, however, the Cu–N distance in the planar complex is not appreciably different from those in 6-coordinate tetragonal and 5-coordinate square-pyramidal complexes.[7,8]

A perspective view of $[CuCl(1,3\text{-chxn})_2]^{+}$ is shown in Fig. 2(c). In addition to the crystallographically imposed mirror plane on which Cu, Cl(1), C(1), C(4), C(5), and C(8) lie, there is an approximate two-fold axis normal to the coordination plane; therefore, the virtual symmetry is regarded as C_{2v}. The Cu atom is displaced by 0.045 Å toward the apical atom, but this deviation is very small in comparison with that (0.33 Å) in chloro(2,7,12-trimethyl-3,7,11,17-tetraazabicyclo-[11.3.1]heptadeca-1(17),2,11,13,15-pentane)copper(II) nitrate dihydrate,[9] which involves the $CuClN_4$ coordination framework. Concomitantly, the Cu–Cl bond in **3** is much longer than that (2.50 Å) in the complex cited for comparison.[9] The $C(1)H_2$ and $C(5)H_2$ groups are in close contact with the Cl(1) atom and prevent the Cl atom from approaching Cu further. The visible spectrum of **3** in methanol ($\tilde{\nu}_{max}=18000$ cm^{-1}) is somewhat different from that in the solid state ($\tilde{\nu}_{max}=18400$ cm^{-1}), suggesting some change in the coordination sphere.

The 6-membered chelate rings in **1** and **2** are of the chair conformation, but those in **3** take the envelope conformation. The N–Cu–N′ coordination angles are greater than 90° in **2** and **3** and are comparable to that in $[Pd(1,3\text{-chxn})_2]Cl_2$.[1] The coordination angle in **1** is significantly smaller than those in **2** and **3**; it has a value of less than 90°. The [Cu,N,N′]–[N,C,C′,N′] interplanar angle in **1** is smallest (Table 3), but is comparable to that in $[Cu(tn)_2](NO_2)_2$ (132.5°)[10] (tn=1,3-propanediamine). In the chair ring, the increase in the interplanar angle gives rise to an enlargement of the coordination angle,[11] and the envelope ring has the largest angle (Table 3). The interplanar angle in the planar complex is thought to be susceptible to its surroundings. The different interplanar angles in **1** and **2** may result from the difference between the crystal packings.

As may be seen from Fig. 2, the 1,3-chxn ligand has the diaxial conformation, in which two C–NH_2 bonds are axial with respect to the cyclohexane ring. A CH_2 group at the 5-position ($C(4)H_2$ in **1**; $C(4)H_2$ and $C(8)H_2$ in **2** and **3**) is located close to the axial coordination site. A chelation of the diaxial 1,3-chxn thus situates the bulky cyclohexane moiety in the proximity of the metal ion, preventing the axial site from ligand access. This is in contrast to the case of the *trans*-1,2-isomer, whose cyclohexane ring is distant from the metal ion and has little influence on the adjacent coordination site.[12] The 1,3-chxn ligand, therefore, tends to give a coordinatively unsaturated complex and prefers a metal ion with tetragonal stereochemistry rather than one with an octahedral one. The steric hindrance of the cyclohexane moiety is responsible for the formation of the 4-coordinate planar Cu(II) complex unusual for the coordination geometry of $Cu(diamine)_2X_2$.

The reaction of $CuCl_2$ with twice as many mols of the 1,3-chxn in methanol yielded a violet compound,

$Cu(1,3\text{-chxn})_2Cl_2$; the violet bromide was also obtained by a similar reaction of $CuBr_2$ with the ligand in ethanol. The reflectance spectra of these compounds were indicative of a 6-coordinate tetragonal geometry.[3] The possible disposition of the 1,3-chxn ligands in this geometry is of the C_{2h} type (*vide supra*), since the C_{2v} disposition is unable to have a coordination number greater than 5 because of the steric interference of the cyclohexane rings. In the "6-coordinate C_{2h}" complex, however, the halide ligands are thought to be displaced greatly from the usual axial coordination sites to avoid the CH_2 groups at the 5-position of the 1,3-chxn. The distortion from tetragonal coordination geometry may be diminished if the cyclohexane ring assumes the boat conformation at the expense of the conformational energy. Unfortunately, no single crystals of the violet compounds have yet been obtained.

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6) The bond lengths and angles in the ClO_4^- ion are as follows: Cl–O(1)=1.37(2), Cl–O(2), Cl–O′(2), Cl–O(3)=1.34(2) Å, O(1)–Cl–O(2)=105(1)°, O(1)–Cl–O′(2)=105(1)°, O(1)–Cl–O(3)=114(1)°, O(2)–Cl–O′(2)=116(2)°, O(2)–Cl–O(3)=108(1)°, O′(2)–Cl–O(3)=108(1)°.

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