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The Structure of Nickel(II) and Copper(II) Complexes with 1,4,8,11-Tetraazacyclotetradecane in Aqueous Solution as Studied by the X-Ray Diffraction Method

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THE STRUCTURE OF NICKEL(II) AND COPPER(II) COMPLEXES WITH 1,4,8,11-TETRAAZACYCLOTETRADECANE IN AQUEOUS SOLUTION AS STUDIED BY THE X-RAY DIFFRACTION METHOD

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ABSTRACT

The structure of 1,4,8,11-tetraazacyclotetradecane (cyclam) complexes with nickel(II) and copper(II) ions in aqueous solution has been determined by the x-ray diffraction method at 25°C. The $[\text{Ni}(\text{cyclam})]^{2+}$ complex has a square-planar structure with four nitrogen atoms of the cyclam, and the Ni—N bond length has been determined to be 198 pm. Upon the addition of ammonia, the color of the nickel(II)-cyclam solution turns to deep purple and the $[\text{Ni}(\text{NH}_3)_2(\text{cyclam})]^{2+}$ complex is formed. The complex has a regular octahedral structure with an additional two NH_3 molecules along the axis vertical of the cyclam plane, and the Ni—N (NH_3 and cyclam) bond lengths are 209 pm. The copper(II)-cyclam complex in the aqueous solution is a distorted octahedron with two water

molecules along the elongated axis. The axial Cu—O and equatorial Cu—N bond lengths are 277 and 210 pm, respectively.

INTRODUCTION

1,4,8,11-Tetraazacyclotetradecane (cyclam) and its homologs draw much attention from analytical, inorganic, and bioinorganic chemists due to their unique coordination properties and the selectivity of metal ions in solution. Although the structure of free cyclam has not been determined by the x-ray crystallographic method, the structures of protonated cyclam [1] and nickel(II) [2–7], copper(II) [8, 9], and zinc(II)–cyclam [6, 10] complexes have been determined by single crystal x-ray diffraction methods. Most of the metal complexes, as well as the protonated cyclam, have the *trans*-III conformation with respect to the cyclam ring; some nickel(II)–cyclam complexes [6] are the *trans*-V and *cis*-V conformers.

Since no structural investigation of cyclam complexes has been carried out in solution by the x-ray diffraction method, probably because the structure of the complexes is too complicated to examine by scattering measurements, we were challenged to elucidate the structure of some metal–cyclam complexes in solution by using x-ray diffraction techniques. The metal–cyclam system is, as far as we know, the most complicated one so far examined by the solution x-ray diffraction method.

For this study we selected nickel(II) and copper(II) ions as the central metal ions of the complexes.

EXPERIMENTAL

Preparation of the Nickel(II)- and Copper(II)-Cyclam Complexes

The $[\text{Ni}(\text{cyclam})]\text{Cl}_2$ [11] and $[\text{Cu}(\text{cyclam})]\text{Cl}_2$ [12] complexes were prepared from nickel(II) chloride and copper(II) chloride, respectively, with cyclam according to the literature. The elemental analyses of the salts gave results which agreed very well with the calculated ones. Sample solutions were prepared by dissolving these salts in water. The $[\text{Ni}(\text{NH}_3)_2(\text{cyclam})]^{2+}$ complex was formed by the addition of 7 mol/dm³ aqueous ammonia solution to an $[\text{Ni}(\text{cyclam})]\text{Cl}_2$ aqueous solution. The color of the solution immediately changed from brownish yellow to deep purple, the color change indicating the structural change of the nickel(II)–cyclam complex from diamagnetic square-planar to paramagnetic

octahedral according to observations reported in the literature. Since the color changed so quickly, ammonia molecules must be coordinating to the axial position of the planar $[\text{Ni}(\text{cyclam})]^{2+}$ complex [13, 14].

The composition of the sample solutions is given in Table 1.

X-Ray Diffraction Measurement and the Treatment of Data

X-ray scattering measurements were carried out with a JEOL θ - θ type diffractometer (JCX-7D) using MoK_α radiation ($\lambda = 71.07$ pm) in a room thermostated at $25 \pm 1^\circ\text{C}$. The scanning range of the scattering angle (2θ) was 2 - 140°C , corresponding to the scattering vector $3 \times 10^{-3} < s, (\text{pm}^{-1}) < 0.16$ ($s = 4\pi \sin \theta/\lambda$). Different slit combinations and step angles were used, and a total amount of 80,000 counts was collected at each angle. Details of the diffractometer and the method of measurements have been described elsewhere [15].

Experimental intensities were corrected for background, absorption, polarization, double scattering, and Compton scattering, and were scaled to absolute units.

The structure function $i(s)$ was obtained by

$$i(s) = I(s) - \sum x_j f_j^2(s) \quad (1)$$

where $I(s)$ is the scaled observed intensities, f_j is the scattering factor of the j th atom corrected for anomalous dispersion, and x_j is the number of the j th atom in the stoichiometric volume containing one metal atom.

The radial distribution function was calculated by the Fourier transform of the $si(s)$ values by using

$$D(r) = 4\pi r^2 \rho_0 + (2r/\pi) \int_{s_{\min}}^{s_{\max}} si(s)M(s) \sin(rs) ds \quad (2)$$

Here, $M(s)$ is the modification function $[\sum x_j f_j(0)^2 / \sum x_j f_j(s)^2] \exp(-0.01s^2)$, and s_{\min} and s_{\max} denote, respectively, the lower and upper limits of the s values available in the experiments.

RESULTS

The structure functions in the form of $si(s)$ and the radial distribution curves $D(r)$ are shown in Figs. 1 and 2, respectively, for the three sample solutions. In the course of data analysis, the structural parameters of

TABLE 1. The Composition of Aqueous and Aqueous Ammoniacal [Ni(cyclam)]Cl₂ and Aqueous [Cu(cyclam)]Cl₂ Solutions at 25°C

	Composition, mol/dm ³		
	[Ni(cyclam)]Cl ₂ aqueous solution	[Ni(cyclam)]Cl ₂ aqueous ammoniacal solution	[Cu(cyclam)]Cl ₂ aqueous solution
Ni ²⁺	0.9503	0.9320	—
Cu ²⁺	—	—	0.9773
Cl ⁻	1.901	1.864	1.955
Cyclam	0.9503	0.9320	0.9773
H ₂ O	43.74	37.24	43.30
NH ₃	—	5.485	—
H	110.4	113.3	110.1
C	9.503	9.320	9.773
N	3.801	9.213	3.909
O	43.78	37.24	43.30
Density, g/cm ³	1.102	1.072	1.107
ν , 10 ⁶ cm ⁻¹ ^a	1747	1781	1699
Color: Crystal	Mauve	Mauve	Violet
Solution	Brownish yellow	Deep purple	Deep purple
λ_{max} , nm	455	340	315 (edge)
		455 (shoulder)	510
		522	
		800 (edge)	

^aStoichiometric volume containing one metal atom.

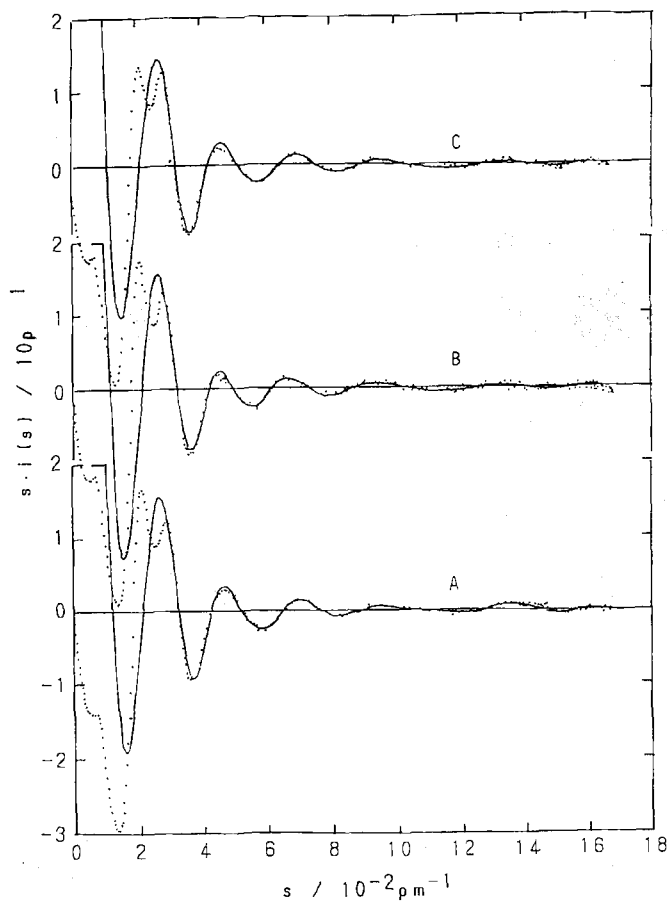


FIG. 1. Structure functions $si(s)$ for (A) $[\text{Ni}(\text{cyclam})]\text{Cl}_2$ aqueous solution, (B) $[\text{Ni}(\text{cyclam})]\text{Cl}_2$ aqueous ammoniacal solution, and (C) $[\text{Cu}(\text{cyclam})]\text{Cl}_2$ aqueous solution. Dotted lines indicate experimental values; solid lines are calculated values of the structural parameters finally obtained.

water and hydrated chloride ions were taken from the literature [16-18]. The intramolecular distances of an ammonia molecule were set to be $r_{\text{N-H}} = 100 \text{ pm}$, $r_{\text{H...H}} = 150 \text{ pm}$, $b_{\text{N-H}} = 100 \text{ pm}^2$, and $b_{\text{H...H}} = 300 \text{ pm}^2$, where b denotes the temperature factor of an atom pair. In this study the contribution of hydrogen atoms to the whole structural data is taken into

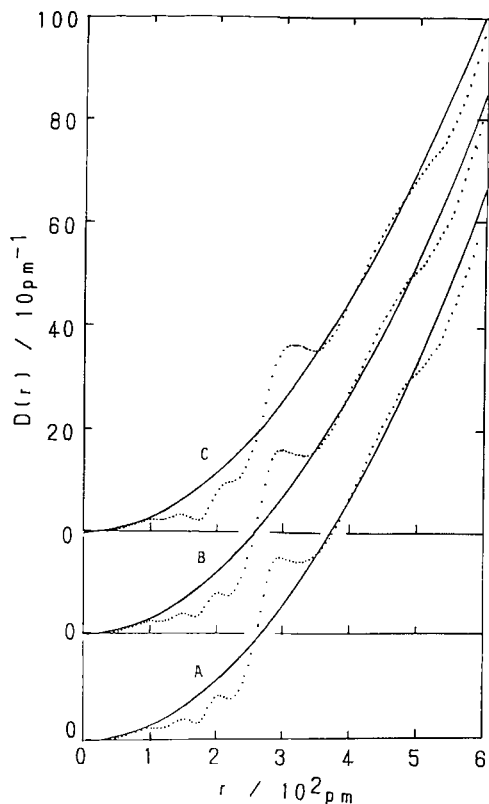


FIG. 2. Radial distribution functions $D(r)$ of (A) $[\text{Ni}(\text{cyclam})]\text{Cl}_2$ aqueous solution, (B) $[\text{Ni}(\text{cyclam})]\text{Cl}_2$ aqueous ammoniacal solution, and (C) $[\text{Cu}(\text{cyclam})]\text{Cl}_2$ aqueous solution. Dotted lines indicate the curves experimentally obtained; solid lines represent $4\pi r^2 \rho_0$.

account in spite of their small scattering ability, because interactions between hydrogen atoms and any other atoms in the cyclam complexes are not negligible when a least-squares refinement is applied to the structural functions.

The ring conformation of cyclam in the complexes is assumed to be *trans*-III throughout this work, because the conformation is most stable in the nickel(II) complexes and those with other ring conformations have

never been synthesized. The structure of $[\text{Ni}(\text{NH}_3)_2(\text{cyclam})]^{2+}$ is known to be in the *trans* form from kinetic investigations [13, 14]. The $[\text{Cu}(\text{cyclam})]^{2+}$ complexes so far synthesized all have *trans*-III conformations [8, 9]. After inserting structural parameters preliminarily obtained from the analysis of the radial distribution curves as the initial values, least-squares calculations were performed to refine the parameters so as to minimize the error-square sum

$$U = \sum_{s_{\min}}^{s_{\max}} s^2 (i_{\text{calc}}(s) - i_{\text{obs}}(s))^2 \quad (3)$$

over the range between $s_{\max} = 16.5 \times 10^{-2} \text{ pm}^{-1}$ and s_{\min} as the minimum value of s . Three different values of s_{\min} , 2.7–2.8, 5.0, and $7.0 \times 10^{-2} \text{ pm}^{-1}$, have been used in order to check the influence of long-range interactions which are not well taken into consideration in the course of the least-squares calculations. No significant change in the final results was observed by varying the s_{\min} value, and the structural parameters obtained from the set of different s_{\min} were averaged to obtain the final values.

The values obtained are summarized in Table 2. Comparisons between the observed and calculated structural functions are shown in Fig. 1. The agreement between observed and calculated curves for the three systems is satisfactory except in the angle range lower than $s = 0.03 \text{ pm}^{-1}$ where long-range atomic interactions, which are not taken into consideration in this study, become significant. A double peak appearing around $s = 0.02\text{--}0.03 \text{ pm}^{-1}$ is not reproduced by the structural parameters obtained. The double peak always appears in aqueous solutions, which arises from the complicated hydrogen-bonded water structure, and it is difficult to reproduce the peak in aqueous solutions containing complex solute species.

The radial distribution curves expressed in the form of $g(r) = D(r)/4\pi r^2 \rho_0$ are shown in Fig. 3. By subtracting the peak shapes estimated from the structural parameters finally obtained, we obtained a smooth background curve in each system, which indicates that the structural parameters thus obtained are reasonable.

The structures of the $[\text{Ni}(\text{cyclam})]^{2+}$, $[\text{Ni}(\text{NH}_3)_2(\text{cyclam})]^{2+}$, and $[\text{Cu}(\text{cyclam})]^{2+}$ complexes are graphically represented in Fig. 4 in which the distances between the central metal and bonding atoms are indicated.

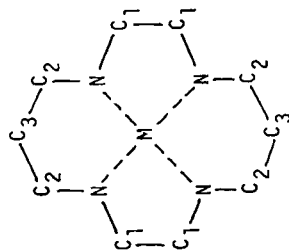
TABLE 2. Structural Parameters of the Coordination Sphere of the Central Metal Ions of the $[\text{Ni}(\text{cyclam})]^{2+}$, $[\text{Ni}(\text{NH}_3)_2(\text{cyclam})]^{2+}$, and $[\text{Cu}(\text{cyclam})(\text{H}_2\text{O})_2]^{2+}$ Complexes in Aqueous Solution at 25°C

Parameter	$[\text{Ni}(\text{cyclam})]^{2+}$	$[\text{Ni}(\text{NH}_3)_2(\text{cyclam})]^{2+}$	$[\text{Cu}(\text{cyclam})(\text{H}_2\text{O})_2]^{2+}$
M—N			
<i>r</i> , pm	197.6(6)	209.0(9)	201.3(6)
<i>b</i> , 10 pm ²	1.8(5)	5.5(9)	2.1(5)
<i>n</i>	4.1(2)	5.8(3)	4.2(2)
M—O			
<i>r</i> , pm	—	—	277(2)
<i>b</i> , 10 pm ²	—	—	6(3)
<i>n</i>	—	—	2.1(3)
M . . . C ₁ ^b			
<i>r</i> , pm	277(1)	282(1)	283(1)
<i>b</i> , 10 pm ²	3(1)	3(1)	4(1)
<i>n</i>	4 ^a	4 ^a	4 ^a
M . . . C ₂ ^b			
<i>r</i> , pm	295(1)	303(2)	301(2)
<i>b</i> , 10 pm ²	6(2)	4(2)	5(1)
<i>n</i>	4 ^a	4 ^a	4 ^a

M . . . C ₃ ^b	<i>r</i> , pm	329(3)	339(6)	335(5)
	<i>b</i> , 10 pm ²	5(3)	6(3)	9(6)
	<i>n</i>	2 ^a	2 ^a	2 ^a

^aFixed during the least-squares calculation.

^bNumbering of carbon atoms:



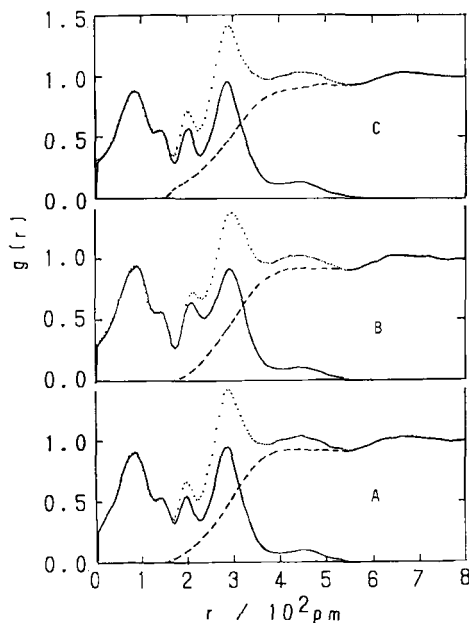


FIG. 3. Radial distribution curves $g(r) = D(r)/4\pi r^2 \rho_0$. (A) $[\text{Ni}(\text{cyclam})]\text{Cl}_2$ aqueous solution, (B) $[\text{Ni}(\text{cyclam})]\text{Cl}_2$ aqueous ammoniacal solution, and (C) $[\text{Ni}(\text{cyclam})]\text{Cl}_2$ aqueous solution. Dotted lines indicate the curves experimentally obtained; solid lines show the peak shapes calculated from the structural parameters finally obtained. The broken lines are the residual curves after subtraction of the theoretical peak shapes from the experimental curves.

DISCUSSION

Ni—N Bond Length

The Ni—N bond lengths in the cyclam complex with various counterions in solution and in crystal are listed in Table 3. The square-planar $[\text{Ni}(\text{cyclam})]^{2+}$ in solution determined in this work has Ni—N bonds shorter than those in crystal except for the perchlorate [7]. No data for the Ni—N bond length have been reported for square-planar nickel(II) complexes coordinated with nitrogen atoms in solution. The Ni—N bond length of square-planar complexes in crystal has been reported to be about 190 pm (see Table 3) which is shorter than the Ni—N bond in the

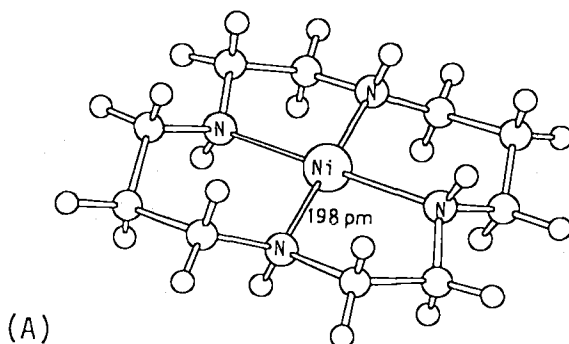
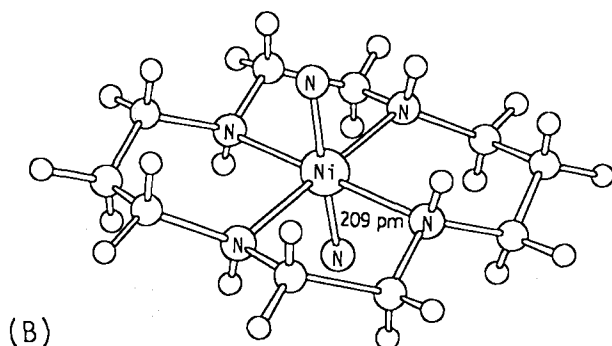
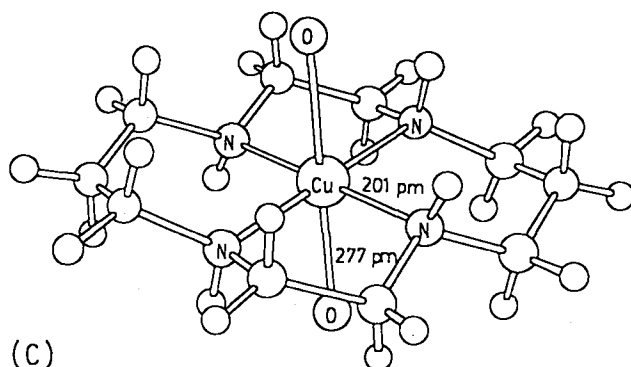


FIG. 4. The structures of (A) [Ni(cyclam)]²⁺, (B) [Ni(NH₃)₂(cyclam)]²⁺, and (C) [Cu(cyclam)(H₂O)₂]²⁺ complexes in solution.

TABLE 3. The Ni—N and Cu—N Bond Lengths in Nitrogen-Coordinated Complexes of Ni(II) and Cu(II) Ions

Metal Ligand	Counterion	r_{M-N} , pm	Form	Ref.
Ni ²⁺				
cyclam	Cl ⁻	197.6	sq, ^a sol ^b	This work
cyclam, NH ₃	Cl ⁻	209.0	oh, ^c sol ^b	This work
cyclam	I ⁻	195	sq, ^a cry ^d	3
cyclam	ClO ₄ ⁻	197	sq, ^a cry ^d	7
cyclam	ZnCl ₂ ²⁻	190, 194	sq, ^a cry ^d	6
cyclam, H ₂ O	Cl ⁻	209–211	oh, ^c cry ^d	6
cyclam, Cl ⁻	Cl ⁻	207	oh, ^c cry ^d	4
cyclam, NCS ⁻	SCN ⁻	{ 206–208(plane) 208–213(axis)	oh, ^c cry ^d	4
cyclam, NO ₃ ⁻	NO ₃ ⁻	205–206	oh, ^c cry ^d	5
en, ^c H ₂ O	NO ₃ ⁻	210	oh, ^c sol ^b	19
en ^c	NO ₃ ⁻	220	oh, ^c sol ^b	19
gly, ^f H ₂ O	NO ₃ ⁻	209	oh, ^c sol ^b	20
gly ^f	Na ⁺	214	oh, ^c sol ^b	20
2,5-dmpz, ^g Br ⁻	Br ⁻	190	sq, ^a cry ^d	21
meso-stdm ^h	Cl ₂ CHCOO ⁻	189	sq, ^a cry ^d	22
glox ⁱ	—	186.8, 188.0	sq, ^a cry ^d	23
3,4-dmpy ^j	ClO ₄ ⁻	189.7	sq, ^a cry ^d	24
N-i-pro-3-esam ^k	—	196.7, 198.0	sq, ^a cry ^d	25

Cu ²⁺				This work
cyclam, H ₂ O	Cl ⁻	201.3	dis-oh, ^l sol ^b	8
cyclam, ClO ₄ ⁻	ClO ₄ ⁻	202	dis-oh, ^l cry ^d	9
cyclam, SC ₆ F ₅ ⁻	C ₆ F ₅ S ⁻	201	dis-oh, ^l cry ^d	26
NH ₃ , H ₂ O	Cl ⁻	193	dis-oh, ^l sol ^b	26
NH ₃ , H ₂ O	Cl ⁻	193, 230	dis-oh, ^l sol ^b	27
en, ^c H ₂ O	NO ₃ ⁻	193	dis-oh, ^l sol ^b	27
en ^c	NO ₃ ⁻	192, 222	dis-oh, ^l sol ^b	28
gly, ^f H ₂ O	NO ₃ ⁻	198	dis-oh, ^l sol ^b	28
gly ^f	Na ⁺	202	oh, ^c sol ^b	28

^aSquare-planar.^bSolution.^cOctahedral.^dCrystal.^eEthylenediamine.^fGlycinate.^g2,5-Dimethylpyrazine.^hmeso-Stilbenediamine.ⁱGlyoximate.^j3,4-Dimethylpyridine.^kN-Isopropyl-3-ethylsalicylaldiminate.^lDistorted octahedral.

cyclam complex. An exception is seen in the bis-(*N*-isopropyl-3-ethylsalicylaldiminato)nickel(II) complex in crystal which has Ni—N bonds of 196.7 and 198 pm [26]; these bond lengths are close to those in the nickel(II)–cyclam complex in solution.

Although the reason why the Ni—N bond in the bis-(*N*-isopropyl-3-ethylsalicylaldiminato)nickel(II) complex is longer than that in other complexes in crystal is not clear, it may be due to a less flexible cyclam ring compared to monodentate and multidentate chain ligands. Effects due to packing of the complex ions in crystal may also account for different Ni—N bond lengths in solution and in solid.

The Ni—N bond in the $[\text{Ni}(\text{cyclam})]^{2+}$ complex is shorter than that in the $[\text{Ni}(\text{NH}_3)_2(\text{cyclam})]^{2+}$ complex which has a larger coordination number than the former. The Ni—N bond length in the latter is close to that in octahedral nickel(II) complexes with cyclam [4–6] and other nitrogen-coordinating ligands (see Table 3).

Cu—N Bond Length

The Cu—N bond length determined for the $[\text{Cu}(\text{cyclam})(\text{H}_2\text{O})_2]^{2+}$ complex in solution is practically the same as those found in the cyclam complex in the crystal [8, 9]. The Cu—N bond length in square-planar complexes of N-coordinated copper(II) complexes in solution is much shorter than that in the cyclam complex (see Table 3). This result again implicates the ring structure of the cyclam.

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