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X-Ray Crystal Structures of Octahedral Diaquabis(*N*,*N*-dialkylethylenediamine)nickel(II) Complexes Possessing Elongated Nickel(II)-Nitrogen Bonds along Axial Direction

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The structures of two diaquabis(*N*,*N*-dialkylethylenediamine)nickel(II) chlorides ($[\mathrm{Ni(H_2O)_2(diamine)_2}]\mathrm{Cl_2}\cdot n\mathrm{H_2O}$) were determined by X-ray crystallographic studies, where diamine is *N*,*N*-dimethylethylenediamine(*NN*-dmen) or *N*,*N*-diethylethylenediamine (*NN*-deen). Both complexes are trans and crystallize in the monoclinic space group $P2_1/n$. The unit cell parameters of the *NN*-dmen complex, $\mathrm{NiCl_2C_8N_4O_4H_{32}}$, are a=7.531(1), b=13.092(1), c=9.591(1) Å, β=107.76(1)°, and Z=2, and those of the *NN*-deen complex, $\mathrm{NiCl_2C_{12}N_4O_2H_{36}}$, are a=9.154(1), b=8.692(1), c=12.395(2) Å, β=104.46(1)°, and Z=2. In *trans*-$[\mathrm{Ni(H_2O)_2}$(*NN*-dmen)$_2]\mathrm{Cl_2}\cdot 2\mathrm{H_2O}$ and *trans*-$[\mathrm{Ni(H_2O)_2}$(*NN*-deen)$_2]\mathrm{Cl_2}$, the Ni–NMe$_2$ and Ni–NEt$_2$ bond distances (2.183 and 2.271 Å) are much longer than the Ni–NH$_2$ distances (2.078 and 2.064 Å), forming tetragonally distorted octahedrons with four close in-plane neighbors($\mathrm{N_2O_2}$) and two remote axial ones($\mathrm{N_2}$). It is apparent that this distortion originates from the steric requirement of N-substituted groups. Such a distortion significantly affects the electronic spectra of these complexes.

We have studied on the coordination structures of various octahedral diaquabis(N- or C-substituted ethylenediamine)nickel(II) complexes and the products of their thermal reactions, and also on the effects of N- or C-substituent group(s) upon their structural changes during thermal treatments.[1–5] In general, the diaqua complexes could readily be characterized to be trans from the feature of their electronic spectra in near IR region, and they changed to the corresponding dianiono species upon thermal deaquation-anation, retaining trans configuration as shown below.[1,2]

$$trans\text{-}[\mathrm{Ni(H_2O)_2(diamine)_2}]\mathrm{X_2} \xrightarrow{-2\mathrm{H_2O}} trans\text{-}[\mathrm{NiX_2(diamine)_2}]$$

The diaqua complexes with *N*,*N*-dialkylated ethylenediamines, however, showed a somewhat obscure splitting or a red shift of the two bands in near IR region, compared with a typical trans spectrum. In addition, some of these complexes peculiarly produced cis dianiono complexes by thermal treatment.[6] Accordingly, to understand the unusual spectra and thermal behaviors of these asymmetric diamine complexes, the structures of the octahedral diaqua complexes with *NN*-dmen (*N*,*N*-dimethylethylenediamine) and *NN*-deen (*N*,*N*-diethylethylenediamine) were determined by X-ray crystallographic studies in the present study.

Experimental

The complexes, *trans*-$[\mathrm{Ni(H_2O)_2}$(*NN*-dmen)$_2]\mathrm{Cl_2}\cdot 2\mathrm{H_2O}$ (**A**) and *trans*-$[\mathrm{Ni(H_2O)_2}$(*NN*-deen)$_2]\mathrm{Cl_2}$ (**B**) were prepared by the known methods.[7,8] The single crystals of the former grew as violet blocks upon slow evaporation from the ethanolic solution containing stoichiometric amounts of the diamine and nickel(II) chloride hexahydrate, and those of the latter were obtained as blue blocks by recrystallization from methanol.

The unit-cell parameters and intensities were measured on a Rigaku AFC-5R automated four-circle diffractometer using graphite-monochromatized Mo $K\alpha$ (λ=0.71073 Å) radiation at room temperature. The 2θ–ω scan mode at a rate of 6° min^{-1} was employed to record the intensities. The intensity data were corrected for Lorentz-polarization and absorption effects. Both structures were solved by the heavy atom method and refined by the block-diagonal least-squares method. Calculations were performed with the TEXSAN Structure Analysis software package on microVax II and with the UNICS III programs[9,10] on a FACOM 760/10 computer at the Kanazawa University Information Processing Center. Tables giving the positional parameters for all atoms, the anisotropic thermal parameters, the observed and calculated

Table 1. Crystal Data of *trans*-$[\mathrm{Ni(H_2O)_2}$(*NN*-dmen)$_2]\mathrm{Cl_2}\cdot 2\mathrm{H_2O}$ (**A**) and *trans*-$[\mathrm{Ni(H_2O)_2}$(*NN*-deen)$_2]\mathrm{Cl_2}$ (**B**)

Complex	**A**	**B**
Formula	$\mathrm{NiCl_2C_8N_4O_4H_{32}}$	$\mathrm{NiCl_2C_{12}N_4O_2H_{36}}$
Fw	377.97	398.05
Crystal system	Monoclinic	Monoclinic
Space group	$P2_1/n$	$P2_1/n$
a/Å	7.531(1)	9.154(1)
b/Å	13.092(1)	8.692(1)
c/Å	9.591(1)	12.395(2)
β/deg	107.76(1)	104.46(1)
V/Å^3	900.1	955.0
Z	2	2
D_c/g cm^{-3}	1.395	1.382
D_m/g cm^{-3}	1.390	1.381
No. of data	2334	2503
No. unique data[a)]	1757	1557
No. parameters	223	173
R	0.0275	0.0327
R_w	0.0257[b)]	0.0254[c)]
μ/cm^{-1}	13.84	12.99
2θ limits/deg	3—55	3—55

a) $I_o > 3\sigma(I_o)$. b) $w=1/\sigma(F)$. c) $w=1/(\sigma(F))^2$.

structure factors, the intramolecular bond distances, the intramolecular bond angles, the interatomic distances in crystal, the intramolecular torsion angles, the least squares planes and deviations therefrom, and Figures showing stereoviews of full cell are deposited as Document No. 8949 at the Office of the Editor of Bull. Chem. Soc. Jpn.

The electronic spectra in solid phase were measured by the diffuse reflectance method with a Hitachi U-3400 spectrophotometer.

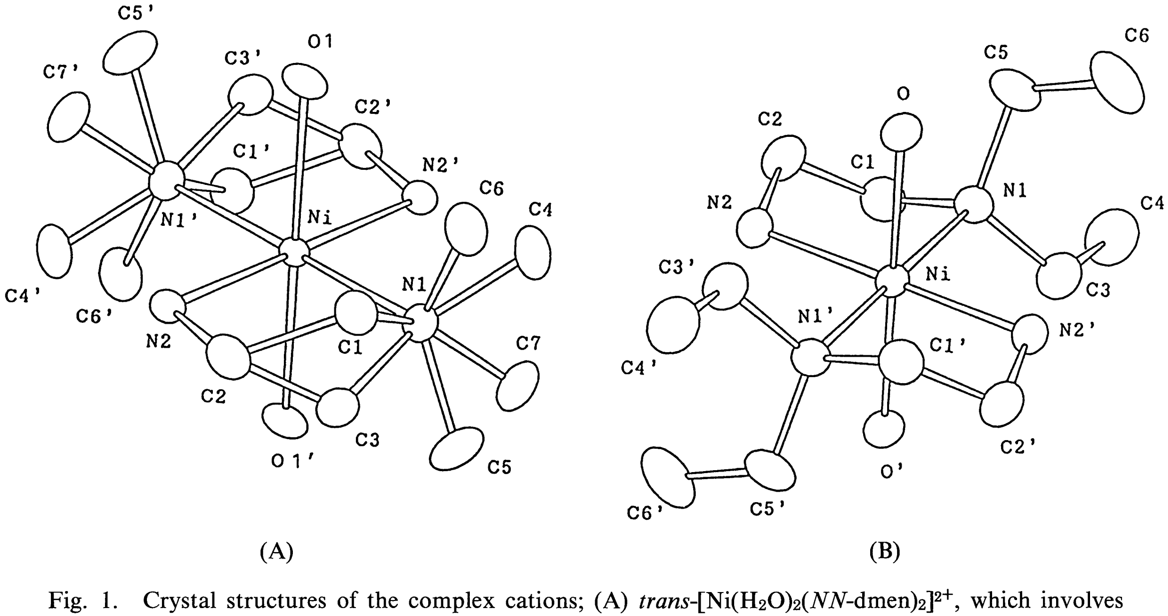
Results and Discussion

Crystal data of *trans*-[Ni(H_2O)$_2$(*NN*-dmen)$_2$]Cl_2·2H_2O (**A**) and *trans*-[Ni(H_2O)$_2$(*NN*-deen)$_2$]Cl_2 (**B**) are given in Table 1. The final atomic coordinates and thermal parameters of non-hydrogen atoms with their estimated deviations are given in Table 2. Figure 1 shows the perspective views of the two complex cations.

Table 2. Atomic Coordinates ($\times 10^4$) and Thermal Parameters of Non-Hydrogen Atoms with Their Estimated Standard Deviations in Parentheses

	Atom	*x*	*y*	*z*	$B/\text{Å}^2$
Complex **A**	Ni	0(0)	0(0)	0(0)	2.21(0)
	Cl	4248(1)	2057(1)	−553(1)	4.33(1)
	O(1)	487(2)	1586(1)	38(2)	4.13(5)
	O(2)[a]	3289(2)	2133(1)	5984(2)	4.92(4)
	N(1)	1690(2)	−97(2)	2295(2)	3.32(9)
	N(2)	−2150(2)	231(1)	905(2)	2.98(12)
	C(1)	645(4)	503(3)	3055(3)	4.08(31)
	C(2)	−1420(3)	241(2)	2516(3)	4.12(0)
	C(3)	168(13)	−354(7)	3020(9)	3.88(0)
	C(4)	3588(4)	354(3)	2583(4)	5.40(0)
	C(5)	1979(6)	−1151(3)	2893(4)	6.00(0)
	C(6)	2557(14)	893(9)	2880(10)	5.04(0)
	C(7)	3094(14)	−870(9)	2565(11)	5.08(0)
Complex **B**	Ni	0(0)	0(0)	0(0)	1.69(1)
	Cl	−4051(1)	2380(1)	−1915(1)	2.93(1)
	O	1355(2)	−141(3)	1629(2)	2.61(5)
	N(1)	1734(3)	1571(3)	−459(2)	2.13(8)
	N(2)	1262(3)	−1702(3)	−499(2)	2.31(9)
	C(1)	2970(3)	470(4)	−438(3)	2.72(8)
	C(2)	2380(4)	−1005(4)	−1024(3)	3.01(0)
	C(3)	2281(4)	2786(4)	399(3)	3.20(0)
	C(4)	3558(4)	3803(5)	232(4)	4.23(0)
	C(5)	1283(4)	2272(4)	−1595(3)	3.18(0)
	C(6)	163(5)	3570(5)	−1712(4)	4.80(0)

a) Lattice water.



(A) (B)

Fig. 1. Crystal structures of the complex cations; (A) *trans*-[Ni(H_2O)$_2$(*NN*-dmen)$_2$]$^{2+}$, which involves disorder, and (B) *trans*-[Ni(H_2O)$_2$(*NN*-deen)$_2$]$^{2+}$.

The nickel(II) ion lies at a center of symmetry. Two coordinated waters of the complexes occupy trans positions of the N_4O_2 octahedrons and the two alkylated nitrogen atoms (N(1)) occupy axial sites apart from each other to minimize their mutual steric hindrance. Complex **A** shows a disorder of gauche and eclipsed five-membered chelate rings: C(4) and C(5) methyl carbon atoms belong to C(1) methylene one of gauche form. The relative occupancy of the dislocated atoms C(1) (C(4), and C(5)) and C(3) (C(6) and C(7)) is 0.75 : 0.25:[11] namely gauche form is predominant in the crystal. All chloride ions (not shown) fall within a distance of hydrogen bonding with adjacent amino group and either coordinated water or lattice water.[12]

The selected bond distances and angles are listed in Tables 3 and 4 for the *NN*-dmen and *NN*-deen complexes, respectively. It can be seen that the common striking characteristic in these structures is the elongated nickel(II)-nitrogen(N(1)) bonds along axial direction: the Ni–N(1) bond distances (2.183(2) Å for the *NN*-dmen and 2.271(3) Å for the *NN*-deen complexes) are much longer than the Ni–N(2) ones (2.078(2) Å for the former and 2.064(3) Å for the latter), so that tetragonally distorted octahedrons with four in-plane neighbors (N(2)N(2′)OO′ or N(2)N(2′)O(1)O(1′)) and two remote axial ones (N(1)N(1′)) are formed rather than familiar N_4(plane)O_2(axial) octahedrons.[13,14] Such distortion is noticeable in the *NN*-deen complex. The relevant bond distances in analogous nickel(II) complexes are collected in Table 5 along with our results. Similar elongated Ni–NR_2 bonds are observed in complexes **1**—**3**, which also contain either *NN*-dmen or *NN*-deen. It is additionally found that the distances of Ni–N bonds increase in the order of Ni–NH_2<Ni–NHR<Ni–NR_2.

Table 3. Selected Interatomic Distances and Angles of *trans*-[Ni(H$_2$O)$_2$(*NN*-dmen)$_2$]Cl$_2$·2H$_2$O

Distances/Å		Angles/deg	
Ni-O(1)	2.108(2)	O(1)-Ni-N(1)	89.7(1)
Ni-N(1)	2.183(2)	O(1)-Ni-N(2)	90.2(1)
Ni-N(2)	2.078(2)	N(1)-Ni-N(2)	82.9(1)
N(1)-C(1)	1.455(4)	Ni-N(1)-C(1)	103.6(1)
N(1)-C(3)	1.547(11)	Ni-N(1)-C(3)	100.5(3)
N(1)-C(4)	1.492(4)	Ni-N(1)-C(4)	113.2(2)
N(1)-C(5)	1.486(4)	Ni-N(1)-C(5)	114.5(2)
N(1)-C(6)	1.484(11)	Ni-N(1)-C(6)	112.6(4)
N(1)-C(7)	1.429(11)	Ni-N(1)-C(7)	113.3(4)
N(2)-C(2)	1.473(3)	Ni-N(2)-C(2)	110.5(1)
C(1)-C(2)	1.520(4)	N(1)-C(1)-C(2)	111.2(2)
C(2)-C(3)	1.385(10)	N(1)-C(3)-C(2)	113.5(6)
		N(2)-C(2)-C(1)	112.0(2)
		N(2)-C(2)-C(3)	111.5(4)

Table 4. Selected Interatomic Distances and Angles of *trans*-[Ni(H$_2$O)$_2$(*NN*-deen)$_2$]Cl$_2$

Distances/Å		Angles/deg	
Ni-O	2.093(2)	O-Ni-N(1)	89.7(1)
Ni-N(1)	2.271(3)	O-Ni-N(2)	90.4(1)
Ni-N(2)	2.064(3)	N(1)-Ni-N(2)	83.0(1)
N(1)-C(1)	1.478(4)	Ni-N(1)-C(1)	100.7(2)
N(1)-C(3)	1.493(4)	Ni-N(1)-C(3)	112.2(2)
N(1)-C(5)	1.495(4)	Ni-N(1)-C(5)	115.8(2)
N(2)-C(2)	1.473(5)	Ni-N(2)-C(2)	109.9(2)
C(1)-C(2)	1.505(5)	N(1)-C(1)-C(2)	111.2(2)
C(3)-C(4)	1.520(6)	N(1)-C(3)-C(4)	116.5(3)
C(5)-C(6)	1.507(6)	N(1)-C(5)-C(6)	114.6(3)
		N(2)-C(2)-C(1)	110.0(3)

Table 5. Summary of Relevant Bond Distances

Complex[a]	Bond distance/Å		Reference
t-[Ni(H$_2$O)$_2$(*NN*-dmen)$_2$]Cl$_2$·2H$_2$O (**A**)	Ni-NH$_2$=2.08 Ni-OH$_2$=2.11	Ni-NMe$_2$=2.18	This work
t-[Ni(ONO)$_2$(*NN*-dmen)$_2$] (**1**)	Ni-NH$_2$=2.08 Ni-ONO=2.11	Ni-NMe$_2$=2.22	16
c-[Ni(NO$_2$)(H$_2$O)(*NN*-dmen)$_2$]ClO$_4$ (**2**)	Ni-NH$_2$=2.09—2.10 Ni-OH$_2$=2.07	Ni-NMe$_2$=2.19—2.20 Ni-NO$_2$=2.12	17
t-[Ni(H$_2$O)$_2$(*NN*-deen)$_2$]Cl$_2$ (**B**)	Ni-NH$_2$=2.06 Ni-OH$_2$=2.09	Ni-NEt$_2$=2.27	This work
t-[Ni(NCS)$_2$(*NN*-deen)$_2$] (**3**)	Ni-NH$_2$=2.09 Ni-NCS=2.08	Ni-NEt$_2$=2.30—2.33	18
t-[Ni(NO$_2$)$_2$(*NN′*-dmen)$_2$]·H$_2$O (**4**)	Ni-NHMe=2.11—2.12 Ni-NO$_2$=2.13		16
c-[Ni(ONO)(*NN′*-deen)$_2$]BF$_4$ (**5**)	Ni-NHEt=2.10—2.16 Ni-ONO=2.10—2.12		19
t-[Ni(NCS)$_2$(en)$_2$] (**6**)	Ni-NH$_2$=2.09—2.11 Ni-NCS=2.15		20
t-[Ni(NO$_2$)$_2$(en)$_2$] (**7**)	Ni-NH$_2$=2.09—2.10 Ni-NO$_2$=2.13		21
t-[Ni(H$_2$O)$_2$(*m*-stien)$_2$](Cl$_2$CHO$_2$)$_2$·2H$_2$O (**8**)	Ni-NH$_2$=2.03—2.05 Ni-OH$_2$=2.12		13
t-[Ni(H$_2$O)$_2$(*dl*-chxn)$_2$]Cl$_2$ (**9**)	Ni-NH$_2$=2.10 Ni-OH$_2$=2.13		14

a) *NN′*-dmen=*N,N′*-dimethylethylenediamine; *NN′*-deen=*N,N′*-diethylethylenediamine; *m*-stien=*meso*-1,2-diphenyl-1,2-ethanediamine; *dl*-chxn=*dl*-1,2-cyclohexanediamine.

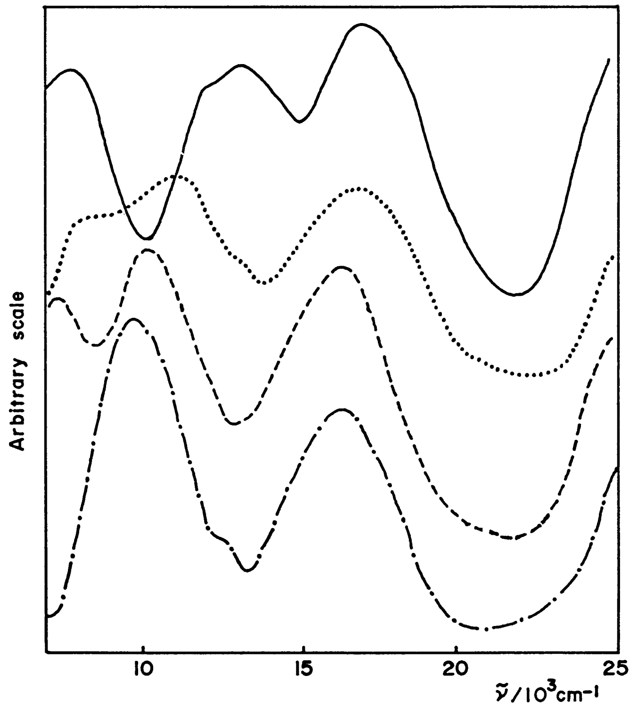


Fig. 2. Electronic spectra of *trans*-$[Ni(H_2O)_2(diamine)_2]Cl_2 \cdot nH_2O$, where diamine is *NN'*-dmen (——), *NN*-dmen (······), or *NN*-deen (– – – –), and of *cis*-$[Ni(H_2O)_2(NN\text{-dmen})_2]I_2$ (— — —). (*NN'*-dmen is *N,N'*-dimethylethylenediamine.)

It is thus apparent that these tetragonal distortions of complexes **A** and **B** originate from the steric requirement of N-substituted groups.

The electronic spectra of the two complexs are shown in Fig. 2, together with those of *trans*-$[Ni(H_2O)_2(NN'\text{-dmen})_2]Cl_2$ and *cis*-$[Ni(H_2O)_2(NN\text{-dmen})_2]I_2$ which are typical of trans and cis configurations, respectively.[15] Compared with the typical trans spectrum, it can be seen that complex **A** shows a somewhat obscure splitting of the two bands in near IR region, and complex **B** shows a red shift of all the bands in their spectra. These spectra can now be interpreted in terms of the above structural results: in comparison with the symmetric diamine complexes, it is anticipated that (1) the difference between ligand field strength along O–O axis and that in N_4 rhombus becomes small because of the elongation of the Ni–NMe_2 (or –NEt_2) bond length, and (2) the overall ligand field strength becomes weak (cf. the data of complexes **4** and **5** in Table 5). The effects of (1) and (2) should be responsible for the somewhat obscure splitting and the red shift of the bands in their spectra, respectively.

Both *trans*-diaqua complexes were transformed into the *cis*-dichloro complexes upon thermal deaquation-anation.[6] This is contrary to the complexes with the symmetric diamines which show simple deaquation-anation retaining a trans configuration. The differences in their reactivities seem to be related to the finding that the bonds between nickel(II) and the alkylated nitrogen atom are much weaker than the other coordination bonds in the asymmetric diamine complexes: it appears reasonable to assume that, in the case of the complexes with the asymmetric diamines, the rupture of a Ni–NR_2 bond precedes the liberation of the coordinated water, providing a driving force for these peculiar reactions.

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