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Articles

Isolation and Vis-Absorption Spectrum of *trans*-[Ni(OH_2)$_2$(cyclam)]Cl_2·4H_2O

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The *trans*-diaqua cyclam−Ni(II) complex was isolated as *trans*-[Ni(OH_2)$_2$(cyclam)]Cl_2·4H_2O, which was confirmed by X-ray crystallography ([Ni(OH_2)$_2$($C_{10}H_{24}N_4$)]Cl_2·4H_2O: triclinic space group $P\bar{1}$ with $a = 7.894(3)$ Å, $b = 7.981(3)$ Å, $c = 9.261(5)$ Å, $\alpha = 65.41(3)°$, $\beta = 79.97(4)°$, $\gamma = 80.76(3)°$, $Z = 1$). Its single-crystal vis-absorption spectrum showed three absorption bands (λ 333 nm (ϵ 3.7), 507 (3.1), 667 (2.4)) in the range 300−800 nm.

Introduction

In aqueous solutions the Ni(II) complex with 1,4,8,11-tetraazacyclotetradecane (cyclam) exists in equilibrium as a mixture of the square-planar low-spin and *trans*-diaqua octahedral high-spin species according to eq 1.[1]

$$[\mathrm{Ni(cyclam)}]^{2+} + 2\mathrm{H_2O} \rightleftharpoons trans\text{-}[\mathrm{Ni(OH_2)_2(cyclam)}]^{2+} \quad (1)$$

The equilibrium can be affected by various factors: addition of salts, temperature, solvent, etc.[1] The addition of $NaClO_4$ displaces the equilibrium to the sqaure-planar side to enable measurements of the vis-absorption spectrum of 100% [Ni(cyclam)]$^{2+}$ even in aqueous solution.[1] The square-planar species has actually been isolated as [Ni(cyclam)](ClO_4)$_2$.[2] On the other hand, it is hard to shift the equilibrium (1) completely to the octahedral side. No electrolytes which shift the equilibrium to the right side have been found so far, and simply decreasing the temperature is insufficient to accomplish the complete shift. Accordingly, the diaqua octahedral form, *trans*-[Ni(OH_2)$_2$(cyclam)]$^{2+}$, has not been isolated and its exact vis-absorption spectrum has not been measured yet, although there have been discussions on its structure[3] and spectrophotometrical evaluation[1] of the equilibrium constant for (1).

In the present study, we have isolated the *trans*-diaqua form as *trans*-[Ni(OH_2)$_2$(cyclam)]Cl_2·4H_2O, **1**, for the first time and revealed its X-ray structure and single-crystal vis-absorption spectrum.

Table 1. Crystallographic Data for *trans*-[Ni(OH_2)$_2$(cyclam)]Cl_2·4H_2O

chem formula	[Ni(OH_2)$_2$($C_{10}H_{24}N_4$)]Cl_2·4H_2O
fw	438.02
crystal system	triclinic
space group	$P\bar{1}$
a, Å	7.894(3)
b, Å	7.981(3)
c, Å	9.261(5)
α, deg	65.41(3)
β, deg	79.97(4)
γ, deg	80.76(3)
V, Å^3	519.9(4)
Z	1
ρ_{calcd}, g cm^{-3}	1.40
λ, Å	0.710 73 (Mo Kα)
T, °C	25
μ, cm^{-1}	12.23
R^a	0.036
$R_w{}^b$	0.033

[a] $R = \Sigma||F_o| - |F_c||/\Sigma|F_o|$. [b] $R_w = \{\Sigma w(|F_o| - |F_c|)^2/\Sigma w|F_o|^2\}$; $w = \exp(10(\sin^2\theta)/\lambda^2)/\sigma^2(F_o)$.

Experimental Section

***trans*-[Ni(OH_2)$_2$(cyclam)]Cl_2·4H_2O (1).** [NiCl_2(cyclam)] was prepared according to the literature.[4] [NiCl_2(cyclam)] was dissolved in a minimum amount of water, which was allowed to stand in an open beaker at room temperature. After ca. 1 week, the diaqua complex **1** separated out as violet plates just before the solution was dried up. The crystals were picked up while they were wet and stored in a sealed glass tube without drying procedures. The crystal large enough for spectroscopy was grown by slow evaporation of the solution in a beaker covered with a filter paper and watch glass, isolated, and stored in the same way as described above. The identification of both small and large crystals used here was performed by X-ray measurements of cell constants.

Vis-Absorption Spectrum Measurement. A large violet plate (size: 0.6 (light path) × 5 × 10 mm) of **1** was fixed between a pair of quartz plates, and its vis-absorption spectrum was quickly measured on a Shimadzu 2200 spectrophotometer at 25 °C.

Crystallography. Crystal data and experimental details are listed in Table 1. To prevent decomposition, a violet crystal (0.60 × 0.50 × 0.30 mm) covered with epoxy resin and further sealed in a glass capillary was used for the X-ray experiments. The determinations of the crystal class, orientation matrix, and accurate unit cell parameters were performed using a MAC Science MXC3k four-circle diffractometer (graphite-monochromatized Mo Kα radiation, λ = 0.710 73 Å). The intensity data were collected by the ω-2θ scan technique in the region 3° < 2θ < 55° at 25 °C, and absorption correction was not applied. A total of 2620 reflections were measured, of which 2007 independent significant reflections ($I \geq 3\sigma(I)$) were assumed to be observed. As a check of the crystal and electronic stability, three representative reflections were monitored every 100 reflections; the intensities of these standards remained constant within experimental error throughout the data collection. The structure was solved by the direct method (SIR92) and refined by the full-matrix least-squares method. All the non-hydrogen atoms were refined with anisotropic

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[⊗] Abstract published in *Advance ACS Abstracts,* November 1, 1995.

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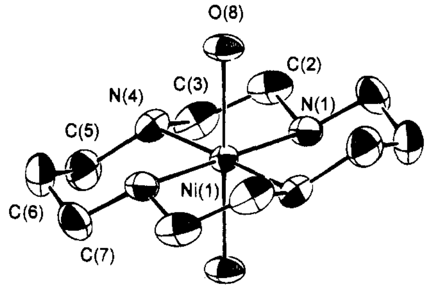

Figure 1. Perspective view of *trans*-$[Ni(OH_2)_2(cyclam)]^{2+}$.

Table 2. Fractional Atomic Coordinates and Equivalent Isotropic Thermal Parameters for Non-Hydrogen Atoms

atom	*x/a*	*y/b*	*z/c*	*U*(iso)^a
Ni(1)	0.500 00	0.500 00	0.500 00	0.028
Cl(1)	0.109 40(9)	0.416 54(11)	0.252 52(8)	0.057
N(1)	0.401 6(3)	0.659 3(3)	0.285 2(2)	0.038
C(2)	0.531 0(4)	0.633 5(5)	0.157 6(3)	0.053
C(3)	0.603 9(3)	0.433 9(5)	0.214 8(3)	0.055
N(4)	0.674 2(2)	0.378 9(3)	0.369 0(3)	0.041
C(5)	0.718 9(4)	0.177 6(4)	0.450 0(5)	0.059
C(6)	0.786 9(4)	0.126 2(4)	0.609 1(5)	0.064
C(7)	0.654 5(4)	0.144 5(4)	0.743 5(4)	0.054
O(8)	0.320 1(3)	0.298 8(3)	0.545 5(2)	0.045
O(9)	1.017 0(4)	0.237 4(3)	0.034 5(3)	0.060
O(10)	0.192 2(4)	0.055 3(4)	0.838 0(3)	0.069

^{a} Equivalent isotropic *U* defined as one-third of the trace of the orthogonalized U_{ij} tensor.

thermal parameters. All hydrogen atoms were located by the difference Fourier syntheses and included in the final refinement with the isotropic thermal parameters. The final *R* indices were $R = 0.036$ and $R_w = 0.033$ (weighting scheme, $\omega = \exp(10(\sin^2 \theta)/\lambda^2)/\sigma^2(F_o)$). All the calculations were carried out using a SUN SPARK 10 workstation (Crystan-GM program system provided by MAC Science).

Results and Discussion

Bosnich et al. reported that the recrystallization of the chloride of the cyclam−Ni(II) complex from methanol yields a *trans*-dichloro complex, the structure of which has already been determined by X-ray crystallography.[5,6] Upon recrystallization of the chloride from water, we obtained the diaqua complex **1** as violet plates, which were different from $[NiCl_2(cyclam)]$.[4,5] If the violet crystal is exposed to air, it easily loses crystal-water and gradually decomposes. The weight loss measurement after drying the crystal over P_2O_5 at 80 °C in vacuum indicated that the diaqua complex is tetrahydrated.

Figure 1 shows the structure of **1** determined by single-crystal X-ray crystallography. The fractional coordinates of the non-hydrogen atoms and internal bond lengths and angles are listed in Table 2 and 3. The structure of **1** is very similar to that of *trans*-$[NiCl_2(cyclam)]$.[5,6] The ligand skeleton of the complex takes the most stable "trans III" conformation with two chair-form six-membered and two gauche five-membered chelate rings. An inversion center exists on the central Ni(II) ion. Two water molecules axially coordinate to the central Ni(II) ion, which is six-coordinate in the high-spin form. The average bond length of Ni−N is 2.069(7) Å, which is similar to those found in *trans*-$[NiX_2(cyclam)]$ (X = Cl, 2.058(8),[5] 2.067(2);[6] NO_3, 2.050(5) and 2.060(6)[3] Å). The Ni−O length is 2.176(2) Å, which is considerably shorter than that of the Ni−Cl (2.492 Å).[5] The molecular mechanics calculation[3] by Hancock for the trans III form of $[Ni(OH_2)_2(cyclam)]^{2+}$ previously predicted that the best-fit Ni−N and Ni−O lengths are 2.065 and 2.16 Å, respectively. These predicted values are in good agreement with those found in the present crystal.

Table 3. Bond Lengths (Å) and Angles (deg) with Estimated Standard Deviations

Ni(1)−N(1)	2.072(2)	Ni(1)−N(4)	2.065(3)
Ni(1)−O(8)	2.176(2)	N(1)−C(2)	1.483(4)
C(2)−C(3)	1.503(5)	C(3)−N(4)	1.489(4)
N(4)−C(5)	1.475(4)	C(5)−C(6)	1.527(6)
C(6)−C(7)	1.520(6)	C(7)−N(1)	1.480(4)
N(1)−Ni(1)−N(4)	85.1(1)	N(1)−Ni(1)−N(4′)	94.9(1)
O(8)−Ni(1)−N(1)	88.5(1)	O(8)−Ni(1)−N(1′)	91.5(1)
O(8)−Ni(1)−N(4)	90.0(1)	Ni(1)−N(1)−C(2)	106.7(2)
Ni(1)−N(1)−C(7)	115.8(2)	Ni(1)−N(4)−C(3)	106.2(2)
Ni(1)−N(4)−C(5)	116.0(2)	N(1)−C(2)−C(3)	108.9(3)
C(2)−C(3)−N(4)	109.4(3)	C(3)−N(4)−C(5)	113.4(3)
N(4)−C(5)−C(6)	111.9(3)	C(5)−C(6)−C(7)	116.1(3)
C(6)−C(7)−N(1)	111.7(3)	C(7)−N(1)−C(2)	114.0(3)

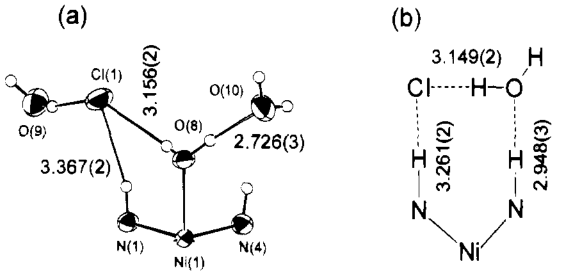

Figure 2. Hydrogen-bond systems of **1** (a) and **2** (b) (from ref 8).

The hexamethylated cyclam 7*R*(*S*),14*S*(*R*)-5,5,7,12,12,14-hexamethyl-1,4,8,11-tetraazacyclotetradecane is known to form an orange Ni(II) complex dihydrate,[7,8] $[NiL]Cl_2{\cdot}2H_2O$ (**2**), which has specific hydrogen-bonding chelate rings comprised of chloride, a water molecule, and secondary amines, as shown in Figure 2b. The hydrogen-bonding chelate rings in the dihydrate prevent the coordination of both the chloride and the water molecule to the central Ni(II) ion. Anticipating obtaining such a dihydrate at first, we recrystallized the chloride of the cyclam−Ni(II) complex from water, although we obtained not an organe but a violet crystal. In the violet crystal, water molecules coordinate to the central Ni(II) ion, accompanied by another water molecule and the chloride which are located close to the coordinated water through a hydrogen-bond network, as shown in Figure 2a.[9] In this case, the hydrogen-bond system appears to play a role in stabilizing the coordination of the water molecule to the central Ni(II) ion, contrary to the function observed in the dihydrate. We assume that the reason that the cyclam−Ni(II) complex forms not a dihydrate but the water-coordinated complex is ascribable to the absence of axial methyl groups on the 5th, 7th, 12th, or 14th positions of the cyclam. Structural and equilibrium studies on the isomers of Ni(II)

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(9) The hydrogen-bond parameters are as follows:

O(8)−O(10)^{i}	2.726(3) Å	O(9)−O(10)^{ii}	2.831(4) Å
O(9)−O(10)^{iii}	2.800(4) Å	Cl(1)−O(8)^{i}	3.156(2) Å
Cl(1)−O(9)^{iv}	3.147(2) Å	Cl(1)−O(9)^{v}	3.101(3) Å
Cl(1)−N(1)^{i}	3.367(2) Å	Cl(1)−N(4)^{iv}	3.439(2)

Key to symmetry operations: (i) *x*, *y*, *z*; (ii) 1 + *x*, *y*, −1 + *z*; (iii) 1 − *x*, −*y*, 1 − *z*; (iv) −1 + *x*, *y*, *z*; (v) 1 − *x*, 1 − *y*, −*z*.

complexes with 5,7,12,14-tetramethylcyclam (Hay),[10] 5,12-dimethylcyclam (MacAuley),[11] and 5,7-dimethylcyclam (Mochizuki)[12] have revealed that the presence of axial methyl groups on these positions prevents the coordination of water molecules to the central Ni(II) ion; that is, the isomers having the axial methyl groups predominantly exist as square-planar species in aqueous solutions, while the isomers with only equatorial methyl groups much prefer water-coordinated octahedral species. When either the dihydrate or anhydride of **2**, which has axial methyl groups on the 5th and 12th positions,[8] is dissolved in water, it actually affords only the square-planar species.[7] On the other hand, there is no interference by axial methyl groups with water coordination to the cyclam−Ni(II) complex. Consequently, water molecules, which form stronger coordination than chloride, as shown in the following vis-absorption spectra, should preferentially coordinate to the central Ni(II) ion.

Very slow evaporation of an aqueous solution containing [NiCl_2(cyclam)] gave a crystal large enough for vis-absorption spectrum measurements. Figure 3 shows the vis-absorption spectrum of *trans*-[Ni(OH_2)$_2$(cyclam)]Cl_2·4H_2O together with that of *trans*-[NiCl_2(cyclam)] in $CHCl_3$. The *trans*-diaqua complex shows three absorption bands (λ 333 nm (ϵ 3.7) ${}^3B_{1g} \rightarrow {}^3E_g$, 507 (3.1) ${}^3B_{1g} \rightarrow {}^3E_g{}^b$, 667 (2.4) ${}^3B_{1g} \rightarrow {}^3B_{2g} + {}^3B_{1g} \rightarrow {}^3A_{2g}{}^a$)[13] in the range 300−800 nm; the molar absorption coefficients in parentheses are estimated from the thickness of the crystal used and the molecular packing of the crystal. All the absorption bands appear at wavelengths shorter than those observed for the *trans*-dichloro complex (λ 345 nm (ϵ 15.6), 520 (7.2), 672 (3.3)), which is reasonably explained by the spectrochemical series ($Cl^- < H_2O$).

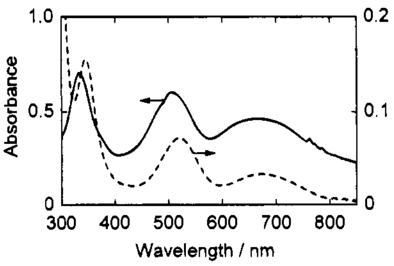

Figure 3. Vis-absorption spectra of *trans*-[Ni(OH_2)$_2$(cyclam)]Cl_2·4H_2O (solid line) and 0.01 M *trans*-[NiCl_2(cyclam)] in $CHCl_3$ (broken line).

In an earlier spectrophotometrical evaluation of the equilibrium constant for eq 1, the molecular extinction coefficient of the octahedral species was treated as 0 around the absorption band of the square-planar species. Although relatively small ϵ values of **1** guarantee that this treatment is essentially valid, it should be noted that **1** shows an absorption maximum at 507 nm, which appears close to that of the square-planar species (ca. 450 nm). This result indicates that the wavelength used for precise calculation should be carefully chosen, if one neglects the contribution of the octahedral species to absorption.

Thus, the *trans*-diaqua complex was isolated, the structure of which was confirmed by X-ray crystallography, and its single-crystal vis-absorption spectrum was obtained.

Supporting Information Available: Tables S1, S2, and S3 listing crystallographic data collection and processing parameters, hydrogen atom coordinates, and anisotropic thermal parameters for non-hydrogen atoms (3 pages). Ordering information is given on any current masthead page.

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