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# Preparation and Molecular Structure of *cis*-Diaqua[(7*S*, 14*S*)-5,5,7,12,12,14-hexamethyl-1,4,8,11-tetraazacyclotetradecane]nickel(II) Chloride

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**Synopsis.** A six-coordinate diaqua nickel(II) complex with the title macrocyclic ligand, $[Ni(H_2O)_2(S,S\text{-}L)]Cl_2$, has been synthesized and its structure has been determined by the X-ray analysis. Coordination geometry about the Ni is of *cis*-$NiO_2N_4$ type with the macrocyclic ligand folded.

It is well known that a certain tetraazamacrocyclic nickel(II) complex exists as an equilibrated mixture of four-coordinate and diaquated six-coordinate species in an aqueous solution. However, in the case of a nickel(II) complex with 5,5,7,12,12,14-hexamethyl-1,4,8,11-tetraazacyclotetradecane, $[NiL]^{2+}$, neither the occurrence of such an equilibrium nor the existence of a diaqua six-coordinate complex had been reported until our previous study[1] on the complex having the optically active ligand. We found in the circular dichroism (CD) spectral study of $[Ni(S,S\text{-}L)]^{2+}$ that a very small amount of six-coordinate diaqua complex exists in a dilute perchloric acid solution of $\alpha$-$[Ni(S,S\text{-}L)](ClO_4)_2$, where *S*,*S*-L denotes 7*S*,14*S*-form of the ligand L and a symbol "$\alpha$" designates in this case that chiral secondary amine nitrogens adopt 1*R*,4*R*,8*R*,11*R*-configuration.[2] From the CD band positions, the structure about the Ni of the six-coordinate species was tentatively assigned to be of *cis*-$NiO_2N_4$ type.

In this study, we isolated successfully the diaqua six-coordinate complex, *cis*-$[Ni(H_2O)_2(S,S\text{-}L)]Cl_2$. The blue diaqua complex is obtained from an acetonitrile solution of *cis*-$[NiCl_2(S,S\text{-}L)]$, which contains an appropriate amount of water. When the acetonitrile contains an insufficient amount of water, green crystals of *cis*-$[NiCl_2(S,S\text{-}L)]$ are recovered. When the water content is too much, a yellow compound (probably four-coordinate $[Ni(S,S\text{-}L)]Cl_2$) is obtained. The diaqua complex was obtained only when secondary amine nitrogens are in the $\alpha$-form.

Figure 1 shows a stereoscopic view of $[Ni(H_2O)_2(S,S\text{-}L)]^{2+}$. Coordination geometry about the Ni is of *cis*-$NiO_2N_4$ type, two water molecules occupying the *cis* positions. The ligand L is folded about N(4)–Ni–N(11), as is in the crystals of $[Ni(OAc)(rac\text{-}L)](ClO_4)$[3] and $[\{Ni(S,S\text{-}L)\}_2(H_2O)(d\text{-}tart)](ClO_4)_2\cdot 2H_2O$.[1] Each chelate ring adopts the most strain free conformation: all the six-membered rings take the chair form with the single methyl groups in equatorial positions; all the five-membered rings are in the gauche conformation. Table 1 lists bond lengths and angles about the Ni. Other structural parameters are deposited as supplementary data.[4] Chloride ions are hydrogen-bonded to coordinated water molecules, giving one dimensional chains along the c-axis.[4]

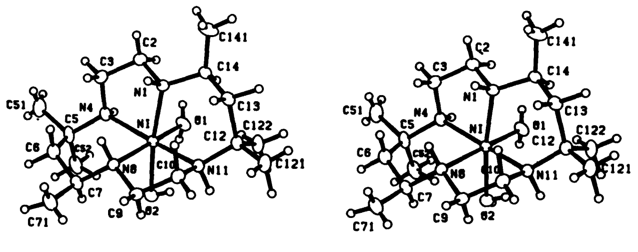

Fig. 1. A stereo view of the structure of *cis*-$[Ni(H_2O)_2\text{-}(S,S\text{-}L)]^{2+}$.

Table 1. Bond lengths ($l$/Å) and angles ($\phi$/°) about the Ni, and their estimated standard deviations

| | | | | | |
|---|---|---|---|---|---|
| NI | -O(1) | 2.162( 3) | NI | -O(2) | 2.142( 3) |
| NI | -N(1) | 2.095( 3) | NI | -N(4) | 2.163( 4) |
| NI | -N(8) | 2.113( 3) | NI | -N(11 | 2.164( 4) |

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| O(1) | -NI | -O(2) | 84.2( 1) | O(1) | -NI | -N(1) | 90.1( 1) |
| O(1) | -NI | -N(4) | 85.3( 1) | O(1) | -NI | -N(11) | 103.5( 1) |
| O(2) | -NI | -N(4) | 100.2( 1) | O(2) | -NI | -N(8) | 87.7( 1) |
| O(2) | -NI | -N(11) | 87.3( 1) | N(1) | -NI | -N(4) | 84.8( 1) |
| N(1) | -NI | -N(8) | 98.7( 1) | N(1) | -NI | -N(11) | 88.6( 1) |
| N(4) | -NI | -N(8) | 88.3( 1) | N(8) | -NI | -N(11) | 84.0( 1) |
| O(1) | -NI | -N(8) | 168.7( 1) | O(2) | -NI | -N(1) | 172.0( 1) |
| N(4) | -NI | -N(11) | 169.1( 1) | | | | |

Table 2. Fractional coordinates ($\times 10^5$) with $B_{eq}$[a]

| Atom | $x$ | $y$ | $z$ | $B_{eq}$/Å$^2$ [5] |
|---|---|---|---|---|
| NI | 10671( 3) | 12643( 3) | 15170( 6) | 2.0 |
| CL(1) | -13189( 9) | 27409( 7) | 14234(18) | 4.6 |
| CL(2) | -31806( 9) | 45145( 7) | 38718(13) | 3.7 |
| O(1) | 24465(21) | 11579(16) | 4645(36) | 3.3 |
| O(2) | 14669(21) | 2721(15) | 26854(33) | 2.9 |
| N(1) | 8682(23) | 22871(17) | 4405(38) | 2.4 |
| N(4) | 5211(23) | 7944(18) | -5514(41) | 2.5 |
| N(8) | -3030(22) | 11418(17) | 24591(36) | 2.1 |
| N(11) | 13686(22) | 18594(17) | 35802(41) | 2.3 |
| C(2) | 7809(33) | 21056(24) | -11813(50) | 3.3 |
| C(3) | 1395(31) | 14403(24) | -13625(50) | 3.1 |
| C(5) | -1344(32) | 1350(25) | -5370(54) | 3.2 |
| C(6) | -9772(33) | 2782(24) | 5231(52) | 3.2 |
| C(7) | -8014(29) | 4148(21) | 21928(51) | 2.6 |
| C(9) | -2017(28) | 13101(24) | 40683(44) | 2.6 |
| C(10) | 4315(31) | 19857(24) | 42690(49) | 2.8 |
| C(12) | 19783(28) | 25457(21) | 35680(54) | 2.7 |
| C(13) | 15961(34) | 31029(23) | 23912(52) | 3.0 |
| C(14) | 15950(31) | 28800(22) | 7270(51) | 2.8 |
| C(51) | -5405(40) | -59(33) | -21256(61) | 4.8 |
| C(52) | 4362(35) | -5476(25) | -745(66) | 4.1 |
| C(71) | -17562(33) | 3694(26) | 30124(61) | 3.9 |
| C(121) | 19788(36) | 29340(28) | 51064(61) | 4.1 |
| C(122) | 29940(31) | 23028(27) | 32009(59) | 3.7 |
| C(141) | 13942(45) | 35671(25) | -2191(61) | 4.8 |

a) Estimated standard deviations are in parentheses.

Figure 2 shows nujol-mull solid state absorption (AB) spectra of *cis*-$[Ni(H_2O)_2(S,S\text{-}L)]Cl_2$ ($\tilde{\nu}_{max}$/cm$^{-1}$: 10100, 17000, 27100) and *cis*-$[NiCl_2(S,S\text{-}L)]$ ($\tilde{\nu}_{max}$/cm$^{-1}$: 8550, 15700, 25400). They are very similar to each other except that the AB maxima of *cis*-$[NiCl_2(S,S\text{-}L)]$ are shifted to longer wavelengths. The green dichloro complex gives the same AB spectrum in the solid state

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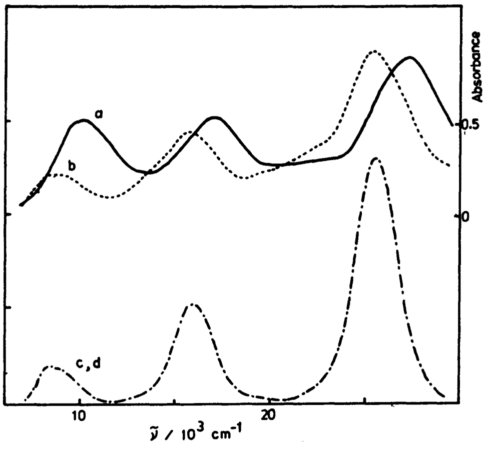

Fig. 2. Nujol-mull solid state absorption spectra of *cis*-[Ni($H_2O$)$_2$(*S*,*S*-L)]$Cl_2$ (a) and *cis*-[$NiCl_2$(*S*,*S*-L)] (b) [right-hand ordinate], and absorption spectra of *cis*-[Ni($H_2O$)$_2$(*S*,*S*-L)]$Cl_2$ (c) and *cis*-[$NiCl_2$(*S*,*S*-L)] (d) in acetonitrile [left-hand ordinate].

as in the acetonitrile solution [$\tilde{\nu}_{max}$/cm$^{-1}$ ($\varepsilon$): 8500(20.9), 15800(53.4), 25600(130)]. On the other hand, when the diaqua complex is dissolved in acetonitrile, nitromethane, or acetone, it gives green solution. The spectrum of the solution is exactly the same as that of *cis*-[$NiCl_2$(*S*,*S*-L)]. The ionic diaqua complex turns the dichloro complex and exists as a chargeless complex in such organic solvents.

The positions of AB maxima of the solid state spectrum of *cis*-[Ni($H_2O$)$_2$(*S*,*S*-L)]$Cl_2$ are the same as those for the triplet species of α-[Ni(*S*,*S*-L)]($ClO_4$)$_2$ in dilute perchloric acid.[2]

## Experimental

*Materials.* cis-[*$NiCl_2$*(S,S-*L*)]: To an acetonitrile solution (50 cm$^3$) containing 0.5 g of α-[Ni(*S*,*S*-L)]($ClO_4$)$_2$[1] was added an excess of tetrabutylammonium chloride (0.5 g). The solution was rotoevaporated to *ca.* 10 cm$^3$. Green precipitates were filtered and washed with a minimum amount of acetonitrile (yield, 0.4 g). Found: C, 45.73; H, 9.02; N, 13.51%. Calcd for $NiC_{16}H_{36}N_4Cl_2$: C, 46.41; H, 8.76; N, 13.53%.

cis-[*Ni($H_2O$)$_2$*(S,S-*L*)]*$Cl_2$*: 0.4 g of *cis*-[$NiCl_2$(*S*,*S*-*L*)] was dissolved in 30 cm$^3$ of acetonitrile containing two drops of water. Blue prismatic crystals of *cis*-[Ni($H_2O$)$_2$(*S*,*S*-L)]$Cl_2$ were obtained upon standing the solution in a refrigerator for a few days. (yield, 0.1 g). Found: C, 42.66; H, 8.87; N, 12.41%. Calcd for $NiC_{16}H_{40}N_4O_2Cl_2$: C, 42.69; H, 8.96; N, 12.45%. When an amount of water present in the solvent acetonitrile is insufficient or too much, the desired compound cannot be isolated.

*X-Ray Analysis.* The intensity measurement and the structure analysis were carried out in the same way as described previously.[1] A specimen with dimensions 0.28 mm × 0.13 mm × 0.10 mm was used for the X-ray work. Crystal data: orthorhombic, $P2_12_12_1$, $a=14.070(3)$, $b=18.022(3)$, $c=8.876(2)$ Å, $U=2250.6(8)$ Å$^3$, $Z=4$, $D_m=1.34$, $D_x=1.33$ g cm$^{-3}$, $\mu$(Mo *K*α) = 11.1 cm$^{-1}$. All the hydrogen atoms located by the difference synthesis were included in the final refinement with the isotropic temperature factors. The final *R* indices were $R=0.033$ and $R_w=0.035$. Table 2 lists the atomic coordinates.[5]

*Measurements.* Absorption spectra in solution were measured with a Hitachi 340 spectrophotometer. Solid state absorption spectra were taken as Nujol mulls on a Hitachi 323 spectrophotometer equipped with an attached integrating sphere.

## References

1) H. Ito, J. Fujita, K. Toriumi, and T. Ito, *Bull. Chem. Soc. Jpn.*, **54**, 2988 (1981).

2) See Ref. 2 and references cited therein for the notation.

3) P. O. Whimp, M. F. Bailey, and N. F. Curtis, *J. Chem. Soc., A*, **1970**, 1956.

4) Tables of atomic parameters, structure factors, bond lengths and angles, and a stereoview of packing of complexes are kept in the Office of the Chemical Society of Japan (Document No. 8235).

5) $B_{eq}=(4/3)\sum_i\sum_j\beta_{ij}\,(\boldsymbol{a}_i\cdot\boldsymbol{a}_j)$, where $\boldsymbol{a}_i$ is a unit cell edge in direct cell and $\beta_{ij}$ is an anisotropic temperature factor in the form of $\exp\{-(\beta_{11}h^2+\beta_{22}k^2+\beta_{33}l^2+2\beta_{12}hk+2\beta_{13}hl+2\beta_{23}kl)\}$.