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The Preparation and the Structure of (1,9-Diamino-1,4,6,6,9-pentamethyl-3,7-diazanona-3-ene) (*l*-propylenediamine)nickel(II) Perchlorate

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A new purple complex of (1,9-diamino-1,4,6,6,9-pentamethyl-3,7-diazanona-3-ene)(*l*-propylenediamine)nickel(II) perchlorate and the known yellow complex, (octamethyl-1,4,8,11-tetraazacyclotetradecadiene)nickel(II) perchlorate, were obtained by the reaction of tris(*l*-propylenediamine)nickel(II) perchlorate and acetone without any irradiation by ultraviolet light. The structure of the purple complex was estimated from its absorption and circular dichroism spectra in acetonitril and in an aqueous solution, and from its infrared spectrum in the solid state. The complex was found to take an octahedral [NiN_6]-type structure in acetonitril and a planar [NiN_4]-type structure in aqueous solution. The (1,9-diamino-1,4,6,6,9-pentamethyl-3,7-diazanona-3-ene)nickel(II) perchlorate and (1,9-diamino-1,4,6,6,9-pentamethyl-3,7-diazanona-3-ene)(ethylenediamine)nickel(II) perchlorate complexes were also prepared.

Since it was reported that tris(ethylenediamine)-nickel(II) perchlorate reacts with acetone to form macrocyclic complexes,[1] a number of analogous complexes have been prepared from various metal-amine complexes and ketones or aldehydes.[2] Some of these complexes have geometrical and/or optical isomers, depending on the positions of such substituents as methyl groups. Curtis *et al.* prepared, for example, two non-interconvertible, isomeric (octamethyl-1,4,8,11-tetraazacyclotetradecadien)nickel(II) perchlorates (yellow and orange) by irradiating an acetone solution of tris(*d*,*l*-propylenediamine)nickel(II) perchlorate with ultraviolet light for several days.[3] Although there are many isomerisms in this ligand, they showed, by X-ray

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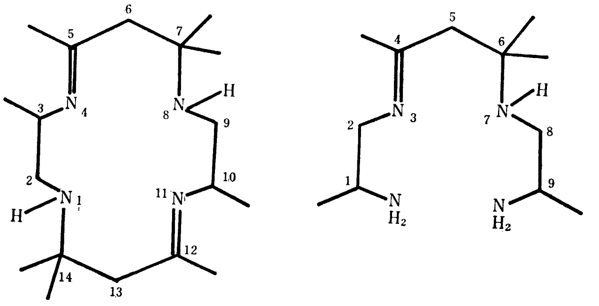
[1] N. F. Curtis, *J. Chem. Soc.*, **1960**, 4409; N. F. Curtis, Y. M. Curtis, and H. K. J. Powell, *J. Chem. Soc. A*, **1966**, 1015.

[2] N. F. Curtis, *Coord. Chem. Rev.*, **3**, 3 (1968).

[3] M. M. Blight and N. F. Curtis, *J. Chem. Soc.*, **1962**, 1204.

analysis,[4] that both isomers have two imino-groups in *trans* positions, but that the two asymmetric carbon atoms of the yellow isomer are racemic (*d,d* or *l,l*), while those of the orange isomer are meso (*d,l*) (Fig. 1). In fact, only the yellow isomer was produced by the reaction of the optically-active tris (*d* or *l*-propylenediamine)-nickel(II) perchlorate and acetone.



$C_{18}H_{36}N_4$ $C_{12}H_{28}N_4$

Fig. 1.

During our study of the effect of methyl groups on the conformation of five- and six-membered chelate rings of metal complexes,[5] we obtained a new purple complex as well as the above yellow complex from the tris(*l*-propylenediamine)nickel(II) perchlorate and acetone without any irradiation by ultraviolet light. This paper will deal with the chemical properties and structure of this purple complex.

Experimental

Preparations. *l*-Propylenediamine was obtained by resolving its commercial racemate according to Dwyer's method.[6]

(1,9-Diamino-1,4,6,6,9-pentamethyl-3,7-diazanona-3-ene) (l-propylenediamine) nickel(II) perchlorate, $[Ni(C_{12}H_{28}N_4)(l\text{-}pn)](ClO_4)_2$: An acetone solution (about 100 m*l*) containing 10 g of $[Ni(l\text{-pn})_3](ClO_4)_2$ was kept at room temperature in a stoppered container. After about two weeks, the purple crystals which had deposited were filtered off and recrystallized from hot water.

The filtrate was kept several more days at room temperature, air-dried until the residue was almost free from acetone, and filtered. A mixture of purple and yellow crystals was then obtained by treating the residue with a small amount of acetone. This mixture can be separated by fractional recrystallization from hot water, because the purple crystals are slightly more soluble in hot water. Recrystallization was effected by adding an aqueous *l*-propylenediamine to the warm aqueous solution from which the yellow crystals had been removed by filtration. Purple complex: Found: C, 31.93; H, 6.76; N, 14.71%. Calcd for $NiC_{15}H_{38}N_6Cl_2O_8$: C, 32.17; H, 6.84; N, 15.00%. The results of the chemical analysis indicated that the yellow complex is the $[Ni(C_{18}H_{36}N_4)](ClO_4)_2$ reported by Curtis *et al.*[4]

(1,9-Diamino-1,4,6,6,9-pentamethyl-3,7-diazanona-3-ene)nickel(II) perchlorate monohydrate, $[Ni(C_{12}H_{28}N_4)](ClO_4)_2\cdot H_2O$: An aqueous solution of $[Ni(C_{12}H_{28}N_4)(l\text{-pn})](ClO_4)_2$ was passed through a cation-exchange column in the Na-form. The column was washed well with water, and the adsorbed yellow band was eluted with a 12% aqueous sodium perchlorate solution. The eluate was concentrated at 50°C under reduced pressure. Yellow crystals were obtained by cooling the solution in a refrigerator.

Found: C, 28.53; H, 5.70; N, 10.94%. Calcd for $NiC_{12}H_{30}N_4Cl_2O_9$: C, 28.60; H, 6.00; N, 11.11%.

(1,9,-Diamino-1,4,6,6,9-pentamethyl-3,7-diazanona-3-ene) (ethylenediamine) nickel(II) perchlorate, $[Ni(C_{12}H_{28}N_4)(en)](ClO_4)_2$: To a concentrated solution of the above eluate, an aqueous ethylenediamine was added, drop by drop. The purple crystals were recrystallized from hot water.

Found: C, 30.31; H, 6.88; N, 14.79%. Calcd for $NiC_{14}H_{36}N_6Cl_2O_8$: C, 30.79; H, 6.64; N, 15.39%.

Measurements. The absorption (AB) and circular dichroism (CD) spectra in the near-infrared region (1400—700 mμ) were obtained with a Hitachi EPS-3 Recording Spectrophotometer and a Shimadzu QV-50 Spectrophotometer with its CD attachment, respectively. The AB and CD spectra in the visible and ultraviolet region (700—200 mμ) were recorded with a Hitachi 124 Spectrophotometer and a Jasco ORD/UV-5 Spectrophotometer with its CD attachment, respectively. The infrared (IR) spectra in the NaCl region were obtained using a Hitachi EPI-2G Infrared Spectrophotometer. All the measurements were made at room temperature.

Results and Discussion

Figure 2 compares the AB and CD spectra of $[Ni(C_{18}H_{36}N_4)](ClO_4)_2$ (the yellow complex (I)) and

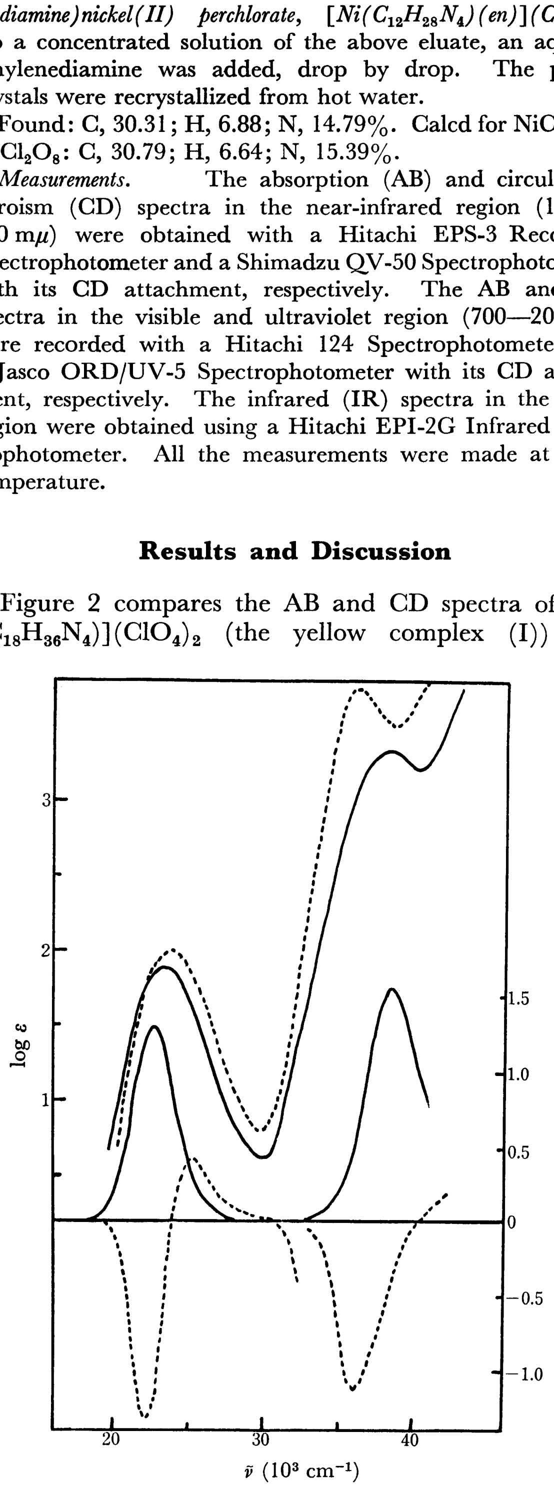


Fig. 2. AB and CD spectra of $[Ni(C_{18}H_{36}N_4)](ClO_4)_2$ (······) and $[Ni(C_{12}H_{28}N_4)(l\text{-pn})](ClO_4)_2$ (——) in water.

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[4] N. F. Curtis, D. S. A. Swann, T. N. Waters, and I. E. Maxwell, *J. Amer. Chem., Soc.*, **91**, 4588 (1969).

[5] S. Yano, H. Ito, Y. Koike, J. Fujita, and K. Saito, This Bulletin, **42**, 3184 (1969); F. Mizukami, H. Ito, J. Fujita, and K. Saito, *ibid.*, **43**, 3633 (1970).

[6] F. P. Dwyer, F. L. Garvan, and A. Shulman, *J. Amer. Chem. Soc.*, **89**, 5780 (1967).

TABLE 1 (a). AB AND CD DATA IN WATER

Complex[a]	$\nu_{max}(\log \varepsilon)$	$\nu_{ext}(\Delta\varepsilon_{ext})$	$\nu_{max}(\log \varepsilon)$	$\nu_{ext}(\Delta\varepsilon_{ext})$
I	23.7(1.99)	22.5(−1.31) 25.3(+0.41)	35.7(3.72)	36.1(−11)
II	23.2(1.88)	22.7(+1.30)	37.9(3.31)	38.5(+ 1.7)
III	23.2(1.89)	22.7(+1.50)	37.9(3.29)	38.5(+ 1.8)

TABLE 1 (b). AB AND CD DATA IN ACETONITRIL

Complex[a]	$\nu_{max}(\log \varepsilon)$	$\nu_{ext}(\Delta\varepsilon_{ext})$	$\nu_{max}(\log \varepsilon)$	$\nu_{ext}(\Delta\varepsilon_{ext})$	$\nu_{max}(\log \varepsilon)$	$\nu_{ext}(\Delta\varepsilon_{ext})$
II	10.9(1.06)	9.9(−0.07) 11.5(+0.24)	18.2(0.97)	18.4(−0.04)	29(sh)	29(−)
IV	10.8(0.98)	9.6(−0.06) 11.5(+0.20)	18.1(0.89)	18.5(−0.03)	29(sh)	29(−)
V	11.1(0.84)	10.3(−0.15) 12.2(+0.10)	18.2(0.80)	17.7(−0.02)	28.8(0.94)	29.4(−0.01)

ν in cm^{-1}; sh shoulder

a) Complexes (I) = $[Ni(C_{18}H_{36}N_4)](ClO_4)_2$; (II) = $[Ni(C_{12}H_{28}N_4)(l\text{-pn})](ClO_4)_2$; (III) = $[Ni(C_{12}H_{28}N_4)](ClO_4)_2 \cdot H_2O$; (IV) = $[Ni(C_{12}H_{28}N_4)(en)](ClO_4)_2$; (V) = $Ni[(l\text{-pn})_3](ClO_4)_2$

$[Ni(C_{12}H_{28}N_4)(l\text{-pn})](ClO_4)_2$ (the purple complex (II)) in water. The purple complex (II) gives a yellow aqueous solution, and its AB spectrum exhibits a pattern typical of a planar $[NiN_4]$-type complex. The purple complex was formed again by the addition of *l*-propylenediamine to the yellow aqueous solution. When the aqueous solution of the purple complex (II) was passed through a cation-exchange column in the Na-form, a yellow band was adsorbed and the eluate was basic. The yellow band was eluted with a 12% aqueous sodium perchlorate solution, and the eluate was concentrated at 50°C under reduced pressure. On cooling, a yellow complex with the composition of $[Ni(C_{12}H_{28}N_4)](ClO_4)_2 \cdot H_2O$ (III) was obtained. The AB and CD spectra of this compound was almost the same as those of the purple complex (II) in water. The addition of aqueous *l*-propylenediamine to the concentrated eluate gave purple crystals which showed the same IR spectrum as that of the original purple complex (II). Purple $[Ni(C_{12}H_{28}N_4)(en)](ClO_4)_2$ (IV) was precipitated by adding aqueous ethylenediamine to the concentrated yellow eluate. These results indicate that the following equilibrium exists in an aqueous solution:

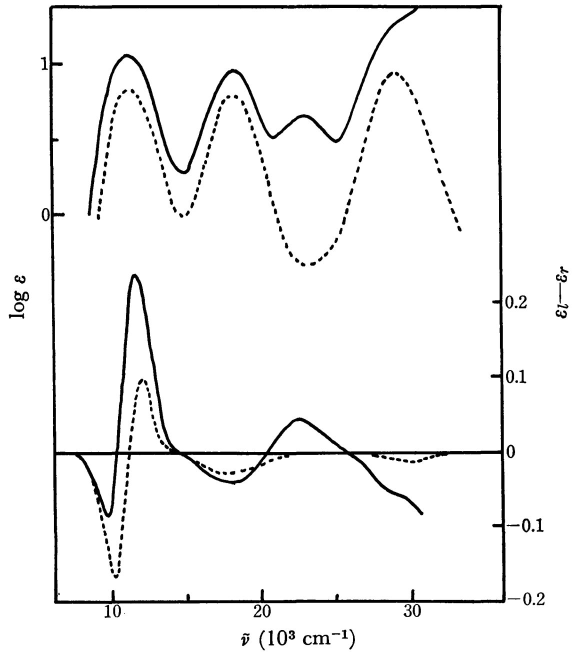


Fig. 3. AB and CD spectra of $[Ni(C_{12}H_{28}N_4)(l\text{-pn})](ClO_4)_2$ (——) and $[Ni(l\text{-pn})_3](ClO_4)_2$(……) in acetonitril.

$$[Ni(C_{12}H_{38}N_4)(l\text{-pn})]^{2+} \rightleftarrows [Ni(C_{12}H_{38}N_4)]^{2+} + l\text{-pn}$$

The AB and CD spectra of the purple complex (II) in acetonitril (purple solution) are compared with those of $[Ni(l\text{-pn})_3](ClO_4)_2$ in Fig. 3. The complex (II) exhibits three absorption peaks at 10900, 18200, and about 29000 cm^{-1}; they correspond to those of the latter complex. This result indicates that the purple complex (II) exists as an octahedral $[NiN_6]$-type complex in acetonitril. A weak peak at about 23000 cm^{-1} seems to come from the planar complex (III) partly formed in this solvent. From the intensity of this absorption band, the quantity of the planar complex is estimated to be only several percent. The AB and CD data are summarized in Table 1. The AB and CD spectra of $[Ni(C_{12}H_{28}N_4)(en)](ClO_4)_2$ are quite similar to those of the corresponding *l*-propylenediamine complex.

The strong band around 36000—38000 cm^{-1} of $[Ni(C_{18}H_{36}N_4)](ClO_4)_2$ (I), $[Ni(C_{12}H_{28}N_4)(l\text{-pn})](ClO_4)_2$ (II) (in water), and $[Ni(C_{12}H_{28}N_4)](ClO_4)_2$ (III) can be attributed to the C=N double bond in the ligands.[1] The absorption intensity of the complex (I) in this region is about twice as strong as those of the complexes (II) and (III), indicating that the ligand $C_{12}H_{28}N_4$ has one C=N double bond.

The IR data of the complexes in the 1600-cm^{-1} region are given in Table 2. The bands at 1603 and 1585 cm^{-1} of $[Ni(l\text{-pn})_3](ClO_4)_2$ can be assigned to the NH_2-deformation vibrations and the band at 1653 cm^{-1} of $[Ni(C_{18}H_{36}N_4)](ClO_4)_2$ (I), to the C=N stretching

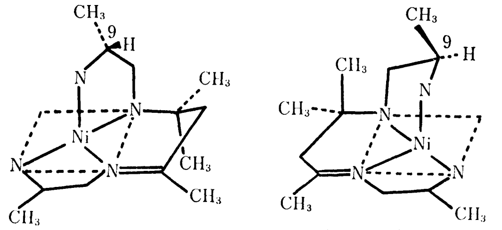
TABLE 2. IR DATA IN 1600 cm^{-1} REGION (cm^{-1})

Complex	$\gamma_{C=N}$	δ_{NH_2}
I	1653	
II	1653	1603
III	1653	1592
IV	1653	1592
V		1603, 1585

vibration. The complexes (II), (III), and (IV), on the other hand, exhibit two strong bands, at 1653 and around 1600 cm^{-1}, which can be assigned to the C=N stretching and the NH_2–deformation vibrations respectively.

On the basis of these data, we concluded that the ligand $C_{12}H_{38}N_4$ is 1,9-diamino-1,4,6,6,9-pentamethyl-3,7-diazanona-3-ene (Fig. 1), although there are four possible isomers, depending on the positions of the methyl groups of the *l*-propylenediamine residues. Their positions are: (1,8), (1,9), (2,8), and (2,9). Of these, however, the isomer (1,9), in which the methyl groups of the *l*-propylenediamine residues are located far from the six-membered chelate ring, may be expected to be most probable.[7] The reasons for this are as follows: (1) The X-ray analysis[4] of the yellow complex (I) showed that the methyl groups of the propylenediamine residues are on the 3 and 10 carbon atoms (Fig. 1). Thus, the repulsion between these methyl groups and the geminal methyl groups on the 7 and 14 carbon atoms seems to be avoided. (2) The reaction of $[Ni(\text{iso-bn})_2]^{2+}$ (iso-bn=iso-butylenediamine) and acetone produced only a complex containing 1,9-diamino-1,1,4,6,6,9,9-heptamethyl-3,7-diazanona-3-ene, in which four methyl groups of iso-butylenediamine residues take 1 and 9 positions.[3] (3) $[Ni(bn)_2]^{2+}$ (bn=2,3-diaminobutane) does not react with acetone.[8]

Curtis[8] described an analogous compound, $[Ni(C_{10}H_{24}N_4)(en)](ClO_4)_2$($C_{10}H_{24}N_4$=1,9-diamino-4,6,6-trimethyl-3,7-diazanona-3-ene), but did not give any details on its structure or chemical properties.

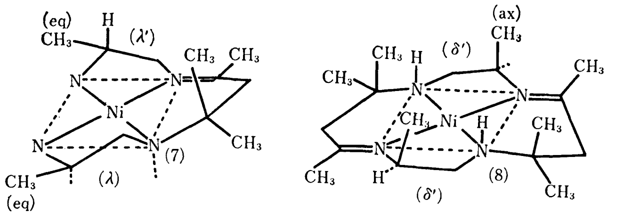


exo-Δ-cis β *endo-Λ-cis β*

Fig. 4

The quadridentate ligand, $C_{12}H_{28}N_4$, in the $[Ni(C_{12}H_{28}N_4)(ch)]^{2+}$ (ch=en and *l*-pn) should give a *cis*-form complex. Although the *cis* form has two different geometrical arrangements, *cis* α and *cis* β,[9] the present complex is probably *cis* β, since the quadridentate ligand involves an imino-nitrogen. In addition, each geometrical isomer has two optical isomers, Δ and Λ. Since both Δ and Λ isomers involve the same asymmetric carbon atoms in the *l*-propylenediamine residues, they form a pair of diastereoisomers. As Fig. 4 illustrates, the methyl group on the 9-carbon atom of the Δ-*cis* β points away (*exo*) from the central six-membered chelate ring, while that of the Λ-*cis* β points toward (*endo*) the six-membered chelate ring. Since the interaction between the nonbonding atoms is expected to be greater in the endo-Λ-*cis* β isomer, the absolute configuration of the purple complexes, (II) and (IV), could be identified as *exo-Δ-cis β*. This assignment is supported further by the facts that the CD spectra in the *d–d* transition region of $[Ni(C_{12}H_{28}N_4)(ch)](ClO_4)_2$ in acetonitril are quite similar to that of Δ-$[Ni(l\text{-pn})_3](ClO_4)_2$ as is shown in Fig. 3, and that they are enantiomeric to that of *fac*(N)-Λ-$[Ni(\text{L-prol})_3]^-$.[10] The positional isomers due to the methyl group of *l*-propylenediamine in $[Ni(C_{12}H_{28}N_4)(l\text{-pn})]^{2+}$ are not clear at present.

As Fig. 2 shows, the CD spectrum of $[Ni(C_{12}H_{28}N_4)]^{2+}$ (III) in water is almost enantiomeric with that of the $[Ni(C_{18}H_{36}N_4)]^{2+}$ (I); the purple complex (II) gives a CD spectrum similar to that of the complex (III) in water, since the former complex liberates the *l*-propylenediamine almost completely in water, as has been stated previously. According to the X-ray analysis,[4] the methyl groups of the *l*-propylenediamine residues in the complex (I) take positions axial to the complex plane. Therefore, the conformation of the *l*-propylenediamine residues in this complex may be described as approximately (pseudo) δ-gauche[5]; the conformation of such five-membered chelate rings involving the imino-nitrogen atom may be somewhat different from the usual gauche structure, as seen in the *l*-propylenediamine chelate. On the other hand, the five-membered chelate rings in the complex (III) may take a pseudo λ- and a usual λ-gauche conformation, since it is known that the methyl group on a puckered chelate ring tends to take an orientation equatorial to the ring unless there is special steric requirement.[11] Therefore the absolute configuration of the secondary amine (7 position) in this complex (III) should become enantiomeric with those of the secondary amines (1, 8 positions) in $[Ni(C_{18}H_{34}N_4)]^{2+}$, as is shown in Fig. 5. The enantiomeric CD curves between the complexes (I) and (III) may be caused by such enantiomeric configurations.



$[Ni(C_{12}H_{28}N_4)]^{2+}$ $[Ni(C_{18}H_{36}N_4)]^{2+}$

Fig. 5. Schematic drawing of $[Ni(C_{12}H_{28}N_4)]^{2+}$ and $[Ni(C_{18}H_{36}N_4)]^{2+}$.

The authors wish to thank Professor Kazuo Saito for his helpful advice and encouragement. They also wish to thank the Ministry of Education for its Grant-in-aid.

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[11] E. J. Corey and J. C. Bailar, Jr., *J. Amer. Chem. Soc.*, **81**, 2620 (1959).