between redox potentials due to the charge effect is greatly reduced for the isoelectronic Mn/Fe pair (d^4–d^5) which does not contain a d-electron configuration of special stability. This correlation between $E_{1/2}$ and d-electron configuration for first-row transition-metal complexes has been described elsewhere.[19]

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Registry No. $\mathrm{Cu(Me_2dtc)_2}$, 137-29-1; $\mathrm{Cu(Et_2dtc)_2}$, 13681-87-3; Cu((*i*-Pr)$_2$dtc)$_2$, 14354-07-5; Cu(Me(*n*-Bu)dtc)$_2$, 59765-84-3; Cu((*n*-Bu)$_2$dtc)$_2$, 13927-71-4; Cu((*i*-Bu)$_2$dtc)$_2$, 51205-55-1; Cu((c-Hx)$_2$dtc)$_2$, 51120-55-9; $\mathrm{Cu(Bz_2dtc)_2}$, 34409-33-1; Cu((pyrr)dtc)$_2$, 23301-60-2; Cu((pip)dtc)$_2$, 15225-85-1; Cu((2-Me(pip))dtc)$_2$, 59765-85-4; Cu((4-Me(pip))dtc)$_2$, 59765-86-5; Cu((2,6-Me$_2$(pip))dtc)$_2$, 59765-87-6; $\mathrm{Cu(Ph_2dtc)_2}$, 15683-27-9; Cu(PhMedtc)$_2$, 38991-27-4; Cu(PhEtdtc)$_2$, 53020-87-4; [Cu((*i*-Pr)$_2$dtc)$_2$]ClO$_4$, 59765-89-8; [Cu((*i*-Pr)$_2$dtc)$_2$]BF$_4$, 59790-37-3; $\mathrm{[Cu(Et_2dtc)_2]BF_4}$, 59796-00-8; Cu((*i*-Pr)$_2$dtc)$_2$I$_3$, 59765-90-1; $\mathrm{[Cu(Et_2dtc)]_4}$, 52133-93-4.

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Contribution from the Chemical Research Institute
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Solution Equilibria of Nickel(II) Complexes with Optically Active Tetraamines Containing Pyrrolidinyl Groups

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The temperature dependence of the square planar–octahedral equilibrium of the nickel(II) complexes with optically active tetraamines including two pyrrolidinyl groups has been studied in water, acetonitrile, and nitromethane. The equilibrium parameters were obtained by variable-temperature spectroscopic measurements. The equilibrium constants disclosed the preferential order in the octahedral-type coordination of these tetraamines to nickel(II) ion: 1,2-bis[2(*S*)-2-aminomethyl-1-pyrrolidinyl]ethane (AMPE) ≃ 1,2-bis[2(*S*)-2-*N*-methylaminomethyl-1-pyrrolidinyl]ethane (MMPE) > 1,3-bis[2(*S*)-2-aminomethyl-1-pyrrolidinyl]propane (AMPP) >> *N*,*N'*-bis[2(*S*)-2-pyrrolidinylmethyl]-1,3-trimethylenediamine (PMTN) > *N*,*N'*-bis[2(*S*)-2-pyrrolidinylmethyl]ethylenediamine (PMEN) > *N*,*N'*-bis[2(*S*)-2-pyrrolidinylmethyl]-1(*S*),2(*S*)-cyclohexanediamine (*SS*-PMCN) > *N*,*N'*-bis[2(*S*)-2-pyrrolidinylmethyl]-1(*R*),2(*R*)-cyclohexanediamine (*RR*-PMCN) (25 °C). This result was compared with the trien and 2,3,2-tet complexes.

Since the investigation of bis(stilbenediamine)nickel(II) by Lifschitz et al.,[1] the equilibrium between blue (octahedral) and yellow (square planar) species of bis(diamine) or tetraamine complexes of nickel(II) ion has been well investigated.[2–8] For example, the 1:1 complex of nickel(II) ion with triethylenetetramine (trien) consists almost entirely of octahedral species in an aqueous solution at room temperature, and its planar species increases with the addition of an excess of neutral salts, or with a rise in temperature.[7]

In the previous papers,[9–11] we have reported that the optically active tetraamines containing two pyrrolidinyl groups as shown in Figure 1 coordinate to nickel(II) ion with a certain stereoselectivity; the tetraamines which have the two pyrrolidinyl groups at their inner parts form mostly blue species in aqueous solutions at room temperature, whereas other tetraamines having the two pyrrolidinyl groups as the terminal groups preferentially form yellow species. It was further recognized that the two species of the tetraamine complexes coexist in solution as represented below

$$\mathrm{Ni(Tet)^{2+} + 2H_2O \rightleftharpoons Ni(Tet)(H_2O)_2{}^{2+}}$$

where Tet is a tetraamine. Similar equilibria have been observed for the mixed complexes of the tetraamines with ethylenediamine (en)

$$\mathrm{Ni(Tet)^{2+} + en \rightleftharpoons Ni(Tet)(en)^{2+}}$$

It was found that these equilibria between the two species depend greatly on the temperature. Then, it appeared of interest to obtain the thermodynamic parameters such as the equilibrium constant by means of the temperature dependence of the absorption spectra, and to further investigate the scope and mechanism of the selective coordination of the tetraamines.

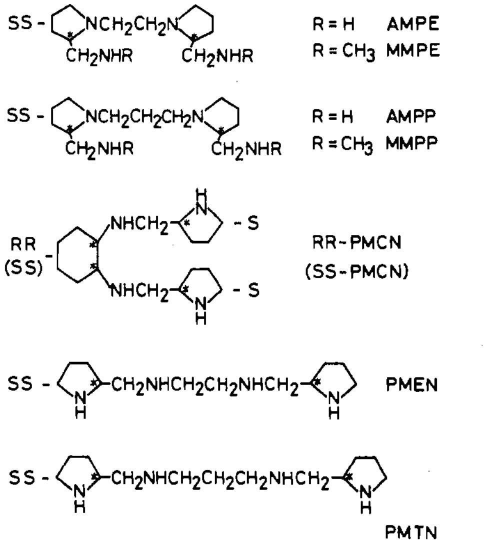

Figure 1. Tetraamines including pyrrolidinyl groups; R and S represent the absolute configurations of asymmetric carbon atoms.

Experimental Section

Compounds. The tetraamine complexes used in this study have been obtained as perchlorates.[10,11] Distilled water, acetonitrile, and nitromethane of spectral grades were used as solvents.

Electronic Spectral Measurements. A Hitachi EPS-3T recording spectrophotometer was used for the measurements of the electronic absorption spectra. The temperature regulation of the solution was done by circulating thermostated (±0.2 °C) water in the range of 3 to 72 °C. Complex solutions for the spectral observation were prepared by dissolving the isolated complexes into water, acetonitrile, or nitromethane. In the case of $[Ni(AMPE)(H_2O)_2]^{2+}$ and $[Ni(MMPE)(H_2O)_2]^{2+}$ which were not isolated, equimolar amounts of nickel(II) perchlorate and each aqueous tetraamine were mixed. The solute concentration was 5×10^{-3}–10^{-2} M.

Calculation of Thermodynamic Parameters. The following two-type equilibria are studied in this paper

$$\mathrm{Ni(Tet)}^{2+} + 2\mathrm{S} \overset{K_S}{\rightleftharpoons} \mathrm{Ni(Tet)(S)_2}^{2+} \tag{1}$$

$$\mathrm{Ni(Tet)}^{2+} + \mathrm{en} \overset{K_{en}}{\rightleftharpoons} \mathrm{Ni(Tet)(en)}^{2+} \tag{2}$$

where S represents a solvent molecule. The equilibrium constants are

$$K_S = [\mathrm{Ni(Tet)(S)_2}^{2+}]/[\mathrm{Ni(Tet)}^{2+}] \tag{3}$$

$$K_{en} = [\mathrm{Ni(Tet)(en)}^{2+}]/[\mathrm{Ni(Tet)}^{2+}][\mathrm{en}] \tag{4}$$

These constants are equal to the formation constants for the octahedral species in these equilibria. The enthalpy and entropy changes, $\Delta H°$ and $\Delta S°$, are related to the equilibrium constant by the following well-known equation

$$(\Delta H°/T) - \Delta S° = -R \ln K \tag{5}$$

The molar extinction coefficient at the peak of the d–d band associated with the planar species was used to determine the equilibrium constant, since this band is more intense than the d–d bands of octahedral species and hence the spectral change accompanied by variation in temperature is very large. When ϵ is the observed coefficient at the peak of the planar band at a certain temperature, the equilibrium constants become

$$K_S = (1 - x)/x \tag{6}$$

$$K_{en} = (1 - x)/cx^2 \tag{7}$$

$$x = (\epsilon - \epsilon_0)/(\epsilon_{100} - \epsilon_0) \tag{8}$$

where ϵ_0 and ϵ_{100} are the molar extinction coefficients at the peak of the limiting spectra containing 100% octahedral and 100% planar species, respectively, and c is the total concentration of the nickel(II) ion. Equation 8 represents the mole fraction (x) of the planar species.

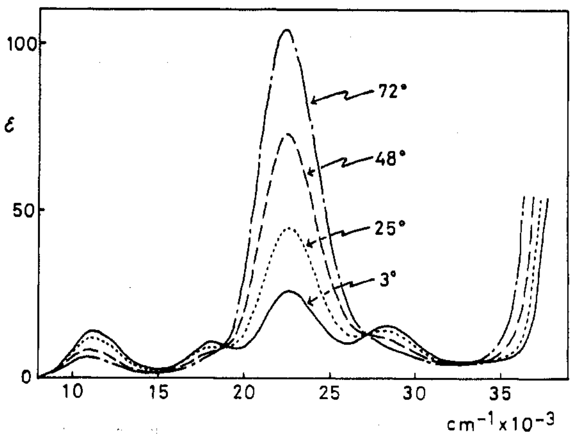

Figure 2. Variable-temperature absorption spectra of the mixed complex of RR-PMCN with ethylenediamine in water.

Table I. Variable-Temperature Molar Extinction Coefficients (ϵ) of the Planar Band and Formation Constants (K_{en}) for the Equilibrium $[Ni(RR\text{-PMCN})]^{2+}$ + en $\rightleftharpoons$ $[Ni(RR\text{-PMCN})(en)]^{2+}$ in Water[a]

T, K	ϵ[b]	x[c]	K_{en}[d]	$\log K_{en}$
276	25.8	0.146	4019	3.60
298	44.6	0.261	1085	3.04
321	72.8	0.434	300	2.48
345	104.3	0.628	94.3	1.98

[a] Total concentration of nickel(II) ion is 1.00×10^{-2} M. [b] At 22 500 cm^{-1}. [c] The limiting values used here are 165 (ϵ_{100}) and $2(\epsilon_0)$ at 22 500 cm^{-1}. [d] K_{en}, mol^{-1}.

In order to calculate the equilibrium constant and other parameters, the two limiting values, ϵ_0 and ϵ_{100}, are required.

The value of ϵ_0 was evaluated to be nearly zero for all complexes.[12] On the other hand, another limiting value, ϵ_{100}, was difficult to estimate experimentally, since the limiting spectra containing 100% planar species could not be obtained within the temperature range accessible to us. In this case, the thermodynamic parameters were calculated by supposing that the enthalpy change ($\Delta H°$) was essentially constant over the narrow range of the temperature employed in this study, that is, that the plot of ln K vs. $1/T$ was linear. Only for the RR-PMCN complex, fortunately, could the value of ϵ_{100} be determined, since the absorption spectra of $[Ni(RR\text{-PMCN})]^{2+}$ in water changed little in the range of 3 to 72 °C.

The dilution effect based on the expansion of the solvent in the measuring cell accompanied by a rise in temperature was neglected, since it was only 1% within the range of the temperature employed in this study. The inherent change of the absorption spectrum with variation in temperature, that is, the spectral change not based on the transformation between the equilibrium species, was also uncorrected.[13]

Results

Figure 2 shows the temperature-dependent absorption spectra of the mixed complex of RR-PMCN with ethylenediamine in an aqueous solution. Some isosbestic points observed support that the equilibrium responsible for this spectral change is a binary system as represented in eq 2. The band at 22 500 cm^{-1} associated with the planar species became markedly greater as the temperature was raised. This indicates that the equilibrium is shifted to the planar species with an increase in temperature. On the other hand, the absorption spectrum of the planar complex of RR-PMCN, $[Ni(RR\text{-PMCN})]^{2+}$, is changed little in the range of 3 to 72 °C in water, suggesting that the equilibrium corresponding to eq 1 is perfectly shifted to the planar species. Then, that molar extinction coefficient ($\epsilon = 165$) at the peak of the planar band can be taken as the value of ϵ_{100} for $[Ni(RR\text{-PMCN})]^{2+}$ in water. Thus, the mole fraction (x) of the planar species and hence the equilibrium constant (K_{en}) at each temperature can be obtained from the spectra depicted in Figure 2. The

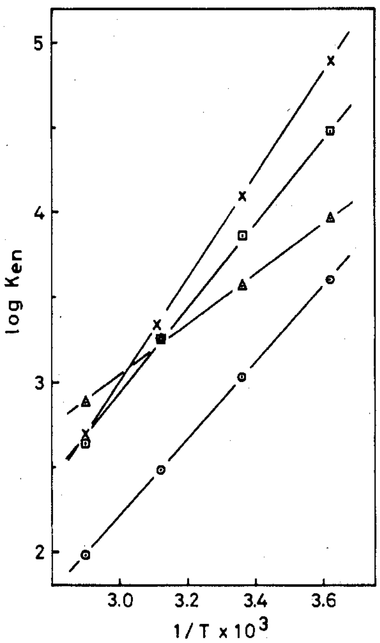

Figure 3. Plots of log K_{en} vs. $1/T$ in water: (◉) [Ni(*RR*-PMCN)(en)]$^{2+}$; (▲) [Ni(*SS*-PMCN)(en)]$^{2+}$; (▣) [Ni(PMEN)(en)]$^{2+}$; (X) [Ni(PMTN)(en)]$^{2+}$.

Table II. Thermodynamic Parameters for the Equilibria $[Ni(Tet)]^{2+} + en \rightleftharpoons [Ni(Tet)(en)]^{2+}$ in Water[a]

Tet		276 K	298 K	321 K	345 K
RR-PMCN	log K_{en}	3.60 ± 0.03	3.04	2.48	1.98 ± 0.05
	ΔH°		10.3 ± 0.1		
	ΔS°	53.8 ± 0.3	48.5	43.4	38.9 ± 0.2
SS-PMCN	log K_{en}	3.96 ± 0.09	3.57	3.26	2.88 ± 0.11
	ΔH°		6.8 ± 0.2		
	ΔS°	42.8 ± 0.3	39.1	36.1	32.9 ± 0.1
PMEN	log K_{en}	4.48 ± 0.08	3.86	3.26	2.60 ± 0.11
	ΔH°		11.4 ± 0.7		
	ΔS°	61.6 ± 2.4	56.0	50.5	44.9 ± 1.6
PMTN	log K_{en}	4.88 ± 0.06	4.10	3.34	2.69 ± 0.07
	ΔH°		13.9 ± 0.1		
	ΔS°	72.6 ± 0.4	65.4	58.5	52.6 ± 0.2

[a] K_{en}, mol^{-1}; ΔH°, kcal mol^{-2}; ΔS°, cal deg^{-1} mol^{-2}.

numerical data of log K_{en} are shown in Table I. The plot of log K_{en} vs. $1/T$ gives a straight line as shown in Figure 3. From the slope of this line, the enthalpy change (ΔH°) is obtained by using the following equation,

$$\ln \frac{K_1}{K_2} = \frac{\Delta H^\circ}{R} \frac{(T_2 - T_1)}{(T_1 T_2)} \qquad (9)$$

and then the entropy change (ΔS°) at each temperature is evaluated by using eq 5. These numerical data are summarized in Table II.

For other complexes of which the limiting spectra containing 100% planar species could not be obtained, the thermodynamic parameters were estimated with a treatment described below. Figure 4 shows the temperature-dependent absorption spectra of the planar and mixed complexes of PMTN, [Ni(PMTN)]$^{2+}$ and [Ni(PMTN)(en)]$^{2+}$, in aqueous solutions. The high temperature dependence in the spectrum of the planar complex of PMTN suggests that its limiting extinction coefficient (ϵ_{100}) is not accessible. In this case, the value of ϵ_{100} is estimated so that both of the plots of log K_{H_2O} vs. $1/T$ and log K_{en} vs. $1/T$ become the best straight lines. In Figure 5 are shown the plots in which the equilibrium constants are calculated on the assumption that the value of ϵ_{100} is 60, 70, or 80. When ϵ_{100} is 70, both plots seem to yield the best lines. Then, the thermodynamic parameters are reasonably calculated by using 70 as ϵ_{100}. The parameters obtained in this way are summarized in Tables II and III. The error inherent in such a treatment is probably large, and hence the errors of the parameters calculated for each system are added in the tables.

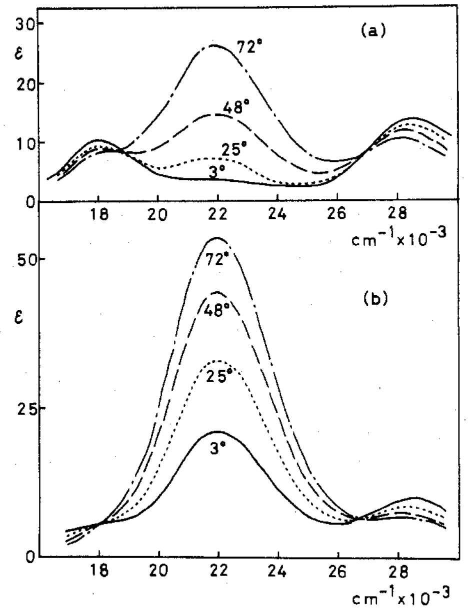

Figure 4. Variable-temperature absorption spectra of the mixed complex with ethylenediamine (a) and planar complex (b) of PMTN in water.

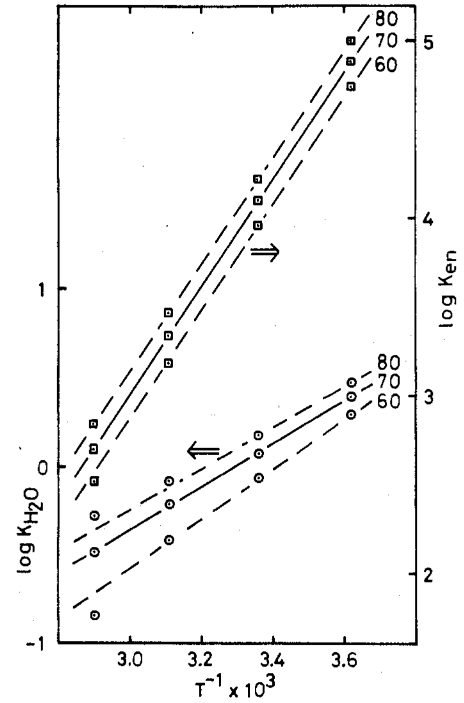

Figure 5. Plots of log K_{H_2O} vs. $1/T$ and log K_{en} vs. $1/T$ for the PMTN complexes in water. The numerical values in this figure are the supposed values of ϵ_{100}.

Table III. Thermodynamic Parameters for the Equilibria $[Ni(Tet)]^{2+} + 2S \rightleftharpoons [Ni(Tet)(S)_2]^{2+}$

Tet	S	T, K	log K_S	ΔH°[a]	ΔS°[b]
SS-PMCN	H_2O	293	−0.28 ± 0.09	3.0 ± 0.6	8.9 ± 1.7
PMTN	H_2O	298	0.07 ± 0.04	5.5 ± 0.2	18.9 ± 0.3
RR-PMCN	CH_3CN	295	−0.67 ± 0.19	3.1 ± 0.8	7.5 ± 1.8
SS-PMCN	CH_3CN	295	0.71 ± 0.08	3.4 ± 0.1	14.8 ± 0.1

[a] ΔH°, kcal mol^{-1}. [b] ΔS°, cal deg^{-1} mol^{-1}.

Besides the equilibrium systems mentioned in Tables II and III, there are some systems for which spectral changes with variation in temperature are so small that their thermodynamic parameters cannot be evaluated. The findings for these systems are described below. In the aqueous solutions of $[\mathrm{Ni(AMPE)(H_2O)_2}]^{2+}$ and $[\mathrm{Ni(MMPE)(H_2O)_2}]^{2+}$, which are not isolated, a new band appeared at about 22 500 $\mathrm{cm^{-1}}$ as a shoulder with increase in temperature (4–72 °C). This suggests that the planar species, $[\mathrm{Ni(AMPE)}]^{2+}$ and $[\mathrm{Ni(MMPE)}]^{2+}$, arise to a small extent at a high temperature. However, the octahedral-type absorption spectrum of the mixed complex of AMPE with ethylenediamine, $[\mathrm{Ni(AMPE)(en)}]^{2+}$, in water was little affected with a rise in temperature (4–72 °C), indicating that the species in this solution is almost octahedral. The planar band of $[\mathrm{Ni}(RR\text{-}\mathrm{PMCN})]^{2+}$ in water did not change as described above. The absorption spectrum of $[\mathrm{Ni(PMTN)}]^{2+}$ in acetonitrile was octahedral type and little changed in the range of 4 to 50 °C, suggesting that the complex is almost octahedral in acetonitrile. In nitromethane, on the other hand, $[\mathrm{Ni(PMTN)}]^{2+}$ and $[\mathrm{Ni}(SS\text{-}\mathrm{PMCN})]^{2+}$ did not exhibit octahedral bands even at 4 °C. This shows that these complexes are almost planar species in nitromethane. The octahedral-type spectrum of $[\mathrm{Ni(AMPP)(en)}]^{2+}$ in water exhibited only a small change, but a new band appeared at 21 300 $\mathrm{cm^{-1}}$ with increase in temperature (4–72 °C). This suggests that the planar species, $[\mathrm{Ni(AMPP)}]^{2+}$, arises to a small extent as temperature is raised.

Discussion

For the tetraamines used in this study, the preference of the octahedral-type coordination to nickel(II) ion decreases in the order (25 °C) AMPE $\simeq$ MMPE > AMPP >> PMTN > PMEN > *SS*-PMCN > *RR*-PMCN. This order holds for both of the two-type equilibria, eq 1 and 2. However, since the enthalpy change for each equilibrium system is different in each case, the above order partly varies with the temperature, as may be seen in Figure 3.

There are some noticeable points in the above order, and they are discussed as follows. The first point is related to *RR*-PMCN and *SS*-PMCN which are diastereomeric; the former prefers remarkably the planar-type coordination to the octahedral-type one compared with the latter. As shown in the previous paper,[10] the planar complex of *SS*-PMCN is forced to contain the envelope-type chelate rings due to the central *SS*-cyclohexane ring. On the other hand, each chelate ring in the planar complex of *RR*-PMCN can take either of gauche forms. The envelope-type chelate rings would mainly reduce the preference of the planar-type coordination of *SS*-PMCN. The small $\Delta H°$ value for the *SS*-PMCN complex may be a reflection of this instability in the planar species. Nevertheless, the formation constant for $[\mathrm{Ni}(SS\text{-}\mathrm{PMCN})(\mathrm{en})]^{2+}$ is not large compared with those for $[\mathrm{Ni(PMEN)(en)}]^{2+}$ and $[\mathrm{Ni(PMTN)(en)}]^{2+}$. This is probably based on the fact that the $\Delta S°$ value for the *SS*-PMCN complex is much smaller than those for the other complexes as shown in Table II and hence it more than makes up for the small $\Delta H°$ value.

It is well-known that 2,3,2-tet forms more readily a planar species of nickel(II) ion than trien, suggesting that the planar form of the tetraamine complex with 5,6,5-membered tri-fused chelate rings is more stable than that with 5,5,5-membered rings.[5,14] This is applicable not only to the tetraamine complexes of nickel(II) ion, but also to other tetradentate ligands and other metal ions.[15–20] However, PMTN which has the skeleton of 2,3,2-tet shows a tendency to form octahedral species more readily than PMEN which has a trien-like skeleton. This may be a manifestation of the steric effect of the pyrrolidine rings. On the other hand, AMPP capable of forming a 5,6,5-membered tri-fused chelate forms a planar species more readily than AMPE. This is similar to the relation between 2,3,2-tet and trien. The unfavorable formation of the planar species with AMPE is probably a reflection on the large strain involved when it takes up a planar configuration.

As to AMPP having a methylene linkage further introduced into AMPE, the molecular models which are relatively strain free can be constructed for the planar configuration. Nevertheless, AMPP hardly forms the planar species. This is indicative of the very large strain of the pyrrolidine rings beyond the expectation on the basis of the molecular models. Other tetraamines which have the two pyrrolidinyl groups at their terminal parts tend to form rather planar species in aqueous solutions. This is a noteworthy finding in comparison with trien and 2,3,2-tet which form octahedral species more readily than planar ones. The pyrrolidine rings as the terminal group may possess a certain steric effect to prefer a planar form to an octahedral one.

As can be seen from Table III, octahedral species of the *SS*-PMCN complex increase in acetonitrile more than in water. This is apparently due to the large $\Delta S°$ value in acetonitrile. In the following order of solvents the octahedral species of the tetraamine complexes are stabilized as described in the Results section

$$\mathrm{CH_3NO_2} < \mathrm{H_2O} < \mathrm{CH_3CN}$$

Also in bis(diamine)nickel(II) complexes, their planar form is stable in nitromethane.[21–23] This suggests that nitromethane hardly coordinates to the planar nickel(II) complexes of diamines or tetraamines. However, the above order does not coincide with the order of the donor number of their solvents, which is a measure of the donor strength (coordination or solvation ability) of the solvents.[24] This problem will be further investigated in the near future.

Registry No. $[\mathrm{Ni}(RR\text{-}\mathrm{PMCN})]^{2+}$, 53553-36-9; $[\mathrm{Ni}(SS\text{-}\mathrm{PMCN})]^{2+}$, 56086-18-1; $[\mathrm{Ni(PMEN)}]^{2+}$, 53553-38-1; $[\mathrm{Ni(PMTN)}]^{2+}$, 59187-65-4; $[\mathrm{Ni(PMCN)(en)}]^{2+}$, 56029-99-3; $[\mathrm{Ni(PMEN)(en)}]^{2+}$, 56029-97-1; $[\mathrm{Ni(PMTN)(en)}]^{2+}$, 59187-67-6; $[\mathrm{Ni}(SS\text{-}\mathrm{PMCN})(\mathrm{H_2O})_2]^{2+}$, 59547-49-8; $[\mathrm{Ni(PMTN)(H_2O)_2}]^{2+}$, 59532-86-4; $[\mathrm{Ni}(RR\text{-}\mathrm{PMCN})(\mathrm{CH_3CN})_2]^{2+}$, 59532-87-5; $[\mathrm{Ni}(SS\text{-}\mathrm{PMCN})(\mathrm{CH_3CN})_2]^{2+}$, 59573-79-4.

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The Tris[(±)-*trans*-1,2-cyclohexanediamine]cobalt(III) System

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The isomers $[\mathrm{Co}((\pm)\mathrm{chxn})_3]\mathrm{Cl}_3$ (chxn = *trans*-1,2-cyclohexanediamine) comprise two catoptric series with the configurations Δ and Λ around the metal ion. The chelate rings formed by the ligands (−)-*R*,*R*-chxn and (+)-*S*,*S*-chxn have the conformations λ and δ, respectively. For each of the configurational series the possible ligand conformations give rise to four diastereoisomers which have been named lel_3, $\mathrm{lel}_2\mathrm{ob}$, $\mathrm{ob}_2\mathrm{lel}$, and ob_3. These eight isomers have been isolated and characterized. The equilibrium between the isomers has been established at 100 °C and the standard free energies for the interconversion between the diastereoisomers have, after a statistical correction, been interpreted in a ring-pair relationship model whose two parameters fully account for the equilibrium data.

Introduction

The two isomers of tris[$(-)_{589}$-*trans*-1(*R*),2(*R*)-cyclohexanediamine]cobalt(III) chloride, $[\mathrm{Co}((-)\mathrm{chxn})_3]\mathrm{Cl}_3$, have been known[1] for some time and the corresponding isomers of rhodium(III),[2] iridium(III),[3] and chromium(III)[4] have recently been isolated. The stereochemical difference between the two isomers may be characterized as an interplay of the conformation of the five-membered chelate rings and the configuration around the central metal ion. The chelate ring formed by the ligand, (−)chxn, has the conformation λ, which when associated with the configurations Δ and Λ gives rise to the diastereoisomer ions Δ-$[\mathrm{Co}((-)\mathrm{chxn})_3\text{-}\lambda\lambda\lambda]^{3+}$ and Λ-$[\mathrm{Co}((-)\mathrm{chxn})_3\text{-}\lambda\lambda\lambda]^{3+}$.

The discussion of the isomerism and nomenclature of tris(diamine) complexes[5,6] containing racemic chxn will be summarized briefly.

The diastereochemical relationship between the conformation of each chelate ring and the configuration of the tris complex can be characterized by the symbols lel and ob defined by

$$\begin{aligned} \mathrm{lel} &\equiv \lambda(\Delta) \text{ or } \delta(\Lambda) \\ \mathrm{ob} &\equiv \delta(\Delta) \text{ or } \lambda(\Lambda) \end{aligned} \qquad (1)$$

The symbols lel and ob refer to the direction of the bond between the carbon atoms attached to the ligating nitrogen atoms, being almost paral*lel* and *ob*lique, respectively, to the threefold axis defined by the three edges of the octahedron which are spanned by the chelate rings. Thus the symbol $\lambda(\Delta)$, for example, means the conformation λ in the configuration Δ. If symmetry operations are applied to the entries of eq 1, it is seen that the symbols lel and ob are invariant to proper as well as to improper rotations,[6] whereas the chirality symbols are changed into their catoptric (= enantiomeric) forms under the latter operations. For example, application of an improper rotation to the lel system $\lambda(\Delta)$ yields $\delta(\Lambda)$, which is also lel. It follows that the complexes mentioned above can be characterized[7] as Δ-lel_3 and Λ-ob_3, respectively. Originally, Corey and Bailar[8] used the designation lel and ob for such isomers, but this notation is not sufficient for the present purpose and has accordingly been modified[7] because we want to consider complexes which simultaneously contain chelate rings of lel and ob type.

In the case when $[\mathrm{Co}(\mathrm{chxn})_3]^{3+}$ is prepared from racemic *trans*-1, 2-cyclohexanediamine, one obtains four racemic pairs of complexes

$$\begin{array}{ll} \Delta\text{-}\lambda_3 \text{ and } \Lambda\text{-}\delta_3 & (\Delta\text{-lel}_3 \text{ and } \Lambda\text{-lel}_3) \\ \Delta\text{-}\lambda_2\delta \text{ and } \Lambda\text{-}\delta_2\lambda & (\Delta\text{-lel}_2\text{ob and } \Lambda\text{-lel}_2\text{ob}) \\ \Delta\text{-}\delta_2\lambda \text{ and } \Lambda\text{-}\lambda_2\delta & (\Delta\text{-ob}_2\text{lel and } \Lambda\text{-ob}_2\text{lel}) \\ \Delta\text{-}\delta_3 \text{ and } \Lambda\text{-}\lambda_3 & (\Delta\text{-ob}_3 \text{ and } \Lambda\text{-ob}_3) \end{array} \qquad (2)$$

In the present work the eight isomers have been separated, the equilibrium ratios have been determined, and the circular dichroism spectra have been measured.

The two isomers Δ-lel_3 and Λ-ob_3 that can be formed from (−)chxn can easily be separated by recrystallization from boiling water by addition of hydrochloric acid, since the lel_3 isomer and the ob_3 isomer have solubility minima in ca 0.4 and ca. 4 M hydrochloric acid, respectively.

A rather special technique is employed for the separation of all eight isomers. A cation exchanger is used with sodium ions as eluting agents but with a suitable anion to effect the separation. Phosphate ions are used in the separation of the four racemic pairs which are eluted in the sequence of (2) with the lel_3 catoptromers leaving the column first. Each racemic pair is then sorbed separately on a new column and separated by the method of Yoshikawa and Yamasaki[9] using ammonium (+)-tartrate. In each case the Λ catoptromer leaves the column first, as also found[9] for the tris(ethylenediamine)cobalt(III) system. The column separations are analogous to those of the tris[(±)-1,2-propanediamine]cobalt(III) system.[5]

Experimental Section

***trans*-1,2-Cyclohexanediamine** was resolved as described by Galsbol, Steenbol, and Sorensen.[2]

Λ-$[\mathrm{Co}((+)\mathrm{chxn})_3\text{-}\delta\delta\delta]\mathrm{Cl}_3\cdot{\sim}4\mathrm{H_2O}$ and Δ-$[\mathrm{Co}((+)\mathrm{chxn})_3\text{-}\delta\delta\delta]\mathrm{Cl}_3\cdot1.5\mathrm{H_2O}$. A 170-g sample of *trans*-$[\mathrm{Co(py)_4Cl_2}]\mathrm{Cl}\cdot6\mathrm{H_2O}$ (0.29 mol) was dissolved in 400 ml of methanol at 40 °C and mixed into a solution of 100 g of (+)chxn (0.88 mol) dissolved in 600 ml of methanol at 40 °C. While being stirred the mixture was allowed to cool and was then filtered. The precipitate was washed with methanol and dried; yield 130 g of tris complex, mainly Λ-lel_3.

Before the separation of the two isomers Λ-lel_3 and Δ-ob_3 it is convenient to establish the equilibrium between them. Accordingly 130 g of the tris complex was dissolved in 1450 ml of water at 100 °C, ca. 1 g of (+)chxn was added, and then the pH was adjusted to 7. After addition of 8 g of charcoal and refluxing for 2 h the hot solution was filtered and partially evaporated in vacuo to yield ca. 100 g of Λ-lel_3. The residue which contains ca. 9 g of Δ-ob_3 (cf. Table II) was also evaporated to dryness.

The crude Λ-lel_3 isomer was reprecipitated using the following general procedure. x g of Λ-lel_3 was dissolved in ca. $8x$ ml of water at 100 °C. After filtration $0.8x$ ml of 4 M hydrochloric acid was added and the solution was cooled on ice and filtered. The precipitate