

**Table III.** Second-Order Rate Constants and Activation Parameters for the Base Hydrolysis of Some Complexes of the type *trans*-[CoLAX]<sup>+</sup>

L	A	X	$k_{OH}(25.0^\circ C)$ , $M^{-1} s^{-1}$	$\Delta H^\ddagger$ , kcal $mol^{-1}$	$\Delta S^\ddagger$ , cal $mol^{-1}$ $K^{-1}$
cyclam <sup>a</sup>	Cl	Cl	$6.7 \times 10^4$	13.7	12
cyclam <sup>b</sup>	NCS	Cl	$9.0 \times 10^2$	21.1	25
cyclam <sup>c</sup>	NCS	Br	$1.5 \times 10^4$	$18.8 \pm 0.3$	$24 \pm 2$
teta <sup>d</sup>	Cl	Cl	$5.7 \times 10^5$		
teta <sup>e</sup>	NCS	Cl	$2.5 \times 10^4$	$16.3 \pm 0.3$	$16 \pm 2$
teta <sup>f</sup>	NCS	Br	$9.8 \times 10^4$	$13.0 \pm 0.4$	$8 \pm 3$
<i>trans</i> [14]diene <sup>d</sup>	Cl	Cl	$2.2 \times 10^5$		
<i>trans</i> [14]diene <sup>e</sup>	NCS	Cl	$1.7 \times 10^5$	$12.6 \pm 0.3$	$8 \pm 2$
<i>trans</i> [14]diene <sup>f</sup>	NCS	Br	$3.9 \times 10^5$	$13.6 \pm 0.5$	$13 \pm 4$
(en) <sub>2</sub> <sup>e,f</sup>	Cl	Cl	$3.2 \times 10^3$	22.6	33
(en) <sub>2</sub> <sup>f,g</sup>	NCS	Cl	$1.3 \times 10$	22.6	22
(NH <sub>3</sub> ) <sub>4</sub> <sup>e</sup>	Cl	Cl	$1.8 \times 10^3$		
(NH <sub>3</sub> ) <sub>4</sub> <sup>b</sup>	NCS	Cl	5.4	29.6	44
<i>RS</i> -2,3,2-tet <sup>h</sup>	Cl	Cl	$4 \times 10^4$		
<i>RR(SS)</i> -2,3,2-tet <sup>h</sup>	Cl	Cl	$8.8 \times 10^4$	13.6	9

<sup>a</sup> C. K. Poon, Ph.D. Thesis, University of London, 1967. <sup>b</sup> K. S. Mok, C. K. Poon, and H. W. Tong, *J. Chem. Soc., Dalton Trans.*, 1701 (1972). <sup>c</sup> This work. <sup>d</sup> At 19.8 °C; J. A. Kernohan and J. F. Endicott, *Inorg. Chem.*, 9, 1504 (1970). <sup>e</sup> R. G. Pearson, R. E. Meeker, and F. Basolo, *J. Am. Chem. Soc.*, 78, 709 (1956). <sup>f</sup> en = ethylenediamine; activation parameters are extracted from J. O. Edwards, F. Monacelli, and G. Ortaggi, *Inorg. Chim. Acta.*, 11, 47 (1974). <sup>g</sup> C. K. Ingold, R. S. Nyholm, and M. L. Tobe, *J. Chem. Soc.*, 1691 (1956). <sup>h</sup> Extrapolated from data published by E. Ahmed, M. L. Tucker, and M. L. Tobe, *Inorg. Chem.*, 14, 1 (1975).

*trans* to the acidic protons. The base hydrolysis of the cyclam series of complexes is most interesting in that the dichloro complex is "limiting" whereas the chloroisothiocyanato complex is still "normal". Accordingly, the kinetic ratio of  $k_{Cl_2}/k_{NCSCl}$  (74) is smaller than the corresponding ratio for bis(ethylenediamine) (250) and tetraamine (330) complexes. Inspection of the rate constant and activation parameters for

*trans*-[Co(cyclam)NCSBr]<sup>+</sup> seems to indicate that the base hydrolysis of this complex is getting close to but has not yet reached the "limiting" condition as shown by the failure to detect general base catalysis (i.e.,  $k_{-1} \gtrsim k_2$ ).

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**Registry No.** *trans*-[Co(cyclam)(NCS)Br]ClO<sub>4</sub>, 59204-55-6; *trans*-[Co(cyclam)(NCS)Cl]<sup>+</sup>, 46931-41-3; *trans*-[Co(teta)(NCS)Cl]<sup>+</sup>, 55032-63-8; *trans*-[Co(teta)(NCS)Br]<sup>+</sup>, 55032-93-4; *trans*-[Co(*trans*[14]diene)(NCS)Cl]<sup>+</sup>, 55032-53-6; *trans*-[Co(*trans*[14]diene)(NCS)Br]<sup>+</sup>, 55032-55-8; *trans*-[Co(cyclam)Br<sub>2</sub>]Br, 34460-16-7.

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- (16) The base hydrolysis of *trans*-[Co(teta)NCSCl]<sup>+</sup> may be just at the borderline between "limiting" and "nonlimiting" as reflected by its relatively slower rate constant and higher  $\Delta H^\ddagger$  than its bromoisothiocyanato and dichloro analogues.
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## Preparation and Circular Dichroism of Nickel(II) Complexes Containing Optically Active Tetraamines with Pyrrolidinyl Groups. Nickel(II) Complexes with a Six-Membered Chelate Ring

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The nickel(II) complexes with 1,3-bis[2(*S*)-aminomethyl-1-pyrrolidinyl]propane (AMPP), 1,3-bis[2(*S*)-*N*-methylaminomethyl-1-pyrrolidinyl]propane (MMPP), and *N,N*-bis[2(*S*)-pyrrolidinylmethyl]-1,3-trimethylenediamine (PMTN) which have the skeleton of 2,3,2-tet were prepared; AMPP and MMPP formed octahedral species, while PMTN formed square-planar ones in aqueous solutions. It was confirmed that whether these tetraamines containing pyrrolidinyl groups form octahedral or planar species of nickel(II) ion depends upon the position of the two pyrrolidinyl groups within the tetraamines themselves. The member of the central chelate ring is not significant for this selective complexation. The mixed complexes of AMPP and PMTN with ethylenediamine were isolated. The CD spectra of these complexes were compared with those of the complexes with the other tetraamines which have the skeleton of trien.

In the previous papers,<sup>2,3</sup> we have reported on the formation of the nickel(II) complexes with the five types of optically active tetraamines which have two pyrrolidinyl groups in each molecule. 1,2-Bis[2(*S*)-aminomethyl-1-pyrrolidinyl]ethane (AMPE)<sup>4</sup> and 1,2-bis[2(*S*)-*N*-methylaminomethyl-1-pyrrolidinyl]ethane (MMPE) formed blue octahedral complexes with nickel(II) ion in aqueous solutions, while *N,N'*-

bis[2(*S*)-pyrrolidinylmethyl]ethylenediamine (PMEN), *N,N'*-bis[2(*S*)-pyrrolidinylmethyl]-1(*R*),2(*R*)-cyclohexanediamine (*RR*-PMCEN), and *N,N'*-bis[2(*S*)-pyrrolidinylmethyl]-1(*S*),2(*S*)-cyclohexanediamine (*SS*-PMCEN) formed yellow square-planar ones. This selectivity may be related to the position of the two pyrrolidinyl groups within the tetraamines; AMPE and MMPE have the two pyrrolidinyl groups

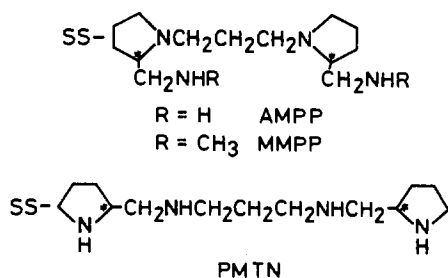


Figure 1. Optically active tetraamines including two pyrrolidinyl groups; *S* represents the absolute configuration of asymmetric carbon atoms.

in their inner parts, whereas the other three tetraamines have them as the terminal groups.

Figure 1 shows the structural formulas of new tetraamines, 1,3-bis[2(*S*)-aminomethyl-1-pyrrolidinyl]propane (abbreviated to AMPP), 1,3-bis[2(*S*)-*N*-methylaminomethyl-1-pyrrolidinyl]propane (MMPP), and *N,N'*-bis[2(*S*)-pyrrolidinylmethyl]-1,3-trimethylenediamine (PMTN), which have the skeleton of 2,3,2-tet (NH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>NHCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>NHC-H<sub>2</sub>CH<sub>2</sub>NH<sub>2</sub>). The central trimethylenediamine linkage in these tetraamines may coordinate to a metal ion to form a six-membered chelate ring. It is of interest to investigate the influence of the six-membered chelate ring on the selective formation of nickel(II) complexes and on the optical activity of the complexes. In this paper, we wish to report on the preparation and circular dichroism (CD) of the nickel(II) complexes containing AMPP, MMPP, and PMTN.

### Experimental Section

**Preparation. Tetraamines.** AMPP and MMPP were prepared with the same procedure as AMPE and MMPE<sup>3</sup> by using 1,3-dibromopropane instead of 1,2-dibromoethane. PMTN was prepared with the procedure mentioned in the preparation of PMEN<sup>3</sup> by using 1,3-trimethylenediamine instead of 1,2-ethylenediamine.

[Ni(PMTN)](ClO<sub>4</sub>)<sub>2</sub>. An aqueous solution containing 1.1 g of nickel(II) perchlorate and 0.75 g of PMTN was allowed to stand at room temperature in an evaporating dish. Within several days, orange needles separated out and were washed with ethanol. The needles were recrystallized from water. Anal. Calcd for [Ni(C<sub>13</sub>H<sub>28</sub>N<sub>4</sub>)](ClO<sub>4</sub>)<sub>2</sub>: C, 31.35; H, 5.66; N, 11.25. Found: C, 31.31; H, 5.63; N, 11.06.

[Ni(PMTN)(en)](ClO<sub>4</sub>)<sub>2</sub>. To a yellow aqueous solution of [Ni(PMTN)](ClO<sub>4</sub>)<sub>2</sub> was added an aqueous ethylenediamine solution, drop by drop, until the solution turned reddish purple. The mixture was allowed to stand for a few days at room temperature in an evaporating dish. The separated deep purple prisms were washed with ethanol and then recrystallized from water. Anal. Calcd for [Ni(C<sub>15</sub>H<sub>36</sub>N<sub>6</sub>)](ClO<sub>4</sub>)<sub>2</sub>: C, 32.29; H, 6.51; N, 15.05. Found: C, 31.93; H, 6.74; N, 14.76.

[Ni(AMPP)(en)](ClO<sub>4</sub>)<sub>2</sub>. To a blue aqueous solution containing equimolar amounts of nickel(II) perchlorate and AMPP was added aqueous ethylenediamine. The purple solution was allowed to stand at room temperature. Within a few days, bluish purple needles separated out. The needles were washed with ethanol and recrystallized from water. Anal. Calcd for [Ni(C<sub>15</sub>H<sub>36</sub>N<sub>6</sub>)](ClO<sub>4</sub>)<sub>2</sub>: C, 32.29; H, 6.51; N, 15.05. Found: C, 32.00; H, 6.42; N, 14.51.

**Measurements.** Visible, ultraviolet, and near-infrared absorption spectra were measured with a Hitachi EPS-3T spectrophotometer. CD spectra in the region of 185–1000 nm were measured with a Jasco J-20A recording spectropolarimeter and those above 1000 nm were obtained by a Jasco J-100 recording spectropolarimeter<sup>5</sup> at room temperature. Each of the complex solutions for spectral observation was prepared by dissolving the isolated complexes in water, methanol, or acetonitrile or by mixing equimolar aliquots of nickel(II) perchlorate with aqueous tetraamines.

### Results and Discussion

The aqueous solution containing equimolar amounts of nickel(II) perchlorate and AMPP or MMPP was blue, indicating that AMPP and MMPP mostly form octahedral

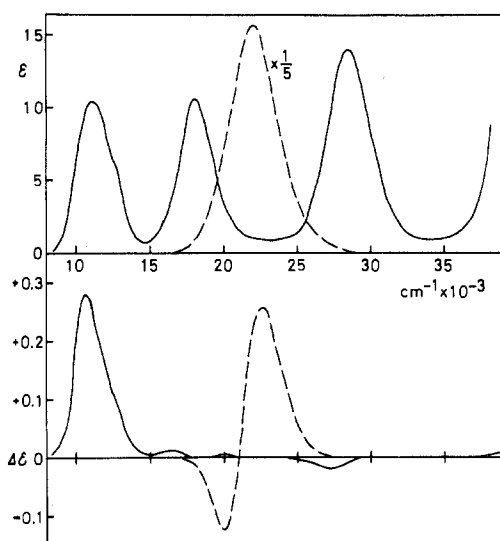


Figure 2. Absorption and CD spectra of [Ni(PMTN)(en)]<sup>2+</sup> (—) in acetonitrile and [Ni(PMTN)]<sup>2+</sup> (---) in methanol.

species of nickel(II) ion. On the other hand, the aqueous solution containing PMTN was yellow, suggesting that PMTN prefers square-planar species to octahedral ones. This selectivity that AMPP and MMPP having the two pyrrolidinyl groups in their inner parts coordinate to nickel(II) ion to form octahedral species whereas PMTN having them as the terminal groups forms planar species agreed with the selectivity previously observed for AMPE, MMPE, *RR*-PMCN, *SS*-PMCN, and PMEN.<sup>3</sup> Therefore, it is reasonable to conclude that the position of the two pyrrolidinyl groups within the tetraamines governs the selectivity in the formation of nickel(II) complexes. Whether the central chelate ring is a five- or six-membered ring is not so significant in the case of the tetraamines with the pyrrolidinyl groups. This is different from the case of 2,3,2-tet and trien; the aqueous solution of Ni(2,3,2-tet)<sup>2+</sup> contains much more of the planar species than that of Ni(trien)<sup>2+</sup> does.<sup>6,7</sup> The pyrrolidinyl groups at the inner parts may give the tetraamines themselves too large strain to coordinate in a plane.

In the absorption spectrum of the isolated planar complex of PMTN, [Ni(PMTN)](ClO<sub>4</sub>)<sub>2</sub>, in an aqueous solution were detected weak bands associated with octahedral species besides a main band at 22 000 cm<sup>-1</sup> typical of square-planar species. This shows that the equilibrium between planar and octahedral species exists in its aqueous solution. The weak bands disappeared entirely in methanol. In Figure 2 are shown the absorption and CD spectra of the PMTN complex in methanol. The PMTN complex exhibited two CD bands, negative at 20 000 cm<sup>-1</sup> and positive at 22 700 cm<sup>-1</sup>. These two CD bands probably correspond to the two magnetically allowed *d-d* transitions (*d*<sub>xz</sub>, *d*<sub>yz</sub> → *d*<sub>x<sup>2</sup>-y<sup>2</sup></sub>, *d*<sub>xy</sub> → *d*<sub>x<sup>2</sup>-y<sup>2</sup></sub>) of a square-planar type nickel(II) complex. For the planar complexes of *RR*-PMCN, *SS*-PMCN, and PMEN, on the other hand, only one positive CD band is observed at about 23 000 cm<sup>-1</sup>.<sup>3,8</sup> In the case of these complexes, the two *d-d* transitions probably impose optical activities with the same sign, or either of the two transitions may contribute little to the optical activity.

When PMTN coordinates in a plane, the two terminal rings should take a *δ*-gauche form which is stable for an (*S*)-diamine moiety and then the central six-membered chelate ring would be forced to adopt a skew-λ form as shown in Figure 3. This conformation is very similar to those expected for the *RR*-PMCN and PMEN complexes except for the distinction between the six- and five-membered rings in the central chelate part. Therefore, the contribution of the six-membered chelate ring to the whole conformation of the complex is expected to

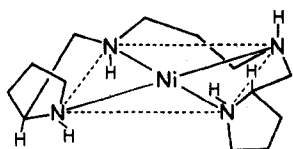


Figure 3. Schematic drawing of the structure of the planar PMTN complex.

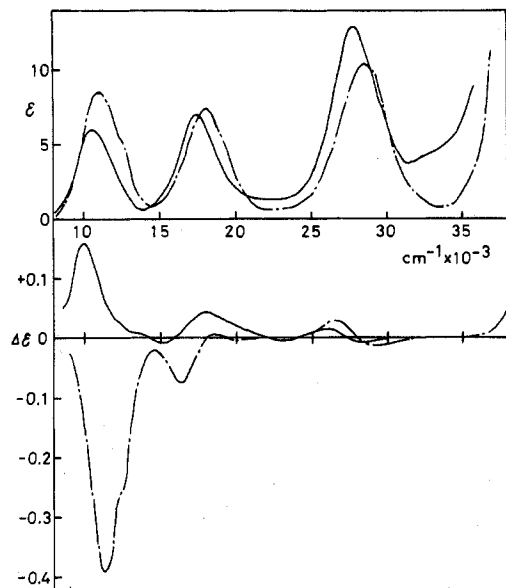


Figure 4. Absorption and CD spectra of  $[\text{Ni}(\text{AMPP})(\text{en})]^{2+}$  (—) and  $[\text{Ni}(\text{AMPE})(\text{en})]^{2+}$  (---) in water.

be responsible for the appearance of the negative CD band in the PMTN complex. Thus, the angle between the nitrogen atoms and the central nickel(II) ion (N-Ni-N) in the six-membered chelate ring will be larger than that in the five-membered ring.<sup>13</sup> It has been theoretically accepted by many investigators that this angle of the chelate ring plays a significant role for the optical activity of metal complexes.<sup>14</sup>

The aqueous solution of the mixed complex of PMTN with ethylenediamine,  $[\text{Ni}(\text{PMTN})(\text{en})](\text{ClO}_4)_2$ , was purple indicative of octahedral  $[\text{Ni}(\text{N})_6]$ -type species, but its absorption spectrum exhibited a small peak at  $22\,000\text{ cm}^{-1}$  which comes from the remaining planar species. The small band entirely disappeared when the mixed complex was dissolved in acetonitrile. This is very similar to the phenomena which have been already found for the mixed complexes of *RR*-PMCN, *SS*-PMCN, and PMEN with ethylenediamine.<sup>3</sup> For the mixed complex of AMPP, on the other hand, no absorption band was detected at about  $22\,000\text{ cm}^{-1}$  in an aqueous solution, similar to the case for the mixed complex of AMPE. As may be seen in Figure 4, the three absorption bands observed for the mixed complex of AMPP locate at much lower wavenumbers than those for all of the other mixed complexes. The wavenumbers of its absorption maxima suggest  $[\text{Ni}(\text{N}_4\text{O}_2)]$ - or  $[\text{Ni}(\text{N}_5\text{O})]$ -type coordination.<sup>3</sup> This implies the dissociation of the ethylenediamine from the mixed complex of AMPP in solution, but it does not seem to be the case. The reason is

the fact that the positions of the absorption bands are almost the same as those in acetonitrile. Moreover, the mixed complex of AMPP is more pale bluish even in the solid state than the other mixed complexes. Therefore, this spectral profile is thought to be characteristic of the mixed complex of AMPP.

The two mixed complexes of PMTN and AMPP exhibited similar CD curves which have one large positive band at the lower wavenumber side within the region of the first (lowest energy) absorption band. These CD spectra are quite different from those for the mixed complexes of the other tetraamines, which exhibit a main negative CD band at the higher wavenumber side. For reference, the CD spectrum of the mixed complex of AMPE, which is very similar to those of the mixed complexes of *RR*-PMCN, *SS*-PMCN, and PMEN,<sup>3</sup> is shown in Figure 4. Then, it can be said that the six-membered chelate ring in the central part affects the optical activity of the mixed complexes.

The structure of the mixed complexes of *RR*-PMCN, *SS*-PMCN, and PMEN has been expected to be  $\Delta$ -cis- $\alpha$  on the basis of their CD spectra and the examination by using molecular models.<sup>3</sup> Recently, it was reported that only  $\Delta$ -cis- $\alpha$  cobalt(III) complexes of PMEN were stereoselectively obtained.<sup>15</sup> This supports our expectation for the structure of the mixed nickel(II) complexes. However, the structures of the mixed complexes of PMTN and AMPP are still poorly characterized. Therefore, there is no explicit decision as to whether this difference in the CD spectra is due to the difference in the whole configuration of the mixed complexes or merely due to the distinction in the central chelate ring. In either of the two cases, however, the six-membered chelate ring in the central part probably plays an important role in the conformation or the optical activity of the complexes.

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**Registry No.**  $[\text{Ni}(\text{PMTN})(\text{ClO}_4)_2]$ , 59187-66-5;  $[\text{Ni}(\text{PMTN})(\text{en})(\text{ClO}_4)_2]$ , 59187-68-7;  $[\text{Ni}(\text{AMPP})(\text{en})(\text{ClO}_4)_2]$ , 59187-70-1; ethylenediamine, 107-15-3.

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