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STEREOSPECIFIC COORDINATION OF SOME OPTICALLY ACTIVE TETRAMINES TO NICKEL(II) ION

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The nickel(II) complexes of optically active tetramines having two pyrrolidinyl groups in each molecules were investigated. 1,2-Bis[2(S)-2-aminomethyl-1-pyrrolidinyl]ethane and 1,2-bis[2(S)-2-N-methylaminomethyl-1-pyrrolidinyl]ethane formed octahedral complexes, while N,N'-bis[2(S)-2-pyrrolidinylmethyl]-1,2-ethylenediamine and N,N'-bis[2(S)-2-pyrrolidinylmethyl]-1(R),2(R)-cyclohexanediamine formed square planar ones.

There have been a large number of studies of "inert" cobalt(III) complexes of linear tetramines, many isomers of which can be isolated. On the other hand, from a stereochemical point of view, not so many has been reported concerning "labile" nickel(II) complexes, because it is much difficult to isolate each of their possible isomers. However, the ligands having a type of steric restriction in themselves may coordinate stereospecifically to the labile nickel(II) ion. In fact, from an aqueous solution containing nickel(II) carbonate and L-proline, fac(N)-Λ-[Ni(L-prolinate)$_3$]$^-$ was predominantly isolated.1) The stereospecificity is attributed to the steric restriction of the pyrrolidine ring in L-proline, the nitrogen of which can coordinate only with the S-configuration. Therefore, it may be expected that other ligands with pyrrolidinyl groups also coordinate to nickel(II) ion stereospecifically.

In this letter, we wish to report the stereospecific coordination of optically active tetramines, which have two pyrrolidinyl groups in each molecules, to nickel(II) ion.

When equimolar amounts of nickel(II) ion and 1,2-bis[2(S)-2-aminomethyl-1-pyrrolidinyl]ethane(AMPE)2) or 1,2-bis[2(S)-2-N-methylaminomethyl-1-pyrrolidinyl]-ethane(MMPE)2) were mixed in aqueous solutions, the solution turned blue. On the other hand, when N,N'-bis[2(S)-2-pyrrolidinylmethyl]-1,2-ethylenediamine(PMEN)[2)] or N,N'-bis[2(S)-2-pyrrolidinylmethyl]-1(R),2(R)-cyclohexanediamine(PMCN)[2)] was used as a ligand, the color of the solution was yellow. Of these four complexes, only [Ni(PMCN)]$(ClO_4)_2$ was isolated as yellow crystals from its aqueous solution. Found: C, 36.2; H, 6.22; N, 10.3 %. Calcd for $C_{16}H_{32}N_4O_8Cl_2Ni$:C, 35.8; H, 5.99; N, 10.3 %.

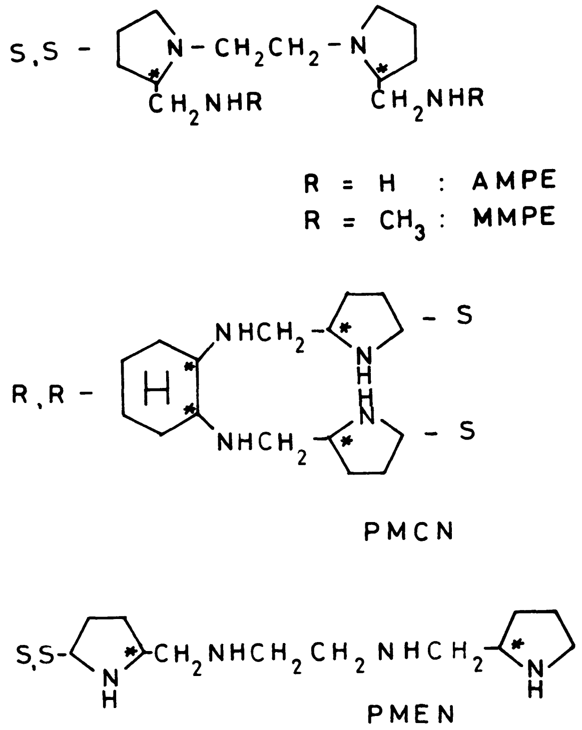

Fig.1 Tetramines

The absorption and circular dichroism(CD) spectra of these solutions are shown in Fig. 2. The blue and yellow nickel(II) complexes are, as well-known, corresponding to the octahedral-type and the square planar-type complexes, respectively. The absorption spectra of the blue complexes have three d-d bands typical of octahedrally coordinated nickel(II) ion. The ν_{max} values of these three bands show the formation of [Ni(N_4O_2)]-type complexes. The CD spectra reveal optical activity in all three absorption bands, but not to the same degree. The lowest energy band ($^3A_{2g} \rightarrow {}^3T_{2g}$) is only one of the three transitions, which is magnetically allowed in the

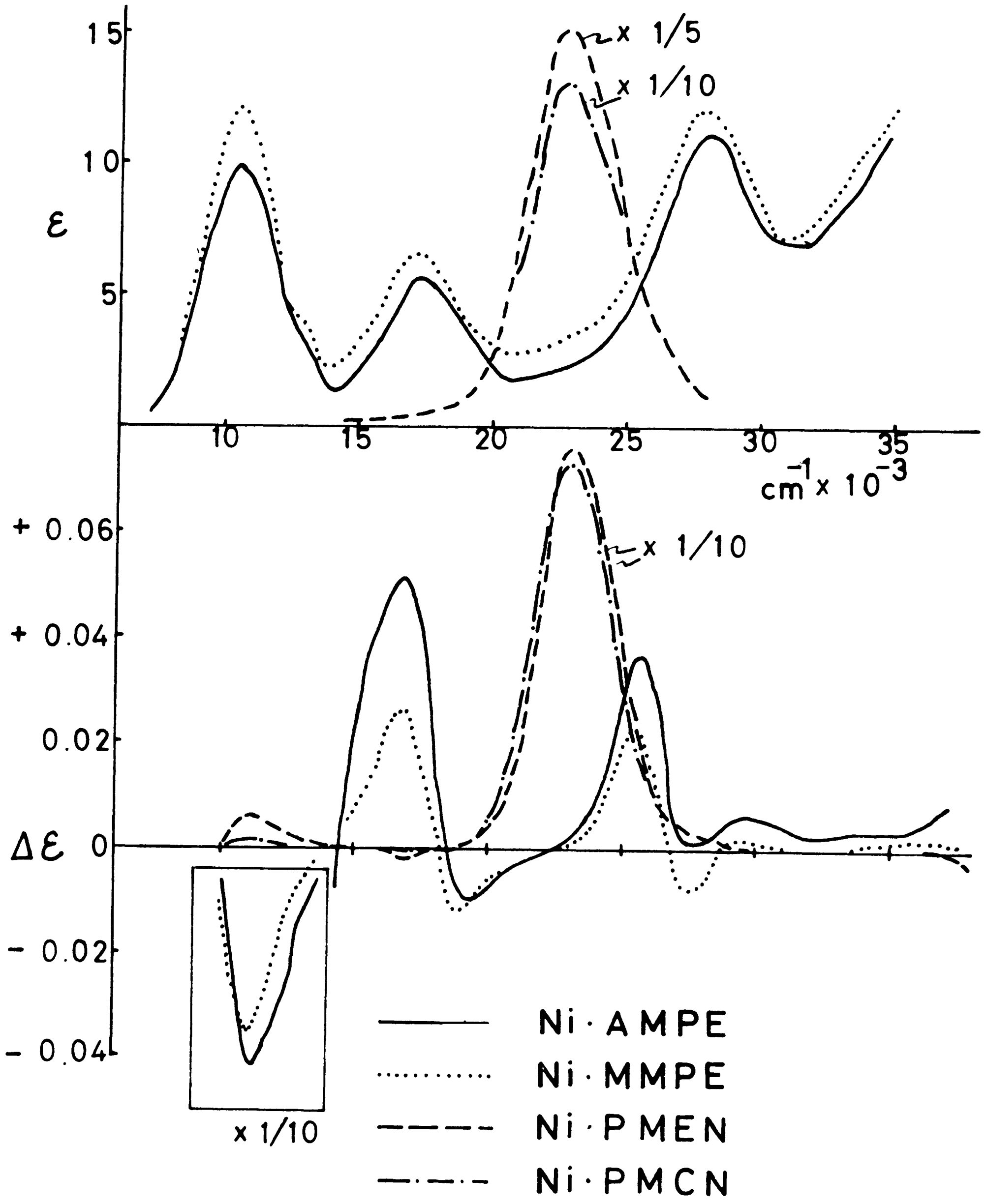

Fig.2 Absorption and CD spectra of nickel(II) complexes with tetramines in aqueous solution

octahedral approximation. Correspondingly, it has the most intense circular dichroism. In addition, from the comparison of the absorption spectra with CD curves, a positive CD component should be observed at lower wavenumber than 10,000 cm^{-1}. Other two bands ($^3A_{2g} \rightarrow {}^3T_{1g}$(F), $^3T_{1g}$(P)) exhibit only weak optical activity. The

CD spectra of the AMPE and MMPE complexes are almost identical with each other, which indicates that the two tetramines coordinate with the same conformations around the central nickel(II) ion. This shows that the terminal N-methyl groups in MMPE do not play an important part of the complex in the conformation.

The yellow complexes exhibit the only one absorption band and CD peak typical of square planar nickel(II) complex. The CD spectra of PMCN and PMEN complexes are also almost identical, and this indicates that these two tetramines coordinate to nickel(II) ion with the same conformations. The fixation of the central chelate ring by the cyclohexane ring may be insignificant for the conformation of the complexes. In addition to the yellow species band, a tiny CD band was also detected at the wavenumber corresponding to the first absorption band in the blue complexes. This shows that in the aqueous solutions of the PMCN and PMEN complexes small quantities of some sorts of octahedrally coordinated species are present.

AMPE and MMPE have two pyrrolidinyl groups in their inner part (Fig. 1), and it is expected that they hardly coordinate in a plane from the consideration with the molecular models. On the other hand, the preference of a square planar-type coordination to an octahedral-type one in the PMCN and PMEN complexes is not well explained, since both of the two types of structures can be easily constructed with the molecular models. In fact, the yellow complexes are converted into the blue complexes by the addition of amino acids or ethylenediamine.

As for triethylenetetramine, both of octahedral- and square planar-type nickel(II) complexes have been obtained.[3,4] Therefore, it is very interesting that our tetramines with similar structures coordinate stereospecifically in different manner to nickel(II) ion.

References

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2) Details on the syntheses of these ligands will be reported elsewhere in the near future.

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