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Discriminating Interaction in the Pfeiffer Effect Developed by L-Tartaric Acid and Its Derivatives. II. Pfeiffer Effect with Tris(5,5′-dimethyl-2,2′-bipyridine)nickel(II) and Tris(3,3′-dimethyl-2,2′-bipyridine) nickel(II) as a Racemic Complex

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In our previous study [1] on the Pfeiffer effect with L-tartaric acid (L-tartH_2) and its derivatives as a chiral environment substance, it was found that L-tartH_2 as well as its dimethyl- and diethyl-esters serves as an environment to $[M(phen)_3]^{2+}$ ($M = Co^{2+}$ or Zn^{2+}, and phen = 1,10-phenanthroline) in water to enrich its Λ-enantiomer, while diacetyl L-tartaric acid does not exhibit the Pfeiffer effect at all for $[M(phen)_3]^{2+}$. This was interpreted to mean that the hydroxyl groups on the asymmetric carbon atoms of the environment substances are essential to the chiral discrimination in the above Pfeiffer systems. Also found was that the protons at 2 and 9 positions of phen in $[Zn(phen)_3]^{2+}$ are subjected to a remarkable PMR line-broadening when mixed with L-tartH_2, but not with its dimethyl- and diethyl-esters. This finding led us to propose that L-tartH_2 approaches the complex along its C_3 axis, while its esters are packed between two phen ligands, the discrimination between the Λ- and Δ-enantiomers of the complex being thereby effected. However, we recently found that the above-mentioned line-broadening does not take place at all for $[Cd(phen)_3]^{2+}$ which of course exhibits the Pfeiffer effect when mixed with L-tartH_2 or its esters. Furthermore, the chemical shift of L-tartH_2 caused by the association with $[Zn(phen)_3]^{2+}$ is not so different from that of dimethyl L-tartrate [1], though the discriminating interaction is supposed to be different between the L-tartH_2 and its ester Pfeiffer systems, as mentioned above. Then, we examined the Pfeiffer effect of some bipyridine complexes having methyl groups which are expected to have some stereochemical influence on the above-mentioned interactions with the environments.

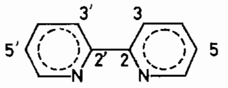
Experimental

5,5′-dimethyl-2,2′-bipyridine (5,5′-dmbpy) and 3,3′-dimethyl-2,2′-bipyridine (3,3′-dmbpy) were prepared from β-picoline by a usual method [2] and their purity was checked by NMR [3]. $[Ni(5,5'\text{-}dmbpy)_3]^{2+}$ and $[Ni(3,3'\text{-}dmbpy)_3]^{2+}$ were synthesized by the method reported by Suzuki and Kimura [4] and their purity was checked by the elemental analysis. $[Co(phen)_3]^{2+}$ was prepared by directly dissolving $CoCl_2 \cdot 6H_2O$ and phen·H_2O in water. To prevent the decomposition of the complex, a small amount of free phen was added. Dimethyl L-tartrate (L-DMT) and diethyl L-tartrate (L-DET) of reagent grade were used without further purification. Di-n-propyl L-tartrate (L-DPT) was prepared [5] from L-tartaric acid and purified on a silica gel column with n-hexane–ethylacetate eluents. Sample solutions containing both a racemic metal complex and an environment substance were prepared by mixing the respective aqueous stock solutions in 25 ml volumetric flasks.

CD and NMR spectra were recorded on a Jasco J-40CS and Varian T-60 spectrometer at ambient temperature.

Results and Discussion

To clarify our present results and discussion, the structure of 2,2′-bipyridine is depicted below.



In Figure 1 are shown the CD spectra developed for the tris-(5,5′-dimethyl-2,2′bipyridine)nickel(II) upon the addition of L-tartaric acid (L-tartH_2), dimethyl L-tartrate (L-DMT), and diethyl L-tartrate (L-DET) as a chiral environment in water. It is seen that the Pfeiffer effect is well developed and the Λ-enantiomer [6] is enriched by all of these environ-

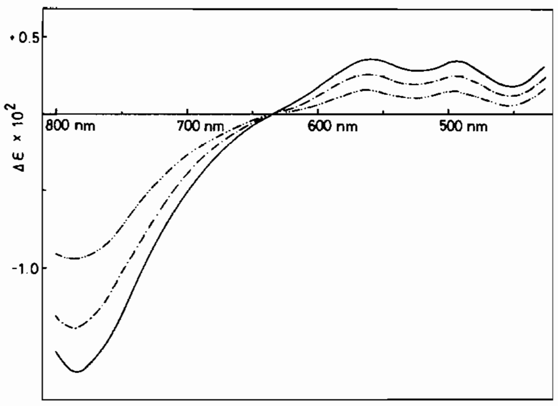


Figure 1. The CD spectra for the $[Ni(5,5'\text{-}dmbpy)_3]^{2+}$ (0.03 *M*)–L-DMT (0.25 *M*) (———), –L-tartH_2 (0.25 *M*) (–·–·–), and –L-DET (0.25 *M*) (–··–··–) systems in water.

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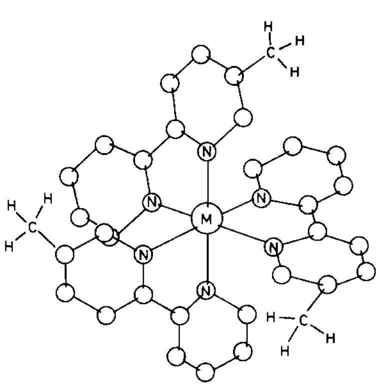

Figure 2. Structure of $[Ni(5,5'\text{-dmbpy})_3]^{2+}$ viewed from C_3 axis (other three methyl groups are not shown).

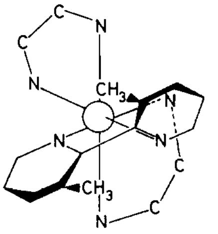

Figure 3. Schematic presentation of $[Ni(3,3'\text{-dmbpy})_3]^{2+}$.

ments. A consideration based on the molecular model leads us to expect that the methyl groups at the 5 and 5′ positions of parent bpy prevent the environment substance from approaching the complex along its C_3 axis (Figure 2). Therefore, it is improbable that these environments develope the Pfeiffer effect by attacking the complex along its C_3 axis.

On the other hand, we proposed in a previous paper [1] that L-DMT and L-DET interact with $[M(phen)_3]^{2+}$ in such a fashion that they are packed between two phen ligands of the complex. Since tris(3,3′-dimethyl-2,2′-bipyridine)nickel(II) ($[Ni(3,3'\text{-dmpby})_3]^{2+}$) has bulky methyl groups along its C_2 axis, as shown in Figure 3, it is expected that the environment cannot be packed between two bpy ligands. As expected, the Pfeiffer effect of $[Ni(3,3'\text{-dmbpy})_3]^{2+}$ is not observed at all with L-DMT and L-DET as an environment, though L-tartH_2 cannot be examined owing to the decomposition of the complex. The same should hold for the corresponding phen complexes (their preparation is relatively tedious, so that they are not examined here). Anyway, the above-mentioned result gives strong evidence for our earlier proposal that the optically active environment is packed between two phen or bpy ligands, and interacts more preferably with one enantiomer of the complex [7].

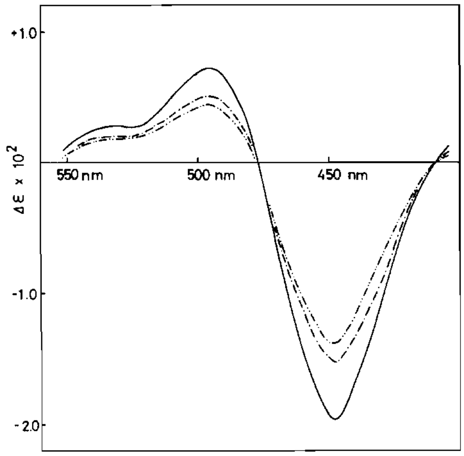

Figure 4. The CD spectra for the $[Co(phen)_3]^{2+}$ (0.0075 *M*)–L-DMT (0.1 *M*) (———), –L-DET (0.1 *M*) (–·–·–), and –L-DPT (0.1 *M*) (–··–··–), systems in water.

In Figure 4 are shown the CD spectra for the system of $[Co(phen)_3]^{2+}$ with dimethyl-, diethyl-, and di-n-propyl-esters of L-tartH_2. It is seen that the more bulky the environment used, the smaller the magnitude of the CD developed. This observation is consistent with our earlier proposal, because steric hindrance between the bulky alkyl groups on the environment and phen ligands of the complex will render the interaction leading to the Pfeiffer effect difficult.

In conclusion, the optically active environments (even L-tartH_2) do not attack $[M(phen)_3]^{2+}$ (or $[M(bpy)_3]^{2+}$) along its C_3 axis, but are packed between two phen (or bpy) ligands, and chiral discrimination in the Pfeiffer effect seems not to be directly related to the PMR line-broadening found for 2 and 9 protons of $[Zn(phen)_3]^{2+}$ in the presence of L-tartH_2. However, the source of the line-broadening observed for $[Zn(phen)_3]^{2+}$ only is still open to question.

References

1 Part 1: Y. Kuroda, K. Miyoshi, and H. Yoneda, *Inorg. Chim. Acta, 28,* 211 (1978).
2 F. H. Case, *J. Am. Chem. Soc., 68,* 2574 (1946); W. H. F. Sasse and C. P. Whittle, *J. Chem. Soc.,* 1347 (1961).
3 T. McL. Spotswood and C. I. Tanzer, *Aust. J. Chem., 20,* 1227 (1967).
4 T. M. Suzuki and T. Kimura, *Bull. Chem. Soc. Jpn., 50,* 391 (1977).
5 P. C. Austin, *J. Chem. Soc.,* 1831 (1928).
6 K. Miyoshi, Y. Kuroda, H. Okazaki, and H. Yoneda, *Bull. Chem. Soc. Jpn., 50,* 1476 (1977).
7 B. Bosnich and D. W. Watts, *Inorg. Chem., 14,* 47 (1975).