Inorganica Chimica Acta, 28 (1978) 211–216

Discriminating Interaction in the Pfeiffer Effect Developed by L-Tartaric Acid and Its Derivatives

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Received September 30, 1977

The Pfeiffer effect was examined on the systems of racemic [Co(phen)$_3$]Cl$_2$ with L-tartaric acid and with its derivatives, L-dimethyltartrate, L-diethyltartrate, L-dimethyldiacetyltartrate, and L-diacetyltartaric acid in water (phen = 1,10-phenanthroline). It was found that the Pfeiffer effect is well developed when L-tartaric acid and its dimethyl- and diethylesters are employed as a chiral environment substance, but not when its diacetyl-derivatives are employed. This result indicates that the alcoholic OH groups of the chiral environment substances play an essential role in the chiral discrimination in these Pfeiffer systems. The NMR study on the corresponding [Zn(phen)$_3$]$^{2+}$ systems suggests that L-tartaric acid attacks the complex along its C$_3$ axis, and that the discriminating interaction in the L-tartaric acid system is different from that in the L-dimethyl- and L-diethyltartrate systems.

Introduction

The Pfeiffer effect [1] is an anomalous change in optical activity observed when a racemic mixture of a labile metal complex is added to a solution containing an optically active compound called an "environment substance". This phenomenon is well interpreted in terms of a shift in equilibrium betwen Δ- and Λ-enantiomers of the complex under their differential interaction with the chiral environment substance. In fact, this equilibrium shift mechanism was decisively confirmed by Kirschner and Ahmad [2] who succeeded in partial resolution of [Ni(phen)$_3$]$^{2+}$ and [Cr(ox)$_3$]$^{3-}$ [3] by exploiting the Pfeiffer effect (phen = 1,10-phenanthroline and ox = oxalate dianion).

Pfeiffer-active systems are tentatively classified into the following three groups as far as tris-phen or tris-bpy complexes are concerned;
1) systems of the same charge; *e.g.*, [M(phen)$_3$]$^{2+}$–(–)-stryH$^+$ and –(+)-cinchoH$^+$ in water,
2) systems of the opposite charge; *e.g.*, [M(phen)$_3$]$^{2+}$–(+)-BCS$^-$ in water and [Cr(ox)$_3$]$^{3-}$–Λ-[Co(phen)$_3$]$^{3+}$ in dioxane–water mixtures [4], and
3) systems with α-hydroxycarboxylic acid as an environment substance; *e.g.*, [M(phen)$_3$]$^{2+}$–D-malic acid and –L-tartaric acid in water, where M = Co(II), Ni(II), or Zn(II), bpy = 2,2′-bipyridine, (–)-stryH$^+$ = levo-strychninium, (+)-cinchoH$^+$ = dextro-cinchoninium, and (+)-BCS$^-$ = dextro-3-bromocamphor-9-sulfonate.
For the first group, we examined the influence of some additives and proposed the hydrophobic bonding [1b] as a driving force for the chiral discrimination [5]. For the last group, Kirschner and Pollock [6, 7] proposed the hydrogen bonding of the three hydroxyl hydrogens (two COOH's and one OH) to the π electron cloud of the phen ligands, notably for the [Ni(phen)$_3$]$^{2+}$–D-malic acid system in water. However, when L-dimethyl- or L-diethyltartrate whose two COOH groups are esterificated is employed as an environment, the Pfeiffer effect is well developed in water. Therefore, the model proposed by Kirschner and Pollock cannot account for the chiral discrimination in these systems. Here, we focus our attention on the Pfeiffer effect developed by L-tartaric acid and its derivatives in a hope to get some insight into the nature of the discriminating interaction in the above Pfeiffer systems.

Experimental

All the environment substances used were of reagent grade except L-dimethyldiacetyltartrate and L-diacetyltartaric acid, which were prepared from L-tartaric acid [8] and whose purity was checked by NMR and elemental analysis. N,N-dimethylformamide (DMF), N,N-dimethylacetamide (DMA), dimethylsulfoxide (DMSO), methanol, ethanol, acetonitrile (AN), and acetone of reagent grade were used as solvents without further purification.

Sample solutions containing both racemic [Co(phen)$_3$]Cl$_2$ and an environment substance were prepared by mixing respective aqueous stock solu-

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tions in 25 ml volumetric flasks. To prevent the decomposition of the complex, a small amount of free phen was added. To some of these solutions were added varying amounts of urea. Sample solutions in nonaqueous solvents were prepared by dissolving weighed samples of the environment substance and of $[Co(phen)_3]Cl_2 \cdot 8H_2O$ for methanol and ethanol and of $[Co(phen)_3](ClO_4)_2$ for others. Absorption (AB), circular dichroism (CD), and NMR spectra were recorded on a Shimadzu UV 200, Jasco J-40CS, and Varian T-60 spectrometer at ambient temperature. For the NMR measurement, weighed samples of $[Zn(phen)_3]Cl_2 \cdot 7H_2O$ were dissolved in D_2O solutions containing a given amount of L-tartaric acid, L-dimethyltartrate, or other environment substances. Tert-butanol was used as an internal standard to measure the chemical shifts of the complex. On the other hand, when the complex concentration was varied, the peak positions of tetramethylsilane, tert-butanol, and 3-trimethylsilyl-1-propanesulfonate were shifted considerably [9], so that the HDO peak was employed as a reference to determine the association constant between the complex and the environment substance. The chemical shifts of each sample were determined from the average of at least 5 different recordings. Furthermore, different runs were repeated 3 times and the averaged values were adopted.

Results and Discussion

The Pfeiffer Effect with L-tartaric Acid and Its Derivatives as an Environment Substance

In Figure 1 are shown the Pfeiffer circular dichroism (PCD) spectra induced in the d–d transition for the systems of racemic $[Co(phen)_3]^{2+}$ with L-tartaric acid (L-$tartH_2$) and with its derivatives, L-dimethyltartrate (L-DMT) and L-diethyltartrate (L-DET) in water. It is noteworthy that the PCD spectra of the $[Co(phen)_3]^{2+}$ ion [10] in the presence of L-$tartH_2$, L-DMT, and L-DET are similar to each other in pattern as well as in magnitude. On the other hand, when L-dimethyldiacetyltartrate (L-DMDAT) and L-diacetyltartaric acid (L-$DATH_2$) are used, the PCD developed is much smaller [11] in magnitude than that in the L-$tartH_2$ system. The difference in the above two sets of environment substances is that the former has free alcoholic OH groups, while the latter has not. Therefore, it is concluded that the alcoholic OH groups on the asymmetric carbon atoms of the environment substances are essential to the chiral discrimination in the above Pfeiffer systems.

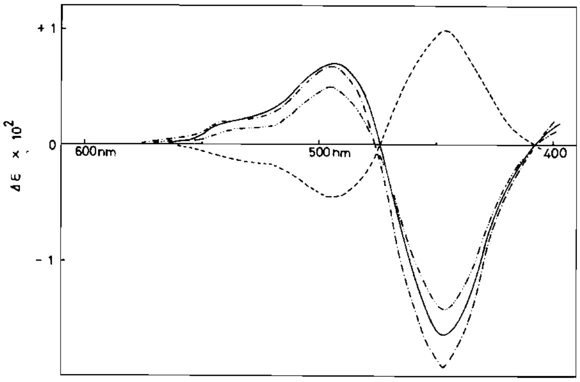

Figure 1. The PCD spectra for the $[Co(phen)_3]^{2+}$ (0.015*M*) –D-$malH_2$ (0.1*M*) (----), –L-$tartH_2$ (0.1*M*) (——), –L-DMT (0.1*M*) (-·-·-), and –L-DET (0.1*M*) (-·····-) systems in water.

A similar conclusion is drawn from the interesting fact that D-malic acid (D-$malH_2$) having only one alcoholic OH group gives rise to the PCD almost equal in magnitude to half the PCD developed in the L-$tartH_2$ system (Figure 1). In contrast, when Na_2L-tart having two alcoholic OH groups is added, the PCD developed is time-dependent and its pattern is different from that exhibited in the L-$tartH_2$ or D-$malH_2$ system, as shown in Figure 2, where the time attached to each spectrum denotes the hours elapsed after the complex is mixed with Na_2L-tart in water. Thus, it is supposed that L-$tart^{2-}$ is coordinated directly to Co(II), thereby making it optically active in the Na_2L-tart system [12]. In fact, the rate of appearance of the PCD in this system is much slower [2] than that of racemization [13] of the $[Co(phen)_3]^{2+}$ ion and in addition, the PCD is not observed if more inert $[Ni(phen)_3]^{2+}$ is used [2] in place of $[Co(phen)_3]^{2+}$.

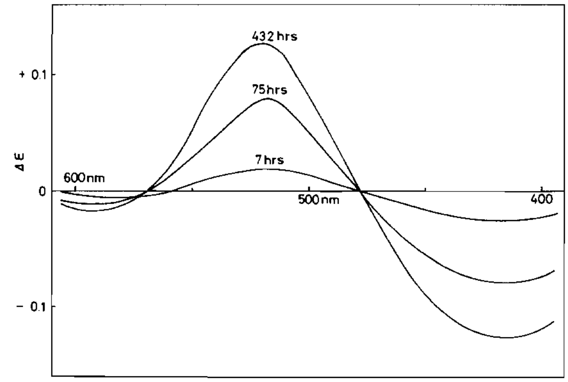

Figure 2. The time dependence of the CD spectrum induced in the $[Co(phen)_3]^{2+}$ (0.015*M*) –Na_2L-tart (0.1*M*) system in water.

The nature of the discriminating interaction [14] in the Pfeiffer-active systems has been discussed by several workers. Particularly, Kirschner and Pollock [6, 7] proposed the hydrogen bonding between the three hydroxyl hydrogens (two COOH's and one OH) and the π electron cloud of the phen ligands for the $[Ni(phen)_3]^{2+}$–D-$malH_2$ or –L-$tartH_2$ system in water. The evidence supporting their proposal is that no Pfeiffer effect is detected if D-malH_2 is replaced by D-malate dianion, though enhanced association is expected between the complex and the environment substance. However, both L-DMT and L-DET having only two alcoholic OH groups serve well as an environment to the $[Co(phen)_3]^{2+}$ ion in water. Accordingly, the chiral discrimination in the L-DMT and L-DET systems is not accounted for by the hydrogen bonding model proposed by Kirschner and Pollock [6, 7], and it needs further study.

The Pfeiffer Effect in Nonaqueous Solvents

A few Pfeiffer-active systems have been so far found in nonaqueous solvents [15]. Here, we examine the Pfeiffer systems in several nonaqueous solvents in an effort to elucidate the discriminating interaction of the above chiral environment substances with $[Co(phen)_3]^{2+}$. Figure 3 shows the PCD of the $[Co(phen)_3]^{2+}$–L-tartH_2 system in methanol, ethanol, DMF, and DMA. It is seen that the PCD is certainly developed in these solvents if L-tartH_2 is employed as an environment (the magnitude of the PCD in these solvents is smaller than that in H_2O), but not in acetone, AN, or DMSO. Whereas, neither L-DMT nor L-DET serves as an environment to $[Co(phen)_3]^{2+}$ at all in each solvent examined here [16]. Thus, it is supposed that the Pfeiffer effect in the L-DMT or L-DET system is not developed via the same mechanism as that proposed by Kirschner and Pollock [6, 7] for the D-malH_2 or L-tartH_2 system.

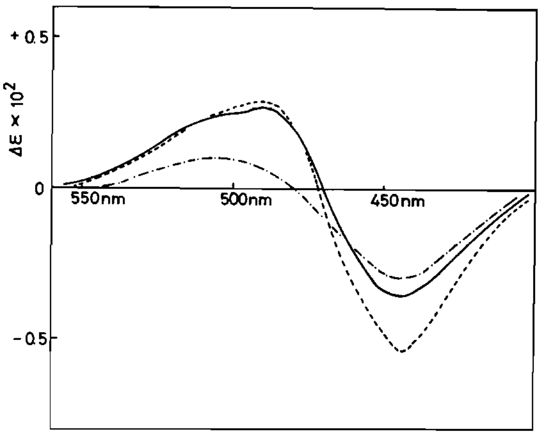

Figure 3. The PCD spectra for the $[Co(phen)_3]^{2+}$ (0.015*M*) –L-tartH_2 (0.05*M*) system in methanol (———), ethanol (----), DMF (-·--·-), and DMA (-·-·-).

Recently, we examined the influence of some additives on the several Pfeiffer-active systems in water. The marked feature revealed is that added urea does not diminish the Pfeiffer effect in the systems of the last group [17], while it does greatly so in the systems of the first group [5a]. In a further attempt to elucidate the nature of the interaction, we examined the influence of urea on the $[Co(phen)_3]^{2+}$–L-tartH_2, –L-DMT, and –L-DET systems in water. In Figures 4–6 are shown the PCD spectra of these systems in the presence of varying amounts of urea. It is found there that added urea has only a small effect on the PCD of the L-tartH_2 system, but it diminishes greatly the PCD of the L-DMT and L-DET systems. This suggests that the discriminating interaction in the L-DMT and L-DET systems is different from that in the L-tartH_2 or D-malH_2 system.

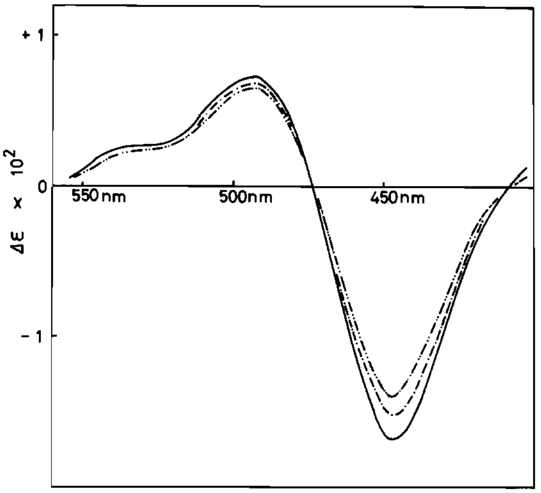

Figure 4. The PCD spectra for the $[Co(phen)_3]^{2+}$ (0.015*M*) –L-tartH_2 (0.1*M*) system in water containing varying amounts of urea. 0*M* (———), 2*M* (-.-.-), 4*M* (-..-..-).

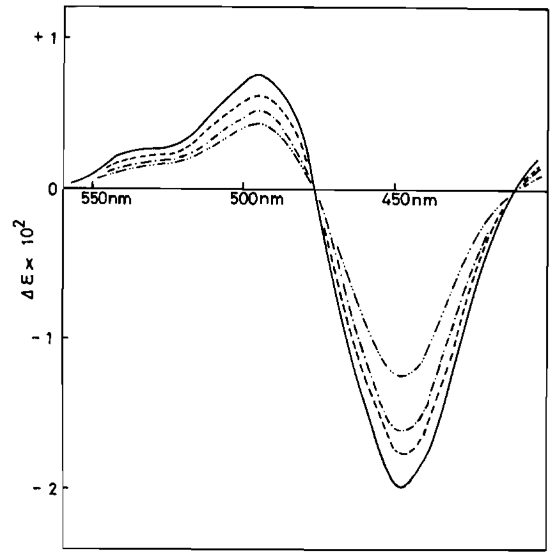

Figure 5. The PCD spectra for the $[Co(phen)_3]^{2+}$ (0.015*M*) –L-DMT (0.1*M*) system in water containing varying amounts of urea. 0*M* (———), 1*M* (----), 2*M* (-·-·-), 4*M* (-··-··-).

NMR Study on the Nature of the Pfeiffer Effect

In order to get some information on the interaction site in the Pfeiffer effect, an NMR investigation was undertaken on the systems of racemic

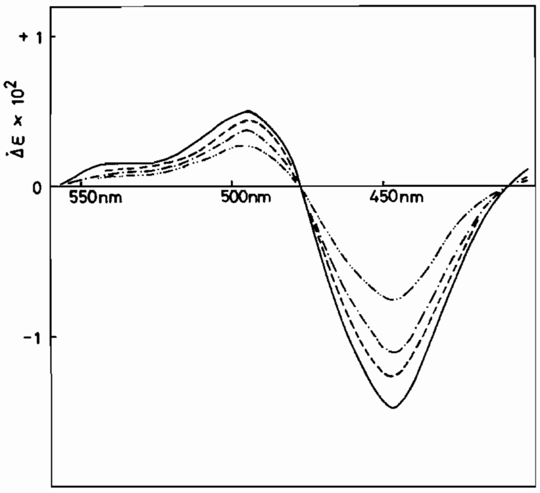

Figure 6. The PCD spectra for the $[Co(phen)_3]^{2+}$ (0.015*M*) –L-DET (0.1*M*) system in water containing varying amounts of urea. 0*M* (———), 1*M* (----), 2*M* (-.-.-), 4*M* (-..-..-).

TABLE I. The Results of the NMR Measurements on the $[Zn(phen)_3]^{2+}$ Systems in D_2O.

Env. Substance	Pfeiffer Effect[a]	Broadening of 2 and 9 Protons[b]
D-$malH_2$	○	○
L-$tartH_2$	○	○
rac-lactic acid	△	○
rac-glyceric acid	△	○
hydroxymalonic acid	×	○
succinic acid	×	×
β-hydroxybutyric acid	×	×
L-DMDAT	×	×
L-DMT	○	×
L-DET	○	×
rac-2,3-butanediol	△	×
Na_2L-tart	×	×
Na_2D-mal	×	×

[a] ○, Pfeiffer-active; ×, Pfeiffer-inactive; △, Pfeiffer-active if an active environment substance is used. [b] ○, the broadening occurs; ×, the broadening does not occur.

$[Zn(phen)_3]^{2+}$ with D-$malH_2$, L-$tartH_2$, and its derivatives in D_2O. The NMR signals of the complex in water were assigned after Miller and Prince [18]. When D-$malH_2$ or L-$tartH_2$ is added, a remarkable PMR line-broadening is observed for the protons at the 2 and 9 positions of the phen in the complex and up-field chemical shifts are observed for all the protons of D-$malH_2$ and L-$tartH_2$, as shown in Figure 7. The fact that the addition of succinic acid (0.1*M*) or acetic acid (0.1*M*) has no effect at all on the PMR spectrum of the complex rules out the possibility that the broadening is due to partial decomposition of the complex in the presence of L-$tartH_2$ or D-$malH_2$.

To clarify the origin of the broadening at the 2 and 9 protons caused by the addition of D-$malH_2$ and L-$tartH_2$, their related compounds were examined as an environment. The results obtained are summarized in Table I. When racemic lactic acid, racemic glyceric acid, and hydroxymalonic acid are added, the broadening at the 2 and 9 protons does occur. When meso and racemic $tartH_2$ are added, the broadening of course occurs. On the other hand, when L-DMDAT, succinic acid, or β-hydroxybutyric acid is added, the broadening is not observed. Then, it follows that the fragment HOOC–C–OH is necessary for the broadening to occur and that the Pfeiffer effect should be developed if active lactic acid and glyceric acid were used. In fact, the $[Co(phen)_3]^{2+}$ –D-mandelic acid system is found Pfeiffer-active in water [7], so that the broadening should be also observed in the $[Zn(phen)_3]^{2+}$–D-mandelic acid system.

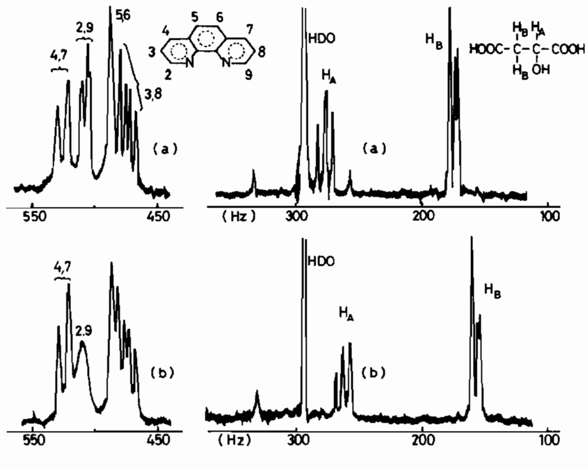

Figure 7. The PMR spectra for the $[Zn(phen)_3]^{2+}$(0.2*M*) –D-$malH_2$ (0.1*M*) system in water (a) before and (b) after the complex is mixed with D-$malH_2$.

Since the 2 and 9 protons are located around the C_3 axis of the complex, it is plausible that D-$malH_2$ and L-$tartH_2$ attack the complex along its C_3 axis. La Mar and Van Hecke [19] pointed out that the pockets of electron density generated at the 2 and 9, and in particular at the 4 and 7 positions of tris-phen complexes can act as a center for the hydrogen bonding with alcohols. Thus, the hydrogen bonding to the 2 and 9 positions is the most probable interaction in the D-$malH_2$ and L-$tartH_2$ systems. On the other hand, Gillard and his coworkers [20] found that the PMR signals due to the 2 and 9 protons of phen complexes and the 6 and 6′ protons of bpy complexes are shifted to higher field upon the addition of some bases, and that their electronic spectra are also changed. Based on these findings, they proposed that the 2 and 9 positions of phen complexes and the 6 and 6′ positions of bpy complexes are subjected to nucleophilic attack by various Lewis bases such as OH^- and CN^- and by H_2O (covalent

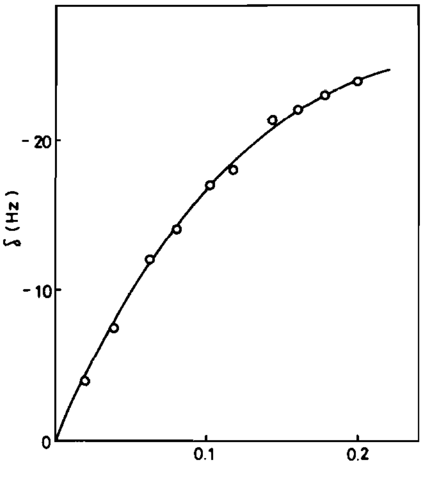

Figure 8. The plot of the chemical shift δ relative to HDO *vs.* the $[Zn(phen)_3]^{2+}$ concentration for the $[Zn(phen)_3]^{2+}$–L-tartH_2 (0.1*M*) system in water.

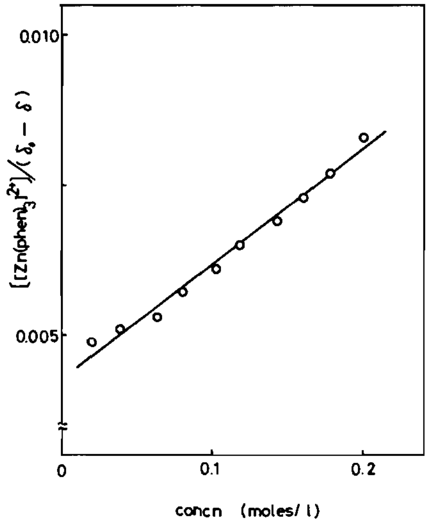

Figure 9. The plot of Eqn (3) *vs.* the $[Zn(phen)_3]^{2+}$ concentration for the $[Zn(phen)_3]^{2+}$–L-tartH_2 (0.1*M*) system in water.

hydration). However, their proposal does not apply to our case, because the signals due to the 2 and 9 protons are shifted slightly to lower field in the $[Zn(phen)_3]^{2+}$–D-malH_2 and –L-tartH_2 systems, and because L-tart^{2-} (Lewis base) has no effect at all on the PMR signals due to the 2 and 9 protons.

A striking feature to be noted in Table I is that the broadening at the 2 and 9 protons of $[Zn(phen)_3]^{2+}$ does not occur when L-DMT or L-DET is added, though both of them serve well as an environment to $[Co(phen)_3]^{2+}$ in water. One interpretation of this observation is to assume as before that the discriminating interaction in the L-DMT and L-DET systems is different from that in the D-malH_2 and L-tartH_2 systems. In fact, a close inspection of Figure 1 reveals that the PCD pattern for the former systems is slightly but definitely different from that for the latter systems, particularly with regard to their isodichroic points.

Bosnich and Watts [21] found that the Pfeiffer effect is developed for the $[Ni(phen)_3]^{2+}$ ion in (−)-2,3-butanediol, and they proposed that (−)2,3-butanediol molecules packed between the phen ligands interact more preferably with one enantiomer (Δ-enantiomer in this case) of the complex than with the other. Since both L-DMT and L-DET are quite similar in structure to 2,3-butanediol, the chiral discrimination in the L-DMT and L-DET systems may be accounted for in a similar manner. In accord with the above assumption, the broadening at the 2 and 9 protons of $[Zn(phen)_3]^{2+}$ is not observed in water upon the addition of racemic 2,3-butanediol (Table I).

In Figure 7 are also shown the PMR spectra of D-malH_2 in D_2O. It is clearly seen that all the protons of D-malH_2 are subjected to up-field chemical shifts when mixed with $[Zn(phen)_3]^{2+}$ in water. Similar up-field shifts are observed for all the environment substances examined except for Na_2L-tart and Na_2D-mal. If these shifts are due to so-called ring current effect of the phen ligands of the complex [22], it follows that the environment substances are situated in the vicinity of the complex to develope the Pfeiffer effect. The fact that the greatest chemical shift is observed for the protons on the asymmetric carbon atoms of the environments, is qualitatively consistent with our earlier conclusion that the OH groups on the asymmetric carbon atoms are essential to the chiral discrimination in the present Pfeiffer systems. In contrast, D-mal^{2-} or L-tart^{2-} seems not to approach the complex closely enough to experience the ring current effect, the true Pfeiffer effect being not developed naturally.

From the discussion presented above, it is possible to determine the association constant between the complex and the environment substance by measuring the chemical shifts as a function of the complex concentration. In Figure 8 is shown a plot of the chemical shift for the protons on the asymmetric carbon atoms of L-tartH_2 relative to that for HDO *vs.* the $[Zn(phen)_3]^{2+}$ concentration. The observed chemical shift δ is given by [23]

$$\delta = [ENV]\delta_0/[ENV]_T + [[Zn(phen)_3]^{2+}\text{–}ENV]\cdot \delta_a/[ENV]_T \qquad (1)$$

where δ_0 and δ_a denote the chemical shift in the bulk solution and in the associated species, respectively, ENV and $[Zn(phen)_3]^{2+}$–ENV refer to the environment substance employed and to its associated species with $[Zn(phen)_3]^{2+}$, respectively, and

TABLE II. The Derived Association Constant K and the Value of $(\delta_0 - \delta_a)$ in Water.

System	$[Zn(phen)_3]^{2+}$–L-tartH_2	$[Zn(phen)_3]^{2+}$–L-DMT
δ_0[a]	294.2	298.8
$(\delta_0 - \delta_a)$[a]	52.4 ± 2.3	40.8 ± 2.2
K	4.47 ± 0.23	6.09 ± 0.41

[a] In Hz.

$$[ENV]_T = [ENV] + [[Zn(phen)_3]^{2+}\text{–}ENV] \quad (2)$$

$$[[Zn(phen)_3]^{2+}]/(\delta_0 - \delta) = [[Zn(phen)_3]^{2+}]/(\delta_0 - \delta_a) + 1/K(\delta_0 - \delta_a) \quad (3)$$

These equations are applicable to the case where the association is limited to 1:1 and $[[Zn(phen)_3]^{2+}$–ENV$] \ll [[Zn(phen)_3]^{2+}]$. Under these conditions, a plot of $[[Zn(phen)_3]^{2+}]/(\delta_0 - \delta)$ *vs.* $[[Zn(phen)_3]^{2+}]$ should yield a straight line, from which the values of $(\delta_0 - \delta_a)$ and the association constant K are derived as (1/slope) and (slope/intercept), respectively.

In Figure 9 is shown the plot of Eqn (3) for the $[Zn(phen)_3]^{2+}$–L-tartH_2 system in water. A similar plot is obtained for the $[Zn(phen)_3]^{2+}$–L-DMT system in water by using the signal due to the protons on the asymmetric carbon atoms of L-DMT, and all the results are listed in Table II. It is surprising that the K values thus obtained for the L-tartH_2 and L-DMT systems are close to that estimated by utilizing the ORD spectra for the systems of the first group in water [24]. However, no distinct difference is detected in the K values of the L-tartH_2 and the L-DMT systems, though the difference in the $(\delta_0 - \delta_a)$ values suggests different interaction modes in the two systems.

In conclusion, the Pfeiffer-active systems should be classified into four groups according to the nature of their discriminating interaction, and the fourth consists of the systems with chiral alcohols as an environment substance, *e.g.*, $[M(phen)_3]^{2+}$–L-DMT or –L-DET system and $[M(phen)_3]^{2+}$–(–)-2,3-butanediol system [21].

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11 Low solubility of L-DMDAT and L-DATH_2 in water makes the quantitative measurement difficult. However, it is certain that the magnitude of the PCD developed in the $[Co(phen)_3]^{2+}$–L-DMDAT and –L-DATH_2 systems is by far smaller than that in the L-tartH_2 system in water.

12 Probably for the same reason, racemic $[Mn(phen)_3]^{2+}$ becomes optically active when mixed with L-tart^{2-} in water. Then, this system is not a true Pfeiffer system. See ref. 15.

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