Inorganic Chemistry, Vol. 18, No. 6, 1979 **1425**

Contribution from the Department of Chemistry, Faculty of Science,
Hiroshima University, Hiroshima 730, Japan

The Pfeiffer Effect with Cinchoninium Ion as a Chiral Environment Substance

KATSUHIKO MIYOSHI, YASUSHIGE KURODA, JUNKO TAKEDA, HAYAMI YONEDA,*[1]
and ICHIRO TAKAGI

Received November 16, 1978

The Pfeiffer effect of tris(oxalato)chromate(III) was examined and compared with that of tris(1,10-phenanthroline)cobalt(II) by using cinchoninium ion and some of its related chiral compounds as an environment substance in water as well as in several mixed solvents with water. It was proposed that $[Cr(ox)_3]^{3-}$ ion attacks the environment substance through electrostatic interaction and is subject to the asymmetry around the C-8 atom of cinchoninium ion, while $[Co(phen)_3]^{2+}$ ion associates with cinchoninium ion through the hydrophobic interaction with the quinolyl group and is subject to the asymmetry around the C-9 atom. The rate of appearance of the Pfeiffer effect was also measured for the $[Cr(ox)_3]^{3-}$ system. It was found that the inversion rate of one enantiomer enriched by the Pfeiffer effect is appreciably retarded by cinchoninium ion, while the other enantiomer is kinetically little affected by it. The same will hold for the corresponding $[Co(phen)_3]^{2+}$ system.

Introduction

When a racemic mixture of a labile metal complex like $[Cr(ox)_3]^{3-}$ or $[Co(phen)_3]^{2+}$ is mixed in solution with a certain chiral compound called an environment substance, new optical activity attributable to the initially racemic complex is sometimes developed. This phenomenon is known as the Pfeiffer effect[2,3] and is usually ascribed to a displacement of the chiral equilibrium between the enantiomers of the complex, viz., to an enrichment of one enantiomer under the influence of the chiral environment substance present. Actually, partial resolution of some metal complexes has been performed by utilizing this phenomenon.[3,4]

Recently, Kirschner et al.[5] found that the enantiomers enriched by the Pfeiffer effect for $[M(phen)_3]^{2+}$ complexes ($M = Fe^{2+}$, Co^{2+}, Ni^{2+}, or Zn^{2+}) have the same absolute configuration (Λ or Δ) if α-hydroxycarboxylic acids of the same absolute configuration (*R* or *S*), e.g., (*S*)-malic acid and (*S*,*S*)-tartaric acid, are used as an environment substance in water. On the basis of this finding, they proposed that the Pfeiffer effect is useful to assign the absolute configuration to labile metal complexes. However, it should be noted that the Λ enantiomer is enriched for the $[M(ox)_3]^{3-}$ system ($M = Cr^{3+}$ or Co^{3+}),[3,6] but the Δ enantiomer is for the $[M(phen)_3]^{2+}$ system ($M = Co^{2+}$ or Ni^{2+}),[7] when cinchoninium ion ($cinchoH^+$) is employed as an environment substance in water. This suggests that the discriminating interaction of $cinchoH^+$ is different between the two systems. In fact, electrostatic repulsion is expected for the $[M(phen)_3]^{2+}$ system,[7] while electrostatic association is apparently favored for the $[M(ox)_3]^{3-}$ system. In this paper, the Pfeiffer effect of the $[Cr(ox)_3]^{3-}$ system is examined by using $cinchoH^+$ and its related compounds as a chiral environment substance and is compared with that of the corresponding $[Co(phen)_3]^{2+}$ system, to elucidate the discriminating interaction of $cinchoH^+$ with these metal complexes in solution.

Results and Discussion

Influence of Additives on the Pfeiffer Effect. In our previous paper,[8] it was reported that the addition of several organic solvents diminishes the Pfeiffer effect of the $[Zn(phen)_3]^{2+}$–$cinchoH^+$ system in water and that the hydrophobic interaction is a main driving force for the two cations, $[Zn(phen)_3]^{2+}$ and $cinchoH^+$, to associate with each other against their mutual electrostatic repulsion to exhibit the Pfeiffer effect. The same is naturally expected for the corresponding $[Co(phen)_3]^{2+}$ system. For the comparison with the above $(phen)_3$ complex system, the influence of similar organic additives was examined here on the $[Cr(ox)_3]^{3-}$–$cinchoH^+$ system in water. The results obtained after chiral equilibration[9-11] are shown in Figure 1 and are summarized in Table I. Similarity of the CD pattern which was developed to that[12] of resolved Λ-$[Cr(ox)_3]^{3-}$ ion indicates that the chiral equilibrium of $[Cr(ox)_3]^{3-}$ is shifted in favor of its Λ enantiomer; that is, the Λ enantiomer is enriched in the presence of $cinchoH^+$ in agreement with the results reported earlier by other workers.[3,6]

Table I. CD Intensity $\Delta\epsilon$ ($\times 10^2$) Obtained for the $[Cr(ox)_3]^{3-}$–$cinchoH^+$ System in Various Mixed Solvents with Water[a]

added solvent	3 mL[b]	λ_{max},[c] nm	5 mL[b]	λ_{max},[c] nm
H_2O	5.09[d]	554		
dioxane	6.47	556	8.72	556
THF	6.41	555	8.76	555
Me_2SO	2.50[e]	557	1.25[e]	565
NMA	2.32	554	1.20	556
DMA	3.95	555	3.42	555
MeOH	4.24	557	3.74	561
EtOH	5.23	557	6.15	556
1-PrOH	5.95	555	7.73	556
acetone			5.33	556
urea	4.31[f]	554		

[a] $[[Cr(ox)_3]^{3-}] = 7.5 \times 10^{-3}$ M; $[cinchoH^+] = 1.5 \times 10^{-2}$ M. [b] Volume of added solvents; total volume = 10 mL. [c] Wavelength at which CD has a maximum intensity. [d] In pure water. [e] Chiral equilibrium is probably not yet established: see S. Sastri and C. H. Langford, *J. Phys. Chem.*, **74**, 3945 (1970). [f] [Urea] = 1.0 M.

It is noteworthy in Figure 1 and Table I that the addition of dioxane and tetrahydrofuran (THF) enhances the Pfeiffer effect of the present system greatly, while other additives, dimethyl sulfoxide (Me_2SO), *N*-methylacetamide (NMA), *N*,*N*-dimethylacetamide (DMA), urea, and alcohols, have a diminishing or relatively small effect. Since dioxane and THF are almost nonpolar (their dielectric constant $\epsilon = 2.2$ and 7.4 at 25 °C, respectively[13]), electrostatically promoted association between $[Cr(ox)_3]^{3-}$ and $cinchoH^+$ is thought to be responsible for the enhanced Pfeiffer effect in these systems. That is, the electrostatic association is one of the important interactions leading to the Pfeiffer effect in these systems, in contrast to the $[M(phen)_3]^{2+}$–$cinchoH^+$ system where it is improbable.[7] In this respect, the present system resembles the $[Cr(ox)_3]^{3-}$–Λ-$[Co(phen)_3]^{3+}$ and $[Cr(ox)_3]^{3-}$–Λ-*cis*-$[Co(en)_2(X)(Y)]^{n+}$ systems reported previously.[14]

In order to confirm the validity of the above assumption, we obtained the association constant K_A for the $[Cr(ox)_3]^{3-}$–$cinchoH^+$ system in water as well as in dioxane–water (36.7 wt % of dioxane) and THF–water (41.0 wt % of THF) mixtures at 25 °C by measuring the intensities of the CD (at 554 nm) developed by the Pfeiffer effect. Then, the K_A value to be obtained is an average of the association constants of Λ- and Δ-$[Cr(ox)_3]^{3-}$ with $cinchoH^+$.

A one-step association is assumed:

0020-1669/79/1318-1425$01.00/0

$$[Cr(ox)_3]^{3-} + cinchoH^+ \rightleftarrows [Cr(ox)_3]^{3-}\text{–}cinchoH^+$$

The association constant K_A is derived from the eq 1[15] if the

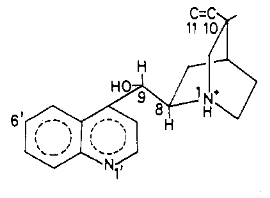
$$C_M(C_E - x)/(CD) = (C_E - x)/\Delta\epsilon_{ME} + 1/K_A\Delta\epsilon_{ME} \qquad (1)$$

concentration of the ion pair is always proportional to the observed CD intensity. In this equation, C_M, C_E, and x refer to the total concentration of $[Cr(ox)_3]^{3-}$, cinchoH$^+$, and the ion pair, respectively, and CD and $\Delta\epsilon_{ME}$ to the observed CD intensity at equilibrium and the proportionality constant (CD = $\Delta\epsilon_{ME}x$), respectively. The values of K_A and $\Delta\epsilon_{ME}$ are derived from the final plots of $C_M(C_A - x)/(CD)$ vs. $(C_A - x)$ attained by a successive approximation, and they are listed in Table II together with those of the final ionic strength μ.

It is seen in Table II that the K_A value obtained in water is close to 26 ± 5 estimated for the $[Cr(ox)_3]^{3-}$–Et$_4$N$^+$ ion pair from the racemization study in water at 25 °C.[11] Also seen is the fact that association between $[Cr(ox)_3]^{3-}$ and cinchoH$^+$ is certainly promoted upon the addition of dioxane and THF and that the K_A values are nearly the same in the two mixed solvents with almost the same dielectric constant, as is expected from a simple electrostatic theory of ion association.[16] These facts strongly suggest that the electrostatic interaction between $[Cr(ox)_3]^{3-}$ and the positive charge on the N(1) atom of cinchoH$^+$ is important to this Pfeiffer system.

On the other hand, the value of $\Delta\epsilon_{ME}$, the ratio of the observed CD intensity to the concentration of the ion pair, is lowered by the addition of dioxane or THF, as seen in Table II. $\Delta\epsilon_{ME}$ consists not only of the CD intensity due to the enriched Λ enantiomer but also of so-called induced CD[17] developed even if the chiral equilibrium is not displaced. Furthermore, since every ion-pair formation with the cinchoH$^+$ does not lead to an enrichment of one enantiomer, the value of $\Delta\epsilon_{ME}$ need not be equal to the CD intensity of optically pure Λ-$[Cr(ox)_3]^{3-}$ ion. However, the magnitude of $\Delta\epsilon_{ME}$ is certainly a measure of chiral discrimination; the higher it is, the better the degree of discrimination. Therefore, it is concluded that the overall Pfeiffer effect of the $[Cr(ox)_3]^{3-}$–cinchoH$^+$ system is certainly enhanced by the addition of dioxane or THF, but the efficiency of chiral discrimination effected by cinchoH$^+$ is conversely diminished to some extent.

Direct Comparison between the $[Cr(ox)_3]^{3-}$ and $[Co(phen)_3]^{2+}$ Systems. cinchoH$^+$ is known to serve as a chiral environment substance to both $[Cr(ox)_3]^{3-}$ and $[Co(phen)_3]^{2+}$ in water to enrich the Λ and Δ enantiomers, respectively.[3,6,7] Here, the two systems are compared by using cinchoH$^+$ and some of its related compounds as an environment substance in water in a hope to find some differences in the discriminating interactions in these systems. The structure of cinchoH$^+$ is depicted.



It should be noted here that when cinchonidinium ion, a stereoisomer of cinchoH$^+$ with respect to the configurations around both the C-8 and C-9 atoms,[18] is used as an environment substance, the enantiomers with completely opposite configuration are enriched, the Δ and Λ enantiomers for $[Cr(ox)_3]^{3-}$ and for $[Co(phen)_3]^{2+}$ or $[Ni(phen)_3]^{2+}$,[19] respectively. This unambiguously means that cinchoH$^+$ interacts with $[Cr(ox)_3]^{3-}$ and $[M(phen)_3]^{2+}$ so that the stereochemical demand due to the asymmetry around its C-8 and/or C-9 atom(s) is exerted upon them, the chiral discrimination being thereby effected.

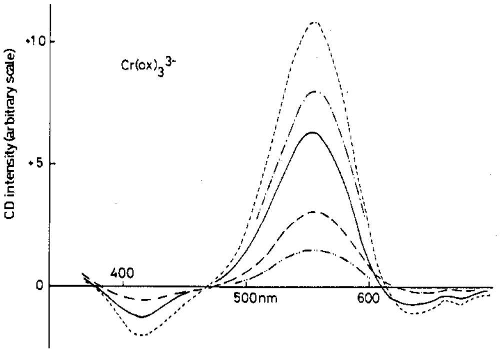


Figure 1. Influence of additives on the CD spectra induced for the $[Cr(ox)_3]^{3-}$ (7.5×10^{-3} M)–cinchoH$^+$ (1.5×10^{-2} M) system (total volume of each sample solution = 10 mL): --- (THF 5 mL); ···· (dioxane 3 mL); — (H$_2$O); – – – (Me$_2$SO 3 mL); –··–·· (NMA 5 mL).

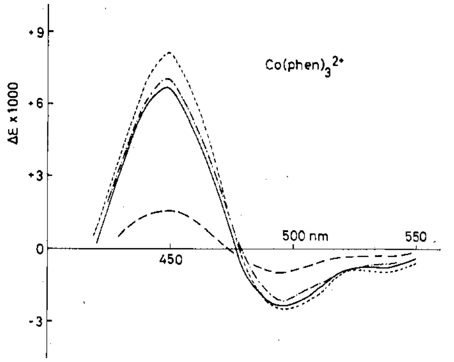


Figure 2. CD spectra induced for $[Co(phen)_3]^{2+}$ (7.5×10^{-3} M) with various environments (1.5×10^{-2} M): — (cinchoH$^+$); ··· (*N*-Me-cinchoH$^+$); –·–· (10,11-H$_2$-cinchoH$^+$); – – – (6′-MeO-cinchoH$^+$).

Table II. Association Constant K_A for the $[Cr(ox)_3]^{3-}$–cinchoH$^+$ System at 25 °C

medium	K_A	$\Delta\epsilon_{ME}$ (554 nm)	$10^2\mu$	ϵ^a
H$_2$O	20.6 ± 1.0	0.41 ± 0.02	3.67 ± 0.04	78.5
dioxane (36.7 wt %)	68.2 ± 1.5	0.26 ± 0.01	3.43 ± 0.09	47.4
THF (41.0 wt %)	62.4 ± 1.9	0.33 ± 0.01	3.45 ± 0.09	47.3

[a] Dielectric constant taken from ref 13.

In Figure 2 are shown the CD spectra developed in the Pfeiffer effect of the $[Co(phen)_3]^{2+}$ system in water. It is seen there that 10,11-H$_2$-cinchoH$^+$ (cinchotinium) and *N*(1)-Me-cinchoH$^+$[20] ions exhibit the Pfeiffer effect similar in magnitude to that developed by cinchoH$^+$, while 6′-MeO-cinchoH$^+$ (quinidinium) ion exhibits a much smaller Pfeiffer effect.[19] This leads to the assumption that the hydrophobic interaction[2b,7,8] of the quinolyl group of cinchoH$^+$ with $[Co(phen)_3]^{2+}$ is important to this system; it is strong enough to force $[Co(phen)_3]^{2+}$ cation to associate with cinchoH$^+$ against the electrostatic repulsion inevitably expected, but the introduction of a methoxy group to the C-6′ position of cinchoH$^+$ will give steric hindrance to the above hydrophobic interaction, leading to the diminished Pfeiffer effect. A similar assumption has been presented by Ogino and Kumagai.[19]

Pfeiffer and Quehl[20] have already found in their earliest study that *N*(1),*N*(1′)-Me$_2$-cinchoH$^+$ does not serve as an environment substance at all to $[Zn(phen)_3]^{2+}$ in water. This finding is to be expected from the above assumption, because the positive charge generated by the addition of a methyl group to the N(1′) atom prohibits electrostatically the above-mentioned interaction of the quinolyl group with $[Zn(phen)_3]^{2+}$, and in addition, the methyl group introduced will

Table III. Absolute Configuration of $[Co(phen)_3]^{2+}$ and $[Cr(ox)_3]^{3-}$ Enriched by the Pfeiffer Effect

	configuration at		enriched enantiomer	
environment (hydrochloride)	C-9	C-8	$[Co(phen)_3]^{2+}$	$[Cr(ox)_3]^{3-}$
cinchonine	*S*	*R*	Δ	Λ
cinchonidine	*R*	*S*	Λ	Δ
cinchoninone		*R*	–[a]	Λ
acetylcinchonine	*S*	*R*	–[a]	Λ

[a] No Pfeiffer effect detected.

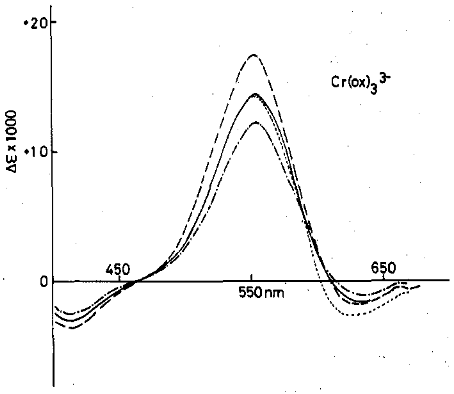


Figure 3. CD spectra induced for $[Cr(ox)_3]^{3-}$ (7.5 × 10^{-3} M) with various environments (7.5 × 10^{-3} M): — (cinchoH$^+$); ··· (*N*-Me-cinchoH$^+$); —·— (10,11-H_2-cinchoH$^+$); --- (6′-MeO-cinchoH$^+$).

also contribute to the steric hindrance like the methoxy group on the C-6′ atom.

In Table III are listed the absolute configurations of the enantiomers of both $[Co(phen)_3]^{2+}$ and $[Cr(ox)_3]^{3-}$ enriched by the Pfeiffer effect when hydrochloride salts of cinchonine, cinchonidine, cinchoninone, and acetylcinchonine are employed as an environment substance in water. Their configurations around C-8 and C-9 atoms are also given.[18] A close inspection of Table III suggests that the direction of the equilibrium shift for $[Co(phen)_3]^{2+}$ is determined by the configuration around the C-9 atom of these environment substances and that the OH group on the C-9 atom is essential to the chiral discrimination between Λ- and Δ-$[Co(phen)_3]^{2+}$. The importance of a hydroxyl group on the asymmetric carbon atom of the environment substance has also been found in the Pfeiffer effect of the $[Co(phen)_3]^{2+}$–(*R*,*R*)-tartaric acid system in water.[21] However, a detailed role of the OH group in the discriminating interaction is not yet known, though some proposals have been made.[5b,21,22] Anyway, it is concluded that $[Co(phen)_3]^{2+}$ associates with cinchoH$^+$ through the hydrophobic interaction with the quinolyl group and is subject to the spatial demand due to the asymmetry around the C-9 atom to which the quinolyl group in question is attached.

On the other hand, $[Cr(ox)_3]^{3-}$ is subject to the asymmetry around the C-8 atom, as is clearly confirmed in Table III. This is consistent with our earlier assumption that $[Cr(ox)_3]^{3-}$ approaches cinchoH$^+$ through the electrostatic interaction with the positive charge on the N(1) atom to which the asymmetric C-8 atom is directly bound. Furthermore, a simple chiral compound, *N*,*N*,*N*′,*N*′-tetramethyl-(*R*)-propylenediammonium ion,[23] serves well as an environment substance to $[Cr(ox)_3]^{3-}$ to enrich its Λ enantiomer, and the CD intensity of this system is enhanced by the addition of dioxane as in the case of the $[Cr(ox)_3]^{3-}$–cinchoH$^+$ system. Therefore, it is concluded that the quinolyl and hydroxyl groups on the C-9 atom of cinchoH$^+$ do not play an essential role in the discriminating interaction with $[Cr(ox)_3]^{3-}$. In contrast, the presence of these groups in the environment substances is indispensable to their stereoselective interaction with $[M(phen)_3]^{2+}$. Qualitatively in accord with the above conclusion, cinchotinium, *N*(1)-Me-cinchoH$^+$, and quinidinium ions all develop the Pfeiffer effect for $[Cr(ox)_3]^{3-}$ almost similar in magnitude to that developed by cinchoH$^+$, as seen in Figure 3.

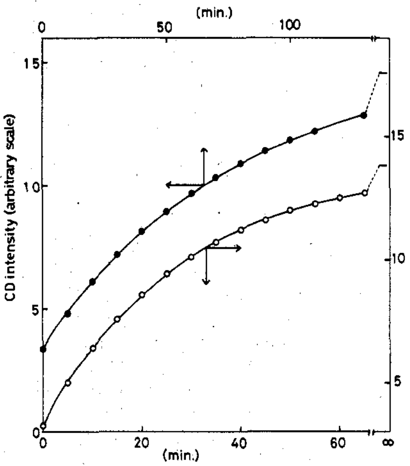


Figure 4. Plots of the CD intensity vs. time (min) for the $[Cr(ox)_3]^{3-}$ (2.86 × 10^{-3} M) –cinchoH$^+$ (3.75 × 10^{-2} M) system in water (○) and for the $[Cr(ox)_3]^{3-}$ (4.63 × 10^{-3} M) –cinchoH$^+$ (3.75 × 10^{-3} M) system in a 20 wt % dioxane–water mixture (●) at 25 °C.

Antiracemization Rate (Rate of Appearance of the Pfeiffer Effect) in the $[Co(ox)_3]^{3-}$–cinchoH$^+$ System. The rate of appearance of the Pfeiffer effect (antiracemization rate) was measured qualitatively by Ahmad[24] for the $[Cr(ox)_3]^{3-}$ and $[Co(ox)_3]^{3-}$ systems with cinchoH$^+$ as an environment substance in water. He found that the former system exhibits the time-dependent Pfeiffer effect, while the latter does not, though both complexes racemize in a usual manner[9a,25] and have been resolved by utilizing the Pfeiffer effect.[3] Here, we reinvestigated the time dependence of the Pfeiffer effect for the $[Cr(ox)_3]^{3-}$ system and analyzed it quantitatively in terms of the inversion rate constants of the Λ and Δ enantiomers in the presence of cinchoH$^+$.

If the following reaction is assumed

$$\Lambda\text{-}[Cr(ox)_3]^{3-} \rightleftarrows \Delta\text{-}[Cr(ox)_3]^{3-}$$

the antiracemization rate constant k_{anti} in the presence of a chiral environment substance is expressed as

$$\ln [(CD_\infty - CD_0)/(CD_\infty - CD_t)] = tk_{anti} = t(k_\Lambda + k_\Delta) \quad (2)$$

and the chiral equilibrium constant K as

$$K = [\Delta\text{-}[Cr(ox)_3]^{3-}]/[\Lambda\text{-}[Cr(ox)_3]^{3-}] = k_\Lambda/k_\Delta \quad (3)$$

where CD_0, CD_t, and CD_∞ refer to the CD intensity observed at $t = 0$, $t = t$, and $t = \infty$ (at equilibrium), respectively, after racemic $[Cr(ox)_3]^{3-}$ is mixed with cinchoH$^+$, and k_Λ and k_Δ refer to the inversion rate constant for the Λ and Δ enantiomers, respectively, in the presence of cinchoH$^+$. The value of K is estimated by the following equation

$$K = (a - x_\infty)/(a + x_\infty)$$

where a is half the total concentration of $[Cr(ox)_3]^{3-}$ and x_∞ is the concentration of Λ-$[Cr(ox)_3]^{3-}$ enriched from Δ-$[Cr(ox)_3]^{3-}$ at equilibrium, which is in turn determined from the values of $(CD_\infty - CD_0)/2$ and Δε for optically pure Λ-[Cr-

Table IV. Antiracemization Rate Constant ($\times 10^3$/min) and Chiral Equilibrium Constant K at 25 °C

system	medium	K	k_{anti}	k_Λ	k_Δ	k_i^a
$[Cr(ox)_3]^{3-}$ (2.86×10^{-3} M)	H_2O	0.909	35.2	16.7	18.5	18.8^b
$cinchoH^+$ (3.75×10^{-2} M)						18.7^c
$[Cr(ox)_3]^{3-}$ (4.63×10^{-3} M)	dioxane (20 wt %)	0.935	14.0	6.76	7.24	6.4^b
$cinchoH^+$ (3.75×10^{-2} M)						6.2^c

[a] Half the racemization rate constant in the absence of $cinchoH^+$. [b] Present work. [c] Reference 11.

$(ox)_3]^{3-}$ ion.[12] In principle, k_Λ and k_Δ can be also estimated from the racemization study for the Λ and Δ enantiomers in the presence of $cinchoH^+$ ion.[22,26]

In Figure 4 are plotted the CD intensities at 554 nm as a function of time (minutes) elapsed after racemic $[Cr(ox)_3]^{3-}$ was mixed with $cinchoH^+$ in water and in a 20 wt % dioxane–water mixture at 25 °C. The values of k_Λ and k_Δ derived from the plots of eq 2 and of the chiral equilibrium constant K are listed in Table IV together with those of the inversion rate constant k_i in the absence of $cinchoH^+$ at 25 °C. Similar experiments were made on the corresponding $[Co(ox)_3]^{3-}$ system, the CD intensity of which definitely increased with time, in disagreement with the earlier study reported by Ahmad.[24] However, quantitative analysis was impossible owing to the gradual decomposition of $[Co(ox)_3]^{3-}$.[25]

It is seen in Table IV that k_Δ in water is only slightly smaller than k_i, while k_Λ is appreciably smaller than k_i and k_Δ. This means that the Λ enantiomer to be enriched by the Pfeiffer effect associates with $cinchoH^+$ considerably, since ion-pair formation with bulky cations like tetraalkylammonium ions is known to retard the inversion rate of $[Cr(ox)_3]^{3-}$.[11] On the other hand, the Δ enantiomer is kinetically little affected by $cinchoH^+$, indicating that it associates only slightly with $cinchoH^+$. In other words, it is a retarded inversion rate of Λ-$[Cr(ox)_3]^{3-}$ brought about by the stereoselective association with $cinchoH^+$ that is responsible for the enrichment of the Λ enantiomer in the Pfeiffer effect of this system. The same should hold for the corresponding $[Co(ox)_3]^{3-}$ system.

Interestingly enough, similar experimental results have been found for the $[Ni(phen)_3]^{2+}$–$cinchoH^+$ system in water by Davies and Dwyer[26] who measured the racemization rates of Λ- and Δ-$[Ni(phen)_3]^{2+}$ in the presence of $cinchoH^+$ (2%). They found that k_Λ of $[Ni(phen)_3]^{2+}$ in the presence of $cinchoH^+$ is almost equal to the inversion rate constant k_i in pure water, while k_Δ is appreciably smaller than k_Λ or k_i, resulting in an enrichment of the Δ enantiomer at equilibrium. The same will hold for the corresponding $[Co(phen)_3]^{2+}$ system, but its inversion is so rapid[27] that this system exhibits the instantaneous Pfeiffer effect and therefore the abovementioned kinetic measurements cannot be carried out. Anyway, it is concluded that $cinchoH^+$ has a kinetically similar influence on $[Cr(ox)_3]^{3-}$ and $[Co(phen)_3]^{2+}$ except that it interacts favorably with their enantiomers of opposite absolute configuration.

On the other hand, it has been found[26] that, in the presence of *d*-3-bromocamphor-9-sulfonate ion (*d*-BCS^-), k_Λ of $[Ni(phen)_3]^{2+}$ is smaller than the corresponding k_Δ, resulting in an enrichment of the Λ enantiomer like in the $[Cr(ox)_3]^{3-}$–$cinchoH^+$ system, but both of the k_Λ and k_Δ are much smaller than k_i (in pure water). This may be ascribed to marked association of *d*-BCS^- with both the Λ and Δ enantiomers of $[Ni(phen)_3]^{2+}$.[28] All these situations are schematically presented in Figure 5.

For the $[Cr(ox)_3]^{3-}$–$cinchoH^+$ system in a 20 wt % dioxane–water mixture, k_Λ is smaller than k_Δ as before, but both of them are greater than k_i, as seen in Table IV. General deacceleration of the inversion rate brought about by the addition of nonpolar solvents[10,11] like dioxane is well interpreted in terms of destabilization of the carboxylate anion generated by one-ended dissociation of ox^{2-} from $[Cr(ox)_3]^{3-}$.[29] However, since k_Λ and k_Δ in this case may be a complicated function of relative compositions of the counterion (K^+ in this case),[11] water, dioxane, and $cinchoH^+$ in the second coordination sphere of $[Cr(ox)_3]^{3-}$, detailed interpretation of these k_Λ and k_Δ values is out of our present knowledge.

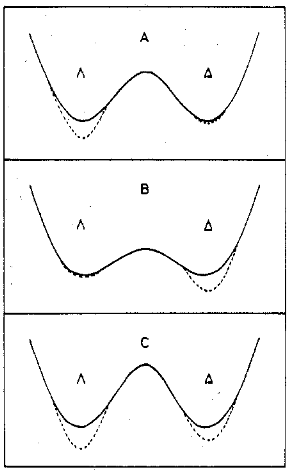


Figure 5. Potential energy curves for (A) Λ- and Δ-$[Cr(ox)_3]^{3-}$ in water (—) and in the presence of $cinchoH^+$ (···), for (B) Λ- and Δ-$[Co(phen)_3]^{2+}$ in water (—) and in the presence of $cinchoH^+$ (···), and for (C) Λ- and Δ-$[Ni(phen)_3]^{2+}$ in water (—) and in the presence of *d*-BCS^- (···).

Experimental Section

Preparation of Metal Complexes. Potassium tris(oxalato)chromate(III) trihydrate was prepared and resolved by a literature method[10] and the corresponding cobalt(III) complex was also prepared by a standard method.[30] An aqueous stock solution of tris(1,10-phenanthroline)cobalt(II) chloride was prepared by dissolving appropriate amounts of cobalt chloride hexahydrate and 1,10-phenanthroline monohydrate in a volumetric flask.

Preparation of Cinchonine Derivatives. 10,11-Dihydrocinchonine hydrochloride was obtained by hydrogenation of cinchonine hydrochloride in ethanol with PtO_2 as a catalyst, and *N*-methylcinchoninium iodide prepared by allowing cinchonine hydrochloride to react with methyl iodide in methanol[20] was converted to the more soluble chloride with an ion-exchange resin. Their purity was checked by NMR and elemental analysis. Cinchoninone was prepared by the method applied to the oxidation of yohimbine[31] and was purified on a silica gel column. Acetylcinchonine was prepared in pyridine by the method of Hilditch.[32] They were neutralized with hydrochloric acid and their purity was checked by NMR and/or IR measurements. Cinchonine, quinidine, and cinchonidine were purchased as hydrochloride salts from Wako Pure Chemical Industries, LTD, and used without purification.

Other Substances. *N,N,N',N'*-Tetramethyl-(*R*)-propylenediamine was prepared by the method of Moshier and Spialter[33] by using resolved (*R*)-propylenediamine[34] as a starting material and was used after neutralization with hydrochloric acid. Organic solvents of reagent grade were used as additives without further purification. Dioxane and THF were purified by distillation over sodium hydroxide.

Measurements. Circular dichroism (CD) and absorption spectra were recorded on a Jasco J-40CS and a Shimadzu UV-200 spectrometer. All the measurements except kinetic runs were carried out after the sample solutions were kept standing in the dark for 3–4 days to attain the chiral equilibrium.[9-11] For the determination of association constants, the concentrations of $K_3[Cr(ox)_3]$ and cinchonine hydrochloride were appropriately varied from 5.5×10^{-3} to 1.5×10^{-3} M and from 6.0×10^{-3} to 30.0×10^{-3} M, respectively, so that the final ionic strength of each sample solution was almost constant. The wavelength chosen for the CD measurement was 554 nm, at which the CD intensity has a maximum in water, and the cell compartment was thermostated at 25 ± 0.1 °C. Antiracemization and racemization were followed at 554 and 552 nm, respectively for at least 2 half-lives in a usual manner.[10,11,22]

Registry No. cinchoH$^+$, 63296-30-0; cinchonidinium, 69847-14-9; cinchoninonium, 69847-15-0; acetylcinchoninium, 69847-16-1; *N*-Me-cinchoH$^+$, 69847-17-2; 10,11-H$_2$-cinchoH$^+$, 69847-18-3; 6′-MeO-cinchoH$^+$, 53264-66-7; *N,N,N′,N′*-tetramethyl-(*R*)-propylenediamine, 36366-15-1; Λ-[Cr(ox)$_3$]$^{3-}$, 34307-04-5; Δ-[Cr(ox)$_3$]$^{3-}$, 67486-80-0; Co(ox)$_3$$^{3-}$, 15053-34-6; Δ-[Co(phen)$_3$]$^{2+}$, 69880-68-8; Λ-[Co(phen)$_3$]$^{2+}$, 69880-69-9; [Cr(ox)$_3$]$^{3-}$, 15054-01-0; [Co(phen)$_3$]$^{2+}$, 16788-34-4.

References and Notes

(1) To whom correspondence should be addressed.
(2) (a) S. Kirschner and N. Ahmad, "Coordination Chemistry", S. Kirschner, Ed., Plenum Press, New York, 1969, p 42; (b) R. C. Brasted, V. Landis, E. J. Kuhajek, P. E. R. Nordquist, and L. Mayer, *ibid.*, p 64.
(3) S. Kirschner, *Rec. Chem. Prog.*, **32**, 29 (1971).
(4) S. Kirschner and N. Ahmad, *J. Am. Chem. Soc.*, **90**, 1910 (1968); N. A. P. Kane-Maguire and D. E. Richardson, *ibid.*, **97**, 7195 (1975); K. Miyoshi, Y. Wada, and H. Yoneda, *Chem. Lett.*, 319 (1977).
(5) (a) N. Ahmad and S. Kirschner, *Inorg. Chim. Acta*, **14**, 215 (1975); (b) S. Kirschner, N. Ahmad, C. Munir, and R. J. Pollock, *Pure Appl. Chem.*, in press.
(6) K. T. Kan and D. G. Brewer, *Can. J. Chem.*, **49**, 2161 (1971).
(7) K. Miyoshi, Y. Kuroda, H. Okazaki, and H. Yoneda, *Bull. Chem. Soc. Jpn.*, **50**, 1476 (1977).
(8) K. Miyoshi, K. Sakata, and H. Yoneda, *J. Phys. Chem.*, **79**, 1622 (1975).
(9) (a) E. Bushra and C. H. Johnson, *J. Chem. Soc.*, 1937 (1939); (b) S. T. Spees and A. W. Adamson, *Inorg. Chem.*, **1**, 531 (1962).
(10) G. K. Schweitzer and J. L. Rose, Jr., *J. Phys. Chem.*, **56**, 428 (1952).
(11) A. L. Odell and D. Shooter, *J. Chem. Soc., Dalton Trans.*, 135 (1972).
(12) A. J. McCaffery, S. F. Mason, and R. E. Ballard, *J. Chem. Soc.*, 2883 (1965); K. R. Butler and M. R. Snow, *J. Chem. Soc., Dalton Trans.*, 251 (1976).
(13) G. J. Janz and R. P. T. Tomkins, "Nonaqueous Electrolytes Handbook", Vol. 1, Academic Press, New York, 1972.
(14) K. Miyoshi, Y. Wada, and H. Yoneda, *Inorg. Chem.*, **17**, 751 (1978); Y. Wada, K. Miyoshi, and H. Yoneda, *Chem. Lett.*, 763 (1978).
(15) T. Taura, H. Nakazawa, and H. Yoneda, *Inorg. Nucl. Chem. Lett.*, **13**, 603 (1977).
(16) R. A. Robinson and R. H. Stokes, "Electrolyte Solutions", Butterworths, London, 1959.
(17) B. Norden, *Acta Chem. Scand.*, **26**, 111 (1972); *Chem. Scr.*, **7**, 14 (1975); K. Miyoshi, C. E. Oh, H. Nakazawa, and H. Yoneda, *Bull Chem. Soc. Jpn.*, **51**, 2946 (1978).
(18) G. G. Lyle and L. K. Keefer, *Tetrahedron*, **23**, 3253 (1967).
(19) K. Ogino and T. Kumagai, *Bull. Chem. Soc. Jpn.*, **47**, 855 (1974).
(20) P. Pfeiffer and K. Quehl, *Ber. Dtsch. Chem. Ges.*, **65**, 560 (1932).
(21) Y. Kuroda, K. Miyoshi, and H. Yoneda, *Inorg. Chim. Acta*, **28**, 211 (1978).
(22) B. Bosnich and D. W. Watts, *Inorg. Chem.*, **14**, 47 (1975).
(23) If (*R*)-propylenediammonium ion is used as an environment substance, [Cr(ox)$_3$]$^{3-}$ ion undergoes a ligand-substitution reaction to give an optically active mixed complex.
(24) N. Ahmad, Ph.D. Dissertation, Wayne State University, 1969.
(25) N. Serpone and D. G. Bickley, *Prog. Inorg. Chem.*, **17**, 391 (1972).
(26) N. R. Davies and F. P. Dwyer, *Trans. Faraday Soc.*, **50**, 24 (1954).
(27) E. L. Blinn and R. G. Wilkins, *Inorg. Chem.*, **15**, 2952 (1976).
(28) A. Jensen, F. Basolo, and H. M. Neumann, *J. Am. Chem. Soc.*, **80**, 2354 (1958).
(29) G. A. Lawrance and D. R. Stranks, *Inorg. Chem.*, **16**, 929 (1977).
(30) J. C. Bailar, Jr., and E. M. Jones, *Inorg. Synth.*, **1**, 35 (1939).
(31) J. D. Albright and L. Goldman, *J. Org. Chem.*, **30**, 1107 (1965).
(32) T. P. Hilditch, *J. Chem. Soc.*, **99**, 224 (1911).
(33) R. W. Moshier and L. Spialter, *J. Org. Chem.*, **21**, 1050 (1956).
(34) F. P. Dwyer, F. L. Garvan, and A. Shulman, *J. Am. Chem. Soc.*, **81**, 290 (1959).

Contribution from the Paul M. Gross Chemical Laboratory,
Duke University, Durham, North Carolina 27706

Synthesis and Structural Isomerism of Some (Silylamino)phosphinimines

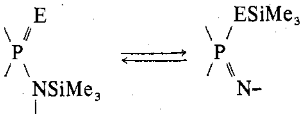
JAMES C. WILBURN, PATTY WISIAN-NEILSON, and ROBERT H. NEILSON*[1]

Received August 17, 1978

The synthesis and NMR (^{1}H and ^{13}C) spectroscopic characterization of several new (silylamino)phosphinimines including $(Me_3Si)_2NP({=}NSiMe_3)PhX$ (**1**, X = Me; **2**, X = F), $(Me_3Si)_2NP[{=}N(t\text{-Bu})]Me_2$ (**3**), $[Me(Me_3Si)N]_nP({=}NSiMe_3)Me_{3-n}$ (**4**, $n = 1$; **5**, $n = 2$; **6**, $n = 3$), $Me_2SiCH_2CH_2SiMe_2NP({=}NSiMe_3)Me_2$ (**7**), and $R(Me_3Si)NP[{=}NSiMe_2(t\text{-Bu})]Me_2$ (**8**, R = Me$_3$Si; **9**, R = Me) are reported. The trisilylated compounds **1** and **2** exhibited reversible [1,3] silyl exchange with $\Delta G^{\ddagger}_{1,3}$ values of 14.2 and 18.3 kcal/mol, respectively. The other phosphinimines **3**–**9** exist as static structures which in some cases (**3**, **8**, and **9**) have resulted from irreversible silyl shifts.

Introduction

It is becoming increasingly apparent that an important feature of the chemistry of four-coordinate silicon–nitrogen–phosphorus compounds is the lability of silyl substituents toward intramolecular migrations.[2]

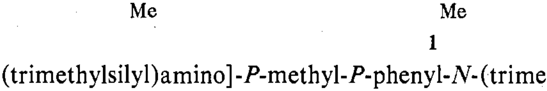


E = O, NR, CR$_2$

With few exceptions,[3] these rearrangements are irreversible for (silylamino)phosphine oxides (E = O)[4] and ylides (E = CR$_2$),[5,6] but the (silylamino)phosphinimines (E = NR)[7] offer greater possibilities for the study of reversible [1,3] silyl shifts. The steric and electronic factors which determine the ease of silyl migration in such compounds as well as their ground-state structures have not been fully elucidated. In this context, we report the synthesis and NMR (^{1}H and ^{13}C) spectroscopic properties of several new di-, tri-, and tetrasilylated phosphinimines.

Results and Discussion

Syntheses. There are two basic preparative routes available for the synthesis of (silylamino)phosphinimines. The first method is an adaptation of the well-known Staudinger reaction of organophosphines with azides.[8] The utility of this approach in Si–N–P chemistry has been broadened by the recent availability of the necessary (silylamino)phosphine reagents.[6] For example, when [bis(trimethylsilyl)amino]methylphenylphosphine was heated with a small excess of trimethylsilyl azide at ca. 100 °C for 20 h in the absence of solvent, the product isolated (eq 1) in 84% yield was *P*-



$$(Me_3Si)_2NP(Ph)Me + Me_3SiN_3 \xrightarrow[\Delta]{-N_2} (Me_3Si)_2N{-}P(Ph)(Me){=}NSiMe_3 \quad (1)$$

1

[bis(trimethylsilyl)amino]-*P*-methyl-*P*-phenyl-*N*-(trimethylsilyl)phosphinimine (**1**).

A second preparative method complements the first by allowing the synthesis of P-halogenated (silylamino)phosphinimines. Treatment of *P,P*-difluoro-*P*-phenyl-*N*-(tri-