

The Pfeiffer Effect Studies in Some Mixed Ligand Complexes of Cobalt (III)

NASIR AHMAD*, EARNEST OBED JOHN
AND CHRISTY MUNIR

*Department of Chemistry, Quaid-i-Azam University,
Islamabad, Pakistan.*

(Received 15th April, 1986)

Summary: The Pfeiffer effect is studied in a series of thirteen coordination compounds of cobalt (III) of type $[\text{Co}(\text{AA})_3]^{n+}$ and $[\text{Co}(\text{AA})_2\text{BB}]^{n+}$ where AA and BB are 1,10-phenanthroline, 2,2'-bipyridyl, oxalate or carbonate ions, $\text{cis-}[\text{Co}(\text{bpy})_2\text{X}_2]^+$ ($\text{X} = \text{Cl}$ or NO_2^-) and $\text{cis-}[\text{Co}(\text{phen})_2\text{Cl}]^+$ ions in presence of (+)-cinchonine hydrochloride and (+)-tartaric acid. Two new chiral environment compounds i.e. (+)-ascorbic acid and (-)-lysine also induce this effect in a few complexes. The effect is used to correlate the absolute configurations of these complexes with that of standard compounds like $\Delta\text{-K}_3[\text{Co}(\text{ox})_3]$.

Introduction

Studies on the Pfeiffer effect in dissymmetric coordination compounds have been in progress for well over 50 years now [1-4]. The Pfeiffer effect is a change in optical rotation of a chiral compound (termed as environment substance) upon addition of a racemic mixture of certain dissymmetric complexes. The Pfeiffer effect was first observed in dissymmetric tris-bidentate complexes of labile metal ions such as Al(III), V(III), Fe(III), Co(II), Ni(II), Cu(II), Zn(II), Cd(II), Hg(II) with ligands like 1,10 phenanthroline (phen), 2,2'-bipyridyl (bpy) and oxalate (ox^{2-}) ion. A number of chiral environment substances such as ammonium (+)- α -bromo- π -camphor-sulphonate, (+)-10-camphorsulphonic acid, (+)-cinchonine hydrochloride (+)-malic acid, (+) and (-)-tartaric acid have been used for inducing this effect. For some time it was believed that this effect was only exhibited in presence of labile dissymmetric complexes but later studies revealed

that inert complexes such as $\text{K}_3[\text{Co}(\text{ox})_3] \cdot 3\text{H}_2\text{O}$ and $\text{K}_3[\text{Cr}(\text{ox})_3] \cdot 3\text{H}_2\text{O}$ also show Pfeiffer activity [5]. Kirschner and Ahmad were able to achieve partial resolution of a few complexes such as $[\text{Ni}(\text{phen})_3]^{2+}$ and $[\text{Co}(\text{ox})_3]^{3-}$ by removing either the complex or chiral environment substance from the Pfeiffer active system [6]. Recently Yoneda et.al. have also partially resolved $[\text{Co}(\text{ox})_3]^{3-}$ and $[\text{Cr}(\text{ox})_3]^{3-}$ ions using $\Delta\text{-}[\text{Co}(\text{phen})_3]^{3+}$ as a chiral environment substance [7]. These studies have provided a strong support to the equilibrium displacement mechanism proposed earlier by Dwyer and Gyarfas for this effect [8].

Most of the studies on Pfeiffer effect have been carried out on racemic, octahedral tris-bidentate complexes of metal ions. A number

of Pfeiffer active complexes cannot be resolved in the laboratory and their Pfeiffer ORD and CD studies are of great value in relating their absolute configurations [5]. Further, most of chiral environment substances used for such studies are common resolving agents. The present investigations were undertaken to explore this effect in mixed ligand complexes of inert metal ions which should be resolvable by conventional means. It was also intended to find new chiral environment substances other than the resolving agents.

We present here investigations on the Pfeiffer effect in a number of complexes of an inert cobalt (III) ion of type $[\text{Co}(\text{AA})_3]^{n+}$, $[\text{Co}(\text{AA})_2\text{BB}]^{n+}$ and $\text{cis-}[\text{Co}(\text{AA})_2\text{X}_2]^{n+}$

where AA, BB are bidentate ligands like phen, bpy, oxalate or carbonate ions and $\text{X} = \text{Cl}^-$ or NO_2^- ions in presence of chiral environment substances such as (+)-cinchonine hydrochloride, (+)-tartaric acid, (-)-lysine, (+)-ascorbic acid and (-)-asparagine. All of these chiral compounds except (-)-asparagine induce Pfeiffer effect in the above noted complexes. The absolute configurations of environment substances and complexes have been related with those of standard dissymmetric complexes and certain relationships have been established.

Experimental

All the reagents used during these studies were of analytical reagent grade. The ligands 1,10-phenanthroline and 2,2'-bipyridyl were obtained from BDH. Doubly distilled water was used as solvent in synthesis as well as in the Pfeiffer effect studies.

The racemic complexes used in these investigations were synthesised by standard literature methods. The green $\text{K}_3[\text{Co}(\text{ox})_3] \cdot 3\text{H}_2\text{O}$ was prepared by the method of Bailar and Jones [9] while $\text{Ba}[\text{Co}(\text{ox})_2(\text{bpy})]_2 \cdot 5\text{H}_2\text{O}$, $[\text{Co}(\text{ox})(\text{phen})_2]\text{Cl} \cdot 4\text{H}_2\text{O}$, $[\text{Co}(\text{phen})_3](\text{ClO}_3)_3 \cdot 2\text{H}_2\text{O}$ and $[\text{Co}(\text{bpy})_3](\text{ClO}_4)_3 \cdot 7\text{H}_2\text{O}$ were synthesised by the method reported by Broomhead *et al.* [10]. The compounds $[\text{Co}(\text{bpy})_2(\text{ox})]\text{Cl} \cdot 2\text{H}_2\text{O}$, $[\text{Co}(\text{bpy})_2\text{CO}_3]\text{Cl} \cdot 3\text{H}_2\text{O}$, $\text{cis-}[\text{Co}(\text{bpy})_2\text{Cl}_2]\text{Cl} \cdot 2\text{H}_2\text{O}$ and $\text{cis-}[\text{Co}(\text{bpy})_2(\text{NO}_2)_2]\text{Cl} \cdot 6\text{H}_2\text{O}$ [11] and $[\text{Co}(\text{phen})_2\text{CO}_3]\text{Cl} \cdot 3\text{H}_2\text{O}$ *cis-}[\text{Co}(\text{phen})_2\text{Cl}]\text{Cl} \cdot 2\text{H}_2\text{O}, $[\text{Co}(\text{phen})_2(\text{bpy})](\text{ClO}_4)_3 \cdot 7\text{H}_2\text{O}$, and $[\text{Co}(\text{phen})(\text{bpy})_2](\text{ClO}_4)_3 \cdot 7\text{H}_2\text{O}$ [12] were also synthesised by reported methods. These compounds were characterized by comparing their infra-red and electronic spectra with the reported ones.*

Preparation of Solutions of Environment Substances:

The solutions of various chiral environment substances were prepared by dissolving requisite amounts in water and diluting to the mark in volumetric flasks. These solutions were stored in the dark. Since (+)-cinchonine is sparingly soluble in water, its solution was prepared as given below.

A 0.04 M solution of (+)-cinchonine hydrochloride was obtained by making a slurry of accurately weighed amount of the alkaloid in water and then dissolving it by dropwise addition of dilute hydrochloric acid. The pH of resulting solution was adjusted to

3.0 - 3.5 by suitable means. The volume of resulting solution was made up in a 500 ml measuring flask. The contents were thoroughly mixed and stored in the dark.

The solutions for the Pfeiffer effect studies were prepared by dissolving calculated amounts of solid racemic complexes in aliquote portions of stock solutions of chiral compounds in volumetric flasks of appropriate size. These solutions were thoroughly mixed and left in the dark for couple of hours before measuring their optical rotations.

Instrumentation:

The electronic spectra of aqueous solutions of complexes and Pfeiffer systems were recorded on Hitachi model 323 spectrophotometer using 1 cm quartz cuvettes. Infra-red spectra of solid complexes in KBr pellets were recorded on a Beckman IR-20A spectrophotometer.

The optical rotations of solutions of chiral environment compounds and Pfeiffer systems were measured on a Perkin Elmer model 241 digital polarimeter. This instrument is equipped with filters to measure rotations at five different wavelengths as 589, 578, 546, 436 and 365 nm. A silica cell of 2 cm length was used to measure rotations. The concentrations of complexes were in the range 1-10mM while those of chiral environment compounds were maintained 2-3 times higher than those of complexes. The molar Pfeiffer rotations were calculated from the difference in rotations in the usual manner [13]. These results are reproduced in Table-1.

Discussion

The Pfeiffer effect was observed in a series of thirteen coordination compounds of cobalt (III) of type

$[\text{Co}(\text{AA})_3]^{n+}$, $[\text{Co}(\text{AA})_2\text{BB}]^{n+}$ (where AA or BB are 2,2'-bipyridyl, 1,10-phenanthroline, oxalate or carbonate ions) and $\text{cis-}[\text{Co}(\text{bpy})_2\text{Cl}]^+$, Cis-

$[\text{Co}(\text{bpy})_2(\text{NO}_2)_2]^+$ and $\text{cis-}[\text{Co}(\text{phen})_2\text{Cl}_2]^+$ ions in presence of chiral

environment compounds like (+)-cinchonine and (+)-tartaric acid. In addition the effect was also induced in a few complexes in presence of two new chiral compounds as (+)-ascorbic acid and (-)-lysine. It was found that (+)-asparagine did not induce this effect in a number of metal complexes. The Pfeiffer rotation (i.e. $\alpha_e - \alpha_{c+e}$)

in these systems is known to be dependent upon concentration of the environment substance, nature of complex ions, temperature and the wavelength of radiation used. These complexes are substitution inert and are not expected to react with environment substances to any appreciable extent under experimental conditions. Further, outer sphere complexation was ruled out by comparing absorption spectra of the Pfeiffer systems with those of aqueous solutions of individual complexes and chiral compounds which matched in every detail.

It was also observed that appearance of the effect in these systems did not depend upon time. In fact the changes in rotation because of the presence of racemate complexes occurred instantaneously. It is evident that an immediate enrichment of one enantiomer occurred as soon as the components were mixed. The Pfeiffer rotations measured at four different wavelengths were found to vary as the wavelength of radiation decreased. The magnitude of the Pfeiffer rotation was appreciably affected in the absorption band region of these metal complexes. The wavelength depen-

dence of the Pfeiffer rotation in these systems is characteristic of metal complexes and indicate the enrichment of one enantiomer of these complexes. It has been earlier reported that ORD and CD spectra of a number of Pfeiffer systems are similar in shape and character to those of their completely resolved enantiomers [14]. These studies also reveal that enrichment of one enantiomer of complexes has occurred in these systems. However, a complete Pfeiffer ORD spectrum is required to make its comparison with that of resolved complexes which could not be obtained.

It is interesting to note that (+)-tartaric acid enriches dextro enantiomers of various complexes indicating that (+) tartaric acid and dextro enantiomers of these complexes are somehow related in terms of their absolute configurations. On the other hand, (+)-cinchonine hydrochloride enriches levo enantiomers of most of these complexes except $[\text{Co}(\text{phen})_3]^{3+}$ and $\text{cis-}[\text{Co}(\text{bpy})_2(\text{NO}_2)_2]^+$ ions. It may be concluded that (+)-tartaric acid and (+) - cinchonine hydrochloride should have opposite absolute configu-

Table-1
Molar Pfeiffer Rotations at 589 nm for some mixed ligand complexes of Cobalt (III).

Complex	Environment Substance	(-)-Lysine HCl	(+)-Tartaric Acid	(+)-Cinchonine HCl.	(+)-Ascorbic Acid.
$[\text{Co}(\text{ox})_3]^{3-}$		- 1100	+ 312.5*	- 14375	
$[\text{Co}(\text{bpy})(\text{ox})_2]^-$		- 375*	+ 153	- 972*	
$[\text{Co}(\text{bpy})_2(\text{ox})]^+$		- 300	+ 93.75*	- 1125	
$[\text{Co}(\text{phen})_2(\text{ox})]^+$		- 200	+ 275	- 1535*	
$[\text{Co}(\text{bpy})_2\text{CO}_3]^+$			+ 31.25	- 586	
$[\text{Co}(\text{phen})_2\text{CO}_3]^+$			+ 85.3*	- 1327	
$[\text{Co}(\text{bpy})_3]^{3+}$		- 200	+ 275	- 1101	+ 826
$[\text{Co}(\text{phen})_3]^{3+}$			+ 595*	+ 1190.5	- 2975
$[\text{Co}(\text{bpy})_2(\text{phen})]^{3+}$			+ 396	- 3956	- 1130
$[\text{Co}(\text{bpy})(\text{phen})_2]^{3+}$			+ 638	- 1160	- 2899.5*
$\text{cis-}[\text{Co}(\text{bpy})_2\text{Cl}_2]^+$				- 2055	
$\text{cis-}[\text{Co}(\text{bpy})_2(\text{NO}_2)_2]^+$				+ 931*	
$\text{cis-}[\text{Co}(\text{phen})_2\text{Cl}_2]^+$			+ 491.5*		

*Optical rotations measured at 578 nm.

Table-2: Absorption spectra, Molar Pfeiffer Rotations at Various Wavelengths and Absolute configuration of the Enriched Enantiomers of some Cobalt (III) Complexes.

Complex	Environment Substance	Absorption maxima λ_{\max}	589 nm	578 nm	Molar Pfeiffer	Rotation	Absolute Configuration of Enriched Enantiomers
$[\text{Co}(\text{ox})_3]^{3-}$	(+)-cinchonine HCl (Cin-HCl)	605 420		- 6166	- 9865	- 13565	Δ
	(-)-lysine		- 1100	- 450	- 375	- 500	Δ
$[\text{Co}(\text{bpy})(\text{ox})_2]^-$	(+)-Cin.HCl	555 390		- 972	- 3159	- 11664	Δ
$[\text{Co}(\text{bpy})_2(\text{ox})]^+$	(+)-Cin.HCl	500		- 750	- 875	- 1000	Δ
$[\text{Co}(\text{phen})_2(\text{ox})]^+$	(+)-Cin.HCl	510		- 1536	- 2304	- 5372	Δ
$[\text{Co}(\text{bpy})_3]^{3+}$	(+)-Cin.HCl	450	- 1101	- 551 + 826	- 1101 + 550	+ 1652	Δ
	(+)-Ascorbic Acid			- 586	- 1107	- 9765	Δ
$[\text{Co}(\text{bpy})_2\text{CO}_3]^+$	(+)-Cin.HCl	504		- 1327	- 1990	- 2654	Δ
$[\text{Co}(\text{phen})_2\text{CO}_3]^+$	(+)-Cin.HCl	512		+ 1190 + 595	+ 1785 + 714	+ 2380 + 1012	Δ
$[\text{Co}(\text{phen})_3]^{3+}$	(+)-Cin.HCl	472		- 4521	- 5086	- 10172	Δ
	(+)-Tartaric Acid		- 3956	- 580	- 4059	- 1160	Δ
$[\text{Co}(\text{phen})(\text{bpy})_2]^{3+}$	(+)-Cin.HCl	462		- 2899 + 638	+ 580	+ 812	Δ
$[\text{Co}(\text{phen})_2(\text{bpy})]^{3+}$	(+)-Cin.HCl	468	- 1160	- 1348	- 1605	- 1926	Δ
	(+)-Ascorbic Acid			+ 931	+ 1163	+ 2870	Δ
	(+)-Tartaric Acid		- 2055	+ 491.5		+ 913	Δ
$\text{Cis-}[\text{Co}(\text{bpy})_2\text{Cl}_2]^+$	(+)-Cin.HCl	520					Δ
$\text{Cis}[\text{Co}(\text{bpy})_2(\text{NO}_2)_2]^+$	(+)-Cin.HCl	453					Δ
$\text{Cis-}[\text{Co}(\text{phen})_2\text{Cl}_2]^+$	(+)-Tartaric Acid	524					Δ

rations around their asymmetric centres. These two chiral compounds have two asymmetric carbon atoms each. The absolute configuration around the two asymmetric atoms of (+)-tartaric is RR while that in (+)-cinchonine is SR. It seems that displacement of equilibrium in these racemates occurred through the R asymmetric centre of (+)-tartaric acid and the S centre of (+)-cinchonine enriching opposite enantiomers in these two chiral compounds. This relationship is further strengthened by the observation that (-)-lysine (which has only one asymmetric centre with S configuration) also enriches levo enantiomers in all the five complexes studied. The dextro enantiomers of these five compounds, i.e. $[\text{Co}(\text{ox})_3]^{3-}$, $[\text{Co}(\text{bpy})(\text{ox})_2]^-$, $[\text{Co}(\text{bpy})_2(\text{ox})]^+$, $[\text{Co}(\text{phen})_2(\text{ox})]^+$ and $[\text{Co}(\text{bpy})_3]^{3+}$ are enriched in presence of (+)-tartaric acid while levo enantiomers are enriched in presence of (+)-cinchonine hydrochloride. The enrichment of dextro enantiomers of $[\text{Co}(\text{phen})_3]^{3+}$ and $\text{cis-}[\text{Co}(\text{bpy})_2(\text{NO}_2)_2]^+$ in presence of (+)-cinchonine hydrochloride indicates that asymmetric centre with R configuration of the chiral compound interacts with these racemates enriching dextro enantiomers.

Another chiral compound (+)-ascorbic acid (RR configuration) induced a positive effect in $[\text{Co}(\text{bpy})_3]^{3+}$ but a negative effect in $[\text{Co}(\text{bpy})_2(\text{phen})]^{3+}$, $[\text{Co}(\text{bpy})(\text{phen})_2]^{3+}$ and $[\text{Co}(\text{phen})_3]^{3+}$ ions. All of these complex ions exhibited a positive Pfeiffer effect in presence of (+)-tartaric acid which has RR configuration. The levo enantiomers of

$[\text{Co}(\text{phen})_3]^{3+}$ and $[\text{Co}(\text{phen})(\text{bpy})_2]^{3+}$ and dextro- $[\text{Co}(\text{phen})_3]^{3+}$ ions are enriched in presence of (+)-cinchonine hydrochloride. If absolute configuration of chiral compounds play any role in enriching a particular enantiomer then (+)-tartaric acid and (+)-ascorbic acid should enrich the same enantiomers because of their similar absolute configuration. It seems that the Pfeiffer effect in these systems does not depend upon the absolute configuration of chiral environment compounds. However, it is difficult to assign a definite reason for their exceptional behaviour.

As opposite enantiomers of these complexes are enriched in (+)-cinchonine hydrochloride and (+)-tartaric acid, certain absolute configurational relationships may be drawn from these studies. The levo enantiomers of $\text{K}_3[\text{Co}(\text{ox})_3] \cdot 3\text{H}_2\text{O}$ and a number of other complexes are enriched in presence of (+)-cinchonine hydrochloride. It has been reported that (+)-cinchonine hydrochloride enriches $\Lambda\text{-K}_3[\text{Co}(\text{ox})_3] \cdot 3\text{H}_2\text{O}$ [15]. Therefore all those compounds exhibiting a negative Pfeiffer effect in (+)-cinchonine hydrochloride should have Λ configuration around the metal ions. On the other hand, (+)-tartaric acid induced positive Pfeiffer effect in all compounds including $\text{K}_3[\text{Co}(\text{ox})_3] \cdot 3\text{H}_2\text{O}$. This chiral compound, therefore, enriches $\Lambda\text{-K}_3[\text{Co}(\text{ox})_3] \cdot 3\text{H}_2\text{O}$ and other compounds of Δ configuration. Similarly $\Lambda\text{-}[\text{Co}(\text{phen})_3](\text{ClO}_4)_3$ is enriched by (+)-tartaric acid and also (+)-cinchonine hydrochloride while $\Delta\text{-cis}[\text{Co}(\text{bpy})_2(\text{NO}_2)_2]^+$ is enriched only by the latter chiral compound. The tentative assignments

of absolute configurations of enriched enantiomers of complexes on the basis of these studies are given in Table-2. It is clear from preceeding discussion that absolute configurations of many dissymmetric complexes may be ascertained by comparing the nature of their Pfeiffer effect in presence of different chiral compounds.

References

1. P. Pfeiffer and K. Quehl, *Ber.*, **64**, 2667 (1931); *ibid.*, **65**, 560 (1932).
2. S. Kirschner, *Rec. Chem. Prog.*, **32**, 29 (1971).
3. P.E. Schipper, *Inorg. Chim. Acta.*, **12**, 199 (1975).
4. R.J. Pollock, S. Kirschner, S. Policec, *Inorg. Chem.*, **16**, 522 (1977).
5. N. Ahmad and S. Kirschner, *Inorg. Chim. Acta.*, **14**, 215 (1975).
6. S. Kirschner and N. Ahmad, *J. Am. Chem. Soc.*, **90**, 1910 (1968).
7. K. Miyoshi, Y. Wada and H. Yoneda, *Inorg. Chem.*, **17**, 751 (1978).
8. E.G. Gyarfás and F.P. Dwyer, *Rev. Pure. Appl. Chem.*, **4**, 73 (1954).
9. J.C. Bailar Jr. and E.M. Jones, *Inorg. Syn.*, **1**, 37 (1939).
10. J.A. Broomhead, M. Dwyer and N. Kane Macguire, *Inorg. Chem.*, **7**, 1388 (1968).
11. D.M. Palade, A.V. Ablove and V.N. Zubareve, *Russ. J. Inorg. Chem.*, **14**, 227 (1969).
12. A.V. Ablove and D.M. Palade, *Zhur. Neorg. Khim.*, **6**, 601 (1961); *ibid.*, **7**, 2514 (1962).
13. S. Kirschner, N. Ahmad, C. Munir and R.J. Pollock, *Pure and App. Chem.*, **51**, 913 (1979).
14. S. Kirschner and N. Ahmad "Coordination Chemistry", Ed.S. Kirschner, Plenum Publishing Corporation, New York, 42, (1969).
15. K. Miyoshi, Y. Kuroda, J. Takeda and H. Yoneda, *Inorg. Chem.*, **18**, 1435 (1979).