Pfeiffer Effect in Covalently Hydrated Molecules

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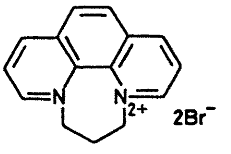
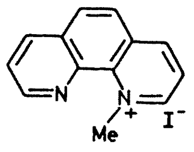
Summary *N*-Heterocyclic complex cations derived from 1,10-phenanthroline and quaternized with alkyl groups, and which are inherently achiral, or metal ions, which are kinetically inert towards racemization, give rise to cation–cation Pfeiffer effects which can be related to covalent hydrate and pseudo-base formation.

SEVERAL explanations have been advanced to explain the origin of the Pfeiffer effect. This effect is the development of additional optical activity when a racemic mixture of a complex is added to a solution containing a certain chiral molecule called an environment compound. Chief among the explanations for this phenomenon are the equilibrium shift or configurational activity (in the thermodynamic sense) mechanism originally put forward by Dwyer *et al.*,[1] and the diastereoisomeric mechanism first proposed by Turner and Harris.[2] The nature of the interactions responsible is not at all well understood.[3]

The Pfeiffer effect in cation–cation systems is seemingly the most unusual since the effect is well observed in spite of the inevitable repulsions between the Pfeiffer and environment (usually alkaloid) ions. We have begun to evaluate the contribution made[4,5] to the Pfeiffer effect by the introduction of new asymmetric centres in complexes of *N*-heterocycles *via* covalent hydrate and pseudo-base formation. We report here two new classes of Pfeiffer-active compounds; first, quaternized derivatives of 1,10-phenanthrolines, and secondly a kinetically inert Ru^{II} complex in which no shift of equilibrium between Δ- and Λ-isomers occurs. Both examples display the cation–cation Pfeiffer effect and both form[6] pseudo-bases and covalent hydrates in aqueous solution. This is the first time that inherently achiral compounds have been shown to be Pfeiffer-active in cation–cation systems. It is also the first time that a cation–cation effect has been observed for a kinetically inert octahedral metal complex.



(1)



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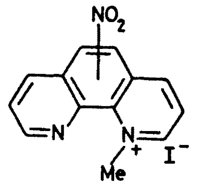


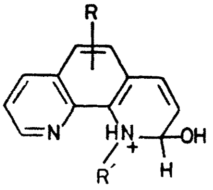
(3)

Results for the organically quaternized compounds (**1**)—(**3**) are given in the Table. Rotations were measured at 298 K using a Thorn-NPL 243 automatic polarimeter at 546·1 nm. The concentration of the environment compound was always 0·01 mol dm^{-3}. The Pfeiffer effect in Ru(5-NO$_2$phen)$_3$$^{2+}$ (phen = 1,10-phenanthroline) was observed through c.d. spectral measurements at 287 K using a Jobin-Yvon CNRS Dichrographe III with strychnine–HCl (0·05 mol dm^{-3}) as the environment compound. Measured values of $\Delta\epsilon$(cm l mol^{-1}) were: at 460 nm, +0·04; 430 nm, 0; 390 nm, −0·07; 360 nm, −0·025; and 330 nm, 0 (±0·01).

All these compounds are known in aqueous solution to form pseudo-bases and covalent hydrates of the type shown in structures (**4**)—(**6**). The newly asymmetric carbon atom may adopt either the *R*- or *S*-configuration, as may the co-ordinated nitrogen atom in the covalent hydrates (**4**) and (**5**). The equilibria are in all cases reversible so that any mixture of hydrates and pseudo-bases can equilibrate to

TABLE. Molar Pfeiffer rotations (see S. Kirschner and K. R. Magnell, *Adv. Chem. Ser.*, 1967, **62**, 366) of some quaternized *N*-heterocycles at 298 K with various environment compounds.

Compound	Concentration/ mol dm^{-3}		$[P_M]_{546\cdot1}$		
		Quinine H+	Strychnine H+	Brucine H+	Cinchonine H+
(**1**)	0·01			1200	
(**2**)	0·01	−4800	−3300		−1900
	0·02			2200	−800
(**3**)	0·01	−5600		3200	−4200
	0·02			1950	



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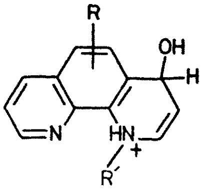

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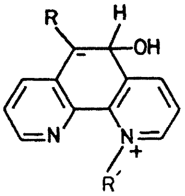

(6)

conform to the most stable distribution for a particular asymmetric environment. This may be principally due to either selective hydrogen bonding (less likely in the case of cation–cation interactions) or to selective interaction with the chiral solvent sheath[5,7] induced at the covalent hydrate by the environment compound. Because the Ru^{II} complex cannot racemize, the only chiral centres in this complex are organic, like those shown in structures (**4**)—(**6**). The Pfeiffer effect can thus be developed in systems where labile racemization at the chiral metal centre is impossible. This case is, we point out, different to those[8] due to strong ion-pairing between inert metal complexes and optically active counter ions.

There have been several reviews[3,9] concerning the kinds of interactions which may be responsible for the Pfeiffer effect. We have limited some variables in active systems in order to probe the phenomenon in a new way. For the Ru^{II} complex configurational activity concepts clearly cannot play any role. For the inherently achiral substrates in the cation–cation system chosen it has been possible to explore the Pfeiffer effect where contact interactions are at a minimum. Consequently it has been possible to isolate a specific and novel *chemical* mechanism for the generation of the Pfeiffer effect which has not been considered previously.

The introduction of new chiral centres in complexes of *N*-heterocyclic molecules *via* the above mechanism may be widespread. It cannot be ignored in compounds of this type, including the most frequently studied Pfeiffer-active systems involving $Ni(phen)_3^{2+}$ and $Zn(phen)_3^{2+}$. It is particularly important, in the context of this new theory, that the only cations which engender cation–cation effects (Pfeiffer's original cases) in water all contain *N*-heterocyclic aromatic ligands.

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