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Circular Dichroism of the Complexes of Quinine with Copper(II), Nickel(II), Cobalt(II), Chromium(III) and Palladium(II) Chlorides

John M. Tsangaris* and **Themistoclis A. Kabanos**

Laboratory of Inorganic and General Chemistry, University of Ioannina,
Ioannina, Greece

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The CD spectrum of the complexes $Q \cdot 2\,CuCl_2$, $Q \cdot 2\,CoCl_2$, $Q \cdot 2\,NiCl_2 \cdot 8\,H_2O$, $Q \cdot 3\,CrCl_3 \cdot 6\,H_2O$, $Q \cdot PdCl_2 \cdot 3\,H_2O$ and $Q \cdot 2\,PdCl_2 \cdot 5\,H_2O$ (where Q = quinine) in *DMF* or *DMSO* solution reveals *Cotton* effects in the d-d absorption range. The *Cotton* effects are relatively strong in the case of Cu(II) and Pd(II) complexes which implies that only in these complexes the hydroxyl group of the quinine molecule possibly participates in the coordination with these metal ions by formation of a chelate ring. The IR spectra of the complexes of Pd(II) are discussed in this respect.

(Keywords: Quinine complexes; Cotton effects; Hydroxyl coordination)

Circular Dichroismus der Komplexe des Chinins mit Kupfer(II)-, Nickel(II)-, Kobalt(II)-, Chrom(III)- und Palladium(II)-chlorid

Die CD-Spektren der Komplexe $Q \cdot 2\,CuCl_2$, $Q \cdot 2\,CoCl_2$, $Q \cdot 2\,NiCl_2 \cdot 8\,H_2O$, $Q \cdot 3\,CrCl_3 \cdot 6\,H_2O$, $Q \cdot PdCl_2 \cdot 3\,H_2O$ und $Q \cdot 2\,PdCl_2 \cdot 5\,H_2O$, ($Q$ = Chinin), in *DMF*- bzw. *DMSO*-Lösungen zeigen *Cotton*-Effekte im Gebiet der d-d-Elektronenübergänge. Die *Cotton*-Effekte sind relativ stark im Falle der Cu(II)- und Pd(II)-Komplexe, was zu der Annahme führt, daß die Hydroxygruppe des Chininmoleküls in diesen Komplexen wahrscheinlich an der Koordination dieser Metallionen durch Chelatringbildung teilnimmt. Unter diesem Aspekt werden die IR-Spektren der Pd(II)-Komplexe untersucht.

Introduction

In a previous paper[1] the synthesis of several complexes of quinine free base with transition metal chlorides was reported. Among the prepared complexes were the following: $Q \cdot 2\,CuCl_2$, $Q \cdot 2\,NiCl_2 \cdot 8\,H_2O$, $Q \cdot 2\,CoCl_2$ and $Q \cdot 3\,CrCl_3 \cdot 6\,H_2O$, where Q = quinine.

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An attempt was made to propose structures for the above complexes either in solution or in the solid state by interpreting their Visible-UV and IR spectra as well as their magnetic properties. The transition metal ions in these complexes are coordinated with the quinolinic and quinuclidinic nitrogens of the quinine molecule. Features shown by the IR spectra of the prepared complexes permit the tentative proposal that the quinine hydroxyl oxygen is participating in the coordination, at least in a few of the prepared complexes, by formation of a chelate ring.

In the present paper, the circular dichroism of the above mentioned complexes was examined in *DMF* solution with the aim to deduce all valuable information which may be relevant to their structure.

In addition, the complexes $Q \cdot PdCl_2 \cdot 3\,H_2O$ and $Q \cdot 2\,PdCl_2 \cdot 5\,H_2O$ were prepared and their Vis-UV and IR spectra were examined together with their circular dichroism in *DMF* or *DMSO* solution.

Results and Discussion

All complexes are soluble in *DMF*, *DMSO*, and relatively soluble in water. Since the complexes are relatively unstable in aqueous solution the reported circular dichroism and absorption measurements were carried out in *DMF* or *DMSO* solutions where the complexes are stable.

Only the complexes of quinine with $CuCl_2$ and $PdCl_2$ display a relatively large circular dichroism in the region of the Cu(II) and Pd(II) d-d absorption range. All other complexes gave minute *Cotton* effects in the d-d absorption range of the corresponding metal ion (Table 1).

Some of the complexes in *DMF* solution have octahedral geometry around the metal ion, as the Cr(III), Ni(II) and Cu(II) complexes. The copper (II) ion in the *DMF* solution is presumably coordinated in the axial positions by *DMF*. The Co(II) complex is of tetrahedral geometry, for the Pd(II) complex a square planar geometry seems more adequate. All this information can easily be deduced from the Vis-UV spectra (Table 1) where all absorption and circular dichroism bands of the complexes are reported.

It is difficult to explain the relatively large values of circular dichroism exhibited in the visible by the Cu(II) and Pd(II) complexes of quinine, in comparison with the complexes of Co(II), Ni(II) and Cr(III). Possibly in these complexes the hydroxyl group of the quinine molecule participates in the coordination to Cu(II) and Pd(II) thus causing the formation of a five membered chelate ring which induces the optical activity originated by the vicinal effect from the chiral quinine molecule to the metal chromophoric centre. In all other complexes the quinine molecule is acting rather as a monodentate ligand.

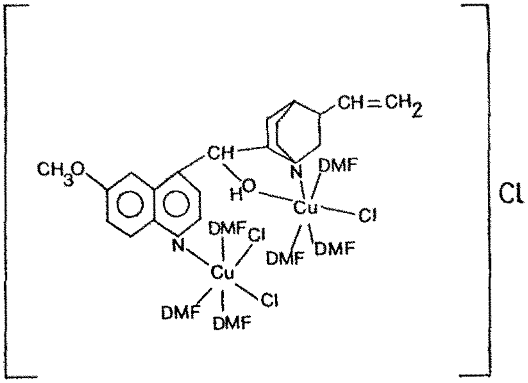
Table 1. *Absorption and circular dichroism in the visible and UV for the quinine free base and its complexes in DMF or DMSO solution; equivalent conductance of the solutions of the same complexes in DMF or DMSO*

Compound	Absorption $\lambda(\varepsilon)$, nm ($mol^{-1}\,cm^{-1}$)	Circular Dichroism $\lambda(\Delta\varepsilon)$, nm ($mol^{-1}\,cm^{-1}$)	Λ_M $Ohm^{-1}\,cm^2\,mol^{-1}$
Q in *DMF*	314 (4595), 296 (4000)	332 (—1.038), 318 (—0.848) 293 (—0.502), 260 (+0.606)	—
Q in *DMSO*	314 (5461), 296 (4866)	332 (—0.946), 320 (—0.79) 307 (—0.516), 268 (+0.71)	—
	790 (98), 723 (102) 316 (4478), 300 (3956)	679 (+0.079), 584 (+0.26) 386 (—0.63), 333sh (—3.90), 323 (—4.26)	84
$Q\cdot 2\,NiCl_2\cdot 8\,H_2O$ in *DMF*	700 (12), 670sh (11), 613 (12) 415 (30)	670 (—0.002), 614 (+0.002)	
	316 (5926), 302 (5370)	337 (—3.64), 326 (—3.05) 294 (—1.06), 282sh (—0.38)	112
$Q\cdot 2\,CoCl_2$ in *DMF*	663 (487), 630sh (277) 607 (302), 528sh (277), 520sh	670 (+0.015), 630 (+0.007) 595 (+0.01)	
	315 (4526), 300 (3823)	335 (—1.25), 324 (—1.06), 301 (—0.53)	50
$Q\cdot 3\,CrCl_3\cdot 6\,H_2O$ in *DMF*	600 (170), 430 (184)	643 (—0.005), 570 (+0.001) 454 (—0.002), 355sh (—0.48)	
	318 (5644), 300 (4844)	336 (—3.31), 325 (—2.72), 295 (—1.0), 264sh (—0.5)	107
$Q\cdot PdCl_2\cdot 3\,H_2O$ in *DMF*	450sh (79)	400 (—0.3), 352 (+2.0) 330sh (—0.24)	
	325 (5482), 280 (6497)	308 (—2.12), 262 (—4.72)	7
$Q\cdot 2\,PdCl_2\cdot 5\,H_2O$ in *DMSO*	500sh (300)	450 (+0.475), 380 (—0.423) 355 (+0.116)	
	319 (4611), 304 (4667)	340 (—1.54), 308 (—1.34)	10

It is noteworthy to point out out that the earlier tentative proposal by *Larsen* and *Olsen*[2] which implies that a chiral molecule produces a *Cotton* effect in the d-d absorption range only if it forms a chelate ring with a transition metal ion, has been proven as incorrect. Many monodentate ligands have been found to exhibit *Cotton* effects[3–8] provided that the circular dichroism measuring devices have an improved sensitivity. From this point of view, we can assume in our case that in the complexes of quinine with $CuCl_2$ and $PdCl_2$ conformational effects in the formed chelated ring may increase the magnitude of the *Cotton* effects.

Except for the complexes $Q \cdot PdCl_2 \cdot 3\,H_2O$ and $Q \cdot 2\,PdCl_2 \cdot 5\,H_2O$ which exhibit very low conductivity all other complexes show remarkable conductivity in *DMF* solution. Their Λ_M values at $10^{-3}\,M$ concentration are relatively close to the range of equivalent conductance of 1:1 electrolytes in *DMF* solution which is 65-90 $\mathrm{Ohm^{-1}\,cm^{-1}\,mol^{-1}}$. This implies that one chloride ion is ionizable from the solid state and is replaced by the solvent[9] in the complexes of quinine with Cu(II), Co(II), Ni(II) and Cr(III). The low value of Λ_M for the palladium complexes is due to the low lability of the Pd—Cl bond.

On the basis of the above results it is very probable that in *DMF* solution the complex $Q \cdot 2\,CuCl_2$ has the structure shown in the formula.



Analogous structures should be given to the complexes $Q \cdot PdCl_2 \cdot 3\,H_2O$ and $Q \cdot 2\,PdCl_2 \cdot 5\,H_2O$ in *DMF* solution.

The IR spectrum of the quinine free base (Table 2) shows one strong broad band at 3230 $\mathrm{cm^{-1}}$ due to the stretching vibration of its secondary hydroxyl group ν (OH). This band is shifted to 3400 $\mathrm{cm^{-1}}$ in both quinine—$PdCl_2$ complexes, becoming very broad since the complexes are examined as hydrates. The shift to higher frequencies indicates a coordination of the hydroxyl group as has been observed in analogous cases[10].

The quinine free base shows a medium broad band at 1335 $\mathrm{cm^{-1}}$ assignable to an in-plane hydroxyl bending vibration δ (OH) of the quinine molecule[1]. This band is sensitive to alterations caused by chelation of the hydroxyl group with metal ions[11]. In the chelated hydroxyl compounds the band shifts to higher frequencies with an increase in intensity. In both quinine—$PdCl_2$ complexes the band is located at 1380 $\mathrm{cm^{-1}}$ also with an increase in its intensity.

The 1045 cm^{-1} band of the quinine free base is due to the secondary hydroxyl stretching vibration ν(C—O). This motion shifts to lower frequencies with a simultaneous decrease of its intensity when the OH is coordinated to metal ions[12]. The band in both $PdCl_2$—quinine complexes appears at 1035 cm^{-1} with a decrease in its intensity.

The 340 and 335 cm^{-1} bands of quinine—$PdCl_2$ complexes, not shown in the IR quinine free base spectrum, are assignable to the ν(Pd—Cl) motion.

It is quite difficult to propose assignments to the visible CD bands of the complexes. From Table 1 it can be seen that the absorption maxima are displaced from those of the circular dichroism in most complexes and especially for $Q \cdot 2\,CuCl_2$, $Q \cdot PdCl_2 \cdot 3\,H_2O$, and $Q \cdot 2\,PdCl_2 \cdot 5\,H_2O$.

Table 2. *IR frequencies of quinine free base and its complexes with* $PdCl_2$ *(s = strong, br = broad, m = medium, w = weak)*

Q (free base)	3230 sbr, 2960 s, 1630 s, 1600 m, 1525 s, 1480 s, 1375 w, 1350 w, 1335 m, 1250 s, 1110 s, 1045 s.
$Q \cdot PdCl_2 \cdot 3\,H_2O$	3400 sbr, 2960 s, 1620 s, 1590 s, 1515 s, 1470 s, 1430 s, 1380 s, 1255 s, 1110 m, 1035 m, 335 m.
$Q \cdot 2\,PdCl_2 \cdot 5\,H_2O$	3400 sbr, 2940 s, 1620 s, 1590 m, 1510 s, 1470 s, 1430 m, 1380 s, 1250 s, 1235 w, 1115 w, 1035 m, 340 m.

This means that the observed CD bands result either from an overlapping or a mutual cancellation of different CD components.

All complexes acquire a very low symmetry which does not permit approximations as, e.g., treating the planar complexes $Q \cdot 2\,CuCl_2$, $Q \cdot PdCl_2 \cdot 3\,H_2O$ and $Q \cdot 2\,PdCl_2 \cdot 5\,H_2O$ in the point groups D_{4h}, D_{2h}, or even C_2. Therefore, it is preferable to consider all transition moments of the visible absorption bands as strictly electric and magnetic dipole allowed. Particular assignments to these bands cannot be given in this case.

All π-π* electronic transitions of the quinine molecule in *DMF* or *DMSO* solution from 314 nm to shorter wavelengths are also observable in all prepared complexes in the same solvents with no considerable change in both the energy and intensity of the absorption.

These transitions are split into three negative and one positive components in the CD spectrum of the quinine free base. In the complexes only negative CD bands were observed in the range of π-π* transitions.

Experimental

All chemicals used were supplied by Fluca Co. The quinine free base (puriss. grade) was used without further purification; m.p. 175°, $[\alpha]_D^{20} = -153 \pm 3°$ ($c = 1.5\%$ in $CHCl_3$).

$Q \cdot PdCl_2 \cdot 3\,H_2O$

0.45 g (0.0014 mol) of quinine free base were dissolved in 6 ml methyl alcohol, and 0.43 g (0.0013 mol) of a warm solution of K_2PdCl_4 were added gradually. The lightly brown precipitate obtained was washed with warm water and alcohol, and dried in vacuum to a solid; m.p. 240° (decomposition).

Found. C 42.52 H 4.42 N 5.23 Pd 19.13.
Calcd. C 43.22 H 5.44 N 5.04 Pd 19.14.

$Q \cdot 2\,PdCl_2 \cdot 5\,H_2O$

0.5 g (0.028 mol) of $PdCl_2$ were dissolved in 5 ml of conc. HCl, and 80 ml of methyl alcohol were added. After filtration a clear solution was obtained and 0.55 g (0.0017 mol) of quinine free base were dissolved. The solution was almost neutralized to $pH = 6.5$–6.8 by slow addition of a methanolic solution of NaOH (0.01 *M*). A brown precipitate was obtained which was washed with water and alcohol, and dried in vacuum to a solid; m.p. 250° (decomp).

Found. C 31.04 H 4.52 N 3.41 Pd 27.33.
Calcd. C 31.23 H 4.45 N 3.64 Pd 27.67.

Pd was determined gravimetrically with dimethylglyoxime and rechecked by atomic absorption.

Visible and UV spectra were obtained with a Shimatzu-Bausch and Lomb Spectronic 210 UV spectrometer. IR spectra were recorded with a Perkin-Elmer 577 spectrometer. Conductivity was measured with a YSI-model 31 conductivity bridge. Circular dichroism was measured with a Jobin-Yvon dichrographe III.

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