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First optically active ferricinium salts: a circular dichroism study

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Abstract

The first CD spectra of optically active ferricinium salts are reported. Cotton effects corresponding to the metal–ligand charge-transfer band have been observed for the compound with planar chirality.

It is known that ferrocenes can be oxidized losing one electron to give ferricinium cations which can be isolated as salts when suitable anions such as fluoroborate or hexafluorophosphate are used. The electronic absorption spectra of these salts have been thoroughly investigated [1]. The main features agree with the general ferrocene pattern, as is shown by the appearence of new bands with the main maximum at 16200 cm^{-1} (617 nm) for the unsubstituted ferricinium ion. It can be assigned to the ligand–metal charge-transfer which is also responsible for the green-blue colour of these salts.

Despite the fact that a wide variety of optically active ferrocenes had been known for years [2], it is only very recently that we have reported the first synthesis of the enantiomeric ferricinium salts having planar (I) or central (II) chirality [3]. Now we report the first CD spectra of ferricinium salts, tetrafluoroborates, in acetonitrile (Fig. 1). The quantitative description of Cotton effects (CE) is given in Table 1.

Two features are worth noting. The charge-transfer "ferricinium" band is optically active, the corresponding CE at 652 nm in I being of the same order of magnitude as the other Cotton effects. This is of special interest because we have previously studied the induced CD spectra of ferricinium hexafluorophosphate included into β-cyclodextrin, and could not detect CE in this region [4]. The

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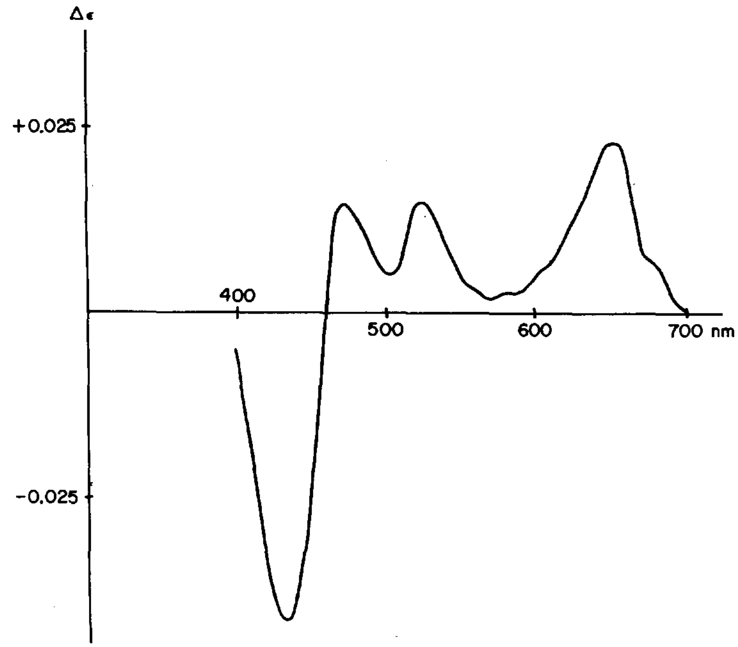

Fig. 1. CD spectra of ferricinium salt in acetonitrile; ——— (−)-S_p-I.

molecular ellipticity induced by β-cyclodextrin appeared to be even higher than that of a related molecule having a plane of chirality; for example, compound I exhibited $\Delta\epsilon = 0.014$ at 469 nm (see Table 1) leading to $[\theta] = 46.2$, whereas the induced CE in ferrocene itself [4] had $[\theta]_{460} = 257$.

The structure of a long-wavelength CE for I appears near to the maximum in the absorption spectrum [1], that consists of several CE's because of the complex structure of this band. In II, the presence of this CE is uncertain, probably because of its low intensity. It is important to note that the CD spectra of II are identical both in CH_3CN and CF_3COOH. This suggests that the double-charged species (the dication with positive charges on both the Fe$^{\bullet}$ and the α-C atoms) is not

Table 1

Cotton effects in the CD spectra of the substituted ferricinium fluoroborates enantiomerically enriched [a]

Derivative	λ_{max} (nm)	$\Delta\epsilon$	solvent (conc.)
1-carboxy-2-methyl	652.5	0.023	
(−)-S_p, I	523.5	0.015	CH_3CN
	469.5	0.014	(1.92 mM/L)
	429.0	−0.042	
1-(1'-hydroxy)benzyl	479.0	−0.035	CF_3COOH
(+)-R_c, II			(1.59 mM/L)
	483.0	−0.021	CH_3CN
			(1.28 mM/L)

[a] Measurements at shorter wavelengths were not possible because of strong absorption

formed in the only modestly acidic CF_3COOH. Solvents bearing an OH group cannot be used for ferricinium salts: methanol affords reduction and thus gives a CD spectrum being similar to that of the corresponding neutral ferrocene, and water gives a completely different CD spectrum, presumably due to decomposition.

The non-symmetrical CE with its maximum around 490 nm in the CD spectrum of I consists mainly of two similar intensities at about 470 and 525 nm, which corresponds neatly to the bands in the absorption spectrum of ferricinium fluoroborate [1] at 467 and 523 nm. One should note that all observable CE's of I do not change their sign as compared with the CD spectrum of the corresponding uncharged ferrocene. The novel, 'ferricinium' CE has the same positive sign as the nearest CE. This reflects most likely the absolute configuration *S*(−) of the chiral plane.

To summarize, in this work we have obtained the first CD spectra of enantiomeric ferricinium salts and observed CE for the 'ferricinium' region in the model compound with planar chirality in which the electronic structure of the ligand is more strongly disturbed.

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