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CIRCULAR DICHROISM OF *IN-SITU* TRINUCLEAR ORGANOTRANSITION METAL COMPLEXES WITH OPTICALLY ACTIVE LIGANDS

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ABSTRACT

Several Cotton effects are developed within absorption bands of trinuclear organotransitionmetal complexes in the presence of acids, diols, amines and aminoalcohols even in the case of bulky substituents on nitrogen; with monohydroxy compounds no circular dichroism could be detected.

Circular dichroism (c.d.) is obtained only within absorption bands. In order to obtain signals from nonabsorbing optically active substances in the range of accessible wavelengths 'cottonogenic derivatives' have to be prepared. One procedure is the *in-situ* formation of chiral complexes by mixing a solution of an achiral transition metal derivative with the substance. An effect is seen provided that this derivative can act as a ligand, that the complex is relatively stable thermodynamically, and that it is labile enough kinetically, so that ligand exchange (eventually at elevated temperature) is possible. The c.d. curves of complexes between transition metal acylates of general formula $[M_2(O_2C.R)_4]^{n+}X_n^-$ (M = Mo, Rh or Ru; n = 0 or 1; X = Cl) and ligands like carboxylates, glycols, amines, aminoalcohols, amides, phosphanes, etc. have recently been reviewed by us.[1] We have now found that trinuclear organometal carboxylate complexes of general formula $[M_3O(O_2C.R)_6L_3]^{n+}$ $(O_2C.R)_n^-$ L'_k (M = Fe or Ru; L = water or pyridine; L′ = pyridine; n,k = 0 or 1) as they have been used for the activation of C—H bonds in saturated hydrocarbons,[2] give several intense Cotton effects between 700 and 250 nm. Spurious small c.d. bands at still longer wavelengths are not reproducible and might be artefacts.

Crystal structures of several such complexes (M = Fe, Mo, Cr, etc.), in which the oxidation state of the metal atoms is either M_3^{III} or $M^{II}M_2^{III}$, are known.[3] In those, which are currently being investigated by us each metal atom is surrounded by 6 ligand positions in an octahedral

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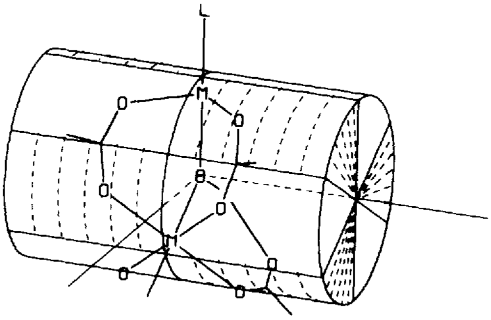
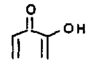


Figure 1. Schematic representation of duodecant rule for the c.d. of optically active acids in the presence of one of the complexes (**1**) to (**4**). Only part of the formula of the complex is drawn, hatched and non-hatched areas contain groups with different signs of their contributions to the c.d.

arrangement, and although the symmetry in the crystal is only D_3, it does not deviate too much from D_{3h}. The pseudoscalar representation in this point group is A''_1 the simplest symmetry-determined sector rule which is appropriate is then a duodecant rule[4] (Figure 1) to which however—at least for some transitions—additional nodal surfaces may have to be added, which are then orbital-determined. These sector rules are only applicable to compounds containing chiral acylate ligands or monoamines; for glycols or amino alcohols as ligands, helicity rules which correlate the sign of the torsional angle (—O—)C—C(—X—) with that of the Cotton effect may be more important than these sector rules (cf. Reference 5), if they act as bidentate ligands.

Table 1. C.d. of *in situ* trinuclear organotransitionmetal complexes (**1**) to (**4**) with some representative optically active substances

Optically active potential ligang	Complex (**1**)	 (**2**)	 (**3**)	 (**4**)
1,2-diols	+	+	+	−
acids	+(a)	+	+	+
-"- in presence of OH^-	−	−	−	+
α-hydroxy acids	+	+	+	+
-"- in presence of OH^-	−	+	+	+
α-amino acids	+(b)	+	0	−
-"- + OH^-	+	+	0	+
-"- + H^+	0 (c)	+	0	−
aminols	+(d)	+	+	+
-"- + H^+	+	+	+	+
prim. amines	−	−	−	+
-"- + H^+	−	−	−	+
tert. amines	+(e)	−	0	+(e)
crossed conj. hydroxy-dienones 	+	+	+	+

+: CD develops after addition of optically active compound to stock solution.
−: no CD could be observed after mixing.
0: not measured.
a) no reaction with 3β-carboxy-cholest-5-ene.
b) only in pyridine solution.
c) not measurable in pyridine under these conditions.
d) no reaction with ephedrine.
e) only in water or after reflux in DMSO.

$[Fe_3O(O_2CCH_3)_6(H_2O)_3]$ (**1**)[6], $[Fe_3O(O_2CCH_3)_6pyr_3]$ (**2**)[6], $[Fe_3O(O_2CCH_3)_6pyr_3]_2pyr$ (**3**)[2], and $[Ru_3O(O_2CCH_3)_6(H_2O)_3]^+$ $CH_3CO_2^-$ (**4**)[7] (pyr = pyridine) have now been used to test the applicability of complexes of this type for our purposes. Table 1 shows our results obtained with representative compounds. As expected, in the presence of each of the 4 complexes appreciable c.d.'s are seen. In general several Cotton effects are obtained with acids, and also with aminols (free bases or hydrochlorides). None of the monohydroxy compounds tried out hitherto showed a c.d. curve under these conditions, nor did thioethers. Glycols gave, however, c.d. curves with the iron containing complexes **1**–**3**. On the other hand the ruthenium complex **4** seems to be more useful for amines and was the only one which gave Cotton effects with carboxylates.

In Figures 2–4 a few such c.d. curves are shown. Since in most cases strong Cotton effects appear between 500 and 400 nm these complexes may even be more useful than the di-metal tetraacetates[1] for the determination of the absolute configuration from c.d. of substances showing their own strong c.d. bands or u.v. absorptions up to 400 nm.

Typical examples: a) the c.d. of a solution of complex **1** in dimethyl sulphoxide DMSO and an aminoalcohol can be measured immediately after mixing. Figure 2 shows the c.d. curves in presence of D- and L-phenyl alaninol, respectively (**5** and **6**). They are enantiomorphic to each other (although no Δε-scale is given, since we do not know the concentration of the optically active complex, it was the same for both enantiomers) and one can recognize 6 c.d. bands around 600, 490, 450, 390, 310, and 265 nm. All Cotton effects besides the fifth one have the same sign for a given enantiomer; e.g. for the D-enantiomer these are positive. The two valinols show the same behaviour.

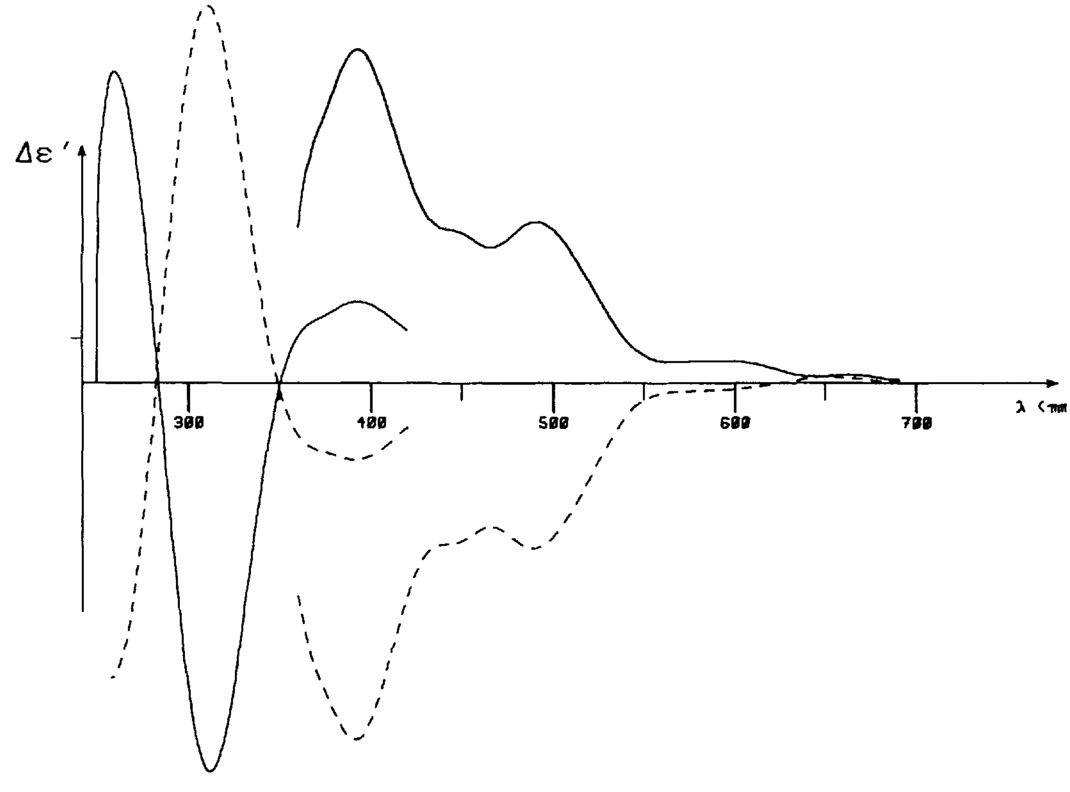


Figure 2. C.d. spectra of D-phenyl alaninol (**5**) (——) and L-phenyl alaninol (**6**) (------) in DMSO, in presence of complex (**1**). 1 Δε'-unit corresponds to 0·02 above 350 nm, to 0·08 below that wavelength

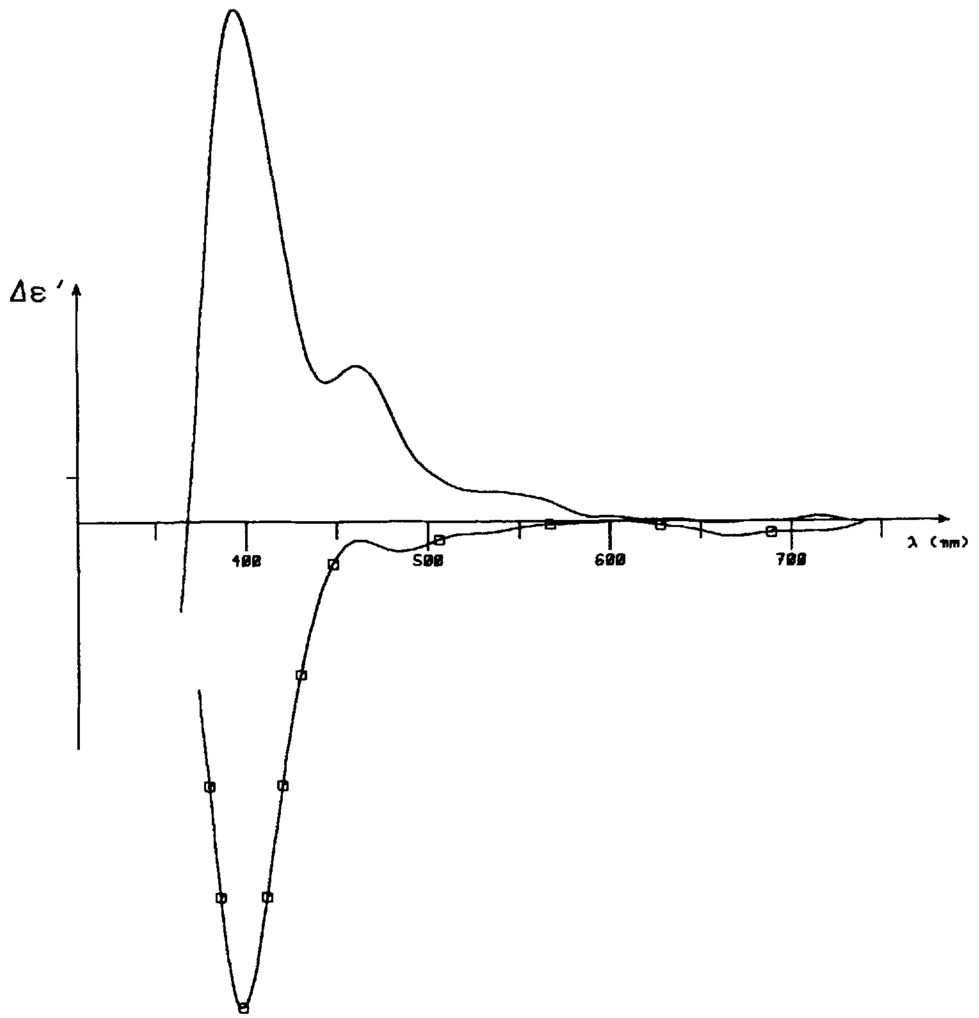
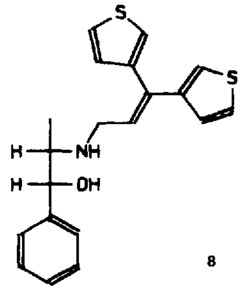


Figure 3. C.d. spectra of (S)-propane-1,2-diol (**7**) (⊟⊟⊟) in presence of complex (**2**) (negative band at shorter wavelengths not shown; 1 Δε'-unit corresponds to 0·025) and of (-)-erythro tinofedrine (**8**) (———, 1 Δε'-unit corresponds to 0·04) in presence of complex (**3**), both in acetonitrile

b) The solution of a glycol like (S)-propane-1,2-diol (**7**) and complex **2** in acetonitrile gives Cotton effects around 520, 480, 397 nm and at still shorter wavelengths, which are negative for the (S)-enantiomer (Figure 3).

c) Complex **3** was also mainly used in acetonitrile solution. In presence of an aminoalcohol like (-)-tinofedrine (**8**) positive Cotton effects are recognized at 550, 460, and 400 nm. At shorter wavelengths another, negative, seems to be present, because of the strong absorption of tinofedrine in this range we were, however, not able to record the full c.d. band (Figure 3). The positions of these Cotton effects are scarcely influenced by a change of the substituent on nitrogen.

d) To a solution of **4** in ethanol is added the optically active acid or base, eventually together with a droplet (amount not critical) of aqueous NaOH or HCl. For (-)-camphanic acid (**9**) a c.d. with a few negative Cotton effects (or one with pronounced vibronic fine structure) is obtained between 700 and 530 nm, a much stronger, positive one around 420 nm, followed by smaller ones around 350 (negative) and 350 nm (positive) (Figure 4). With D-phenylethyl amine (**10**) several positive Cotton effects without clear structure appear between approximately 530 and 300 nm with a negative one following at still shorter



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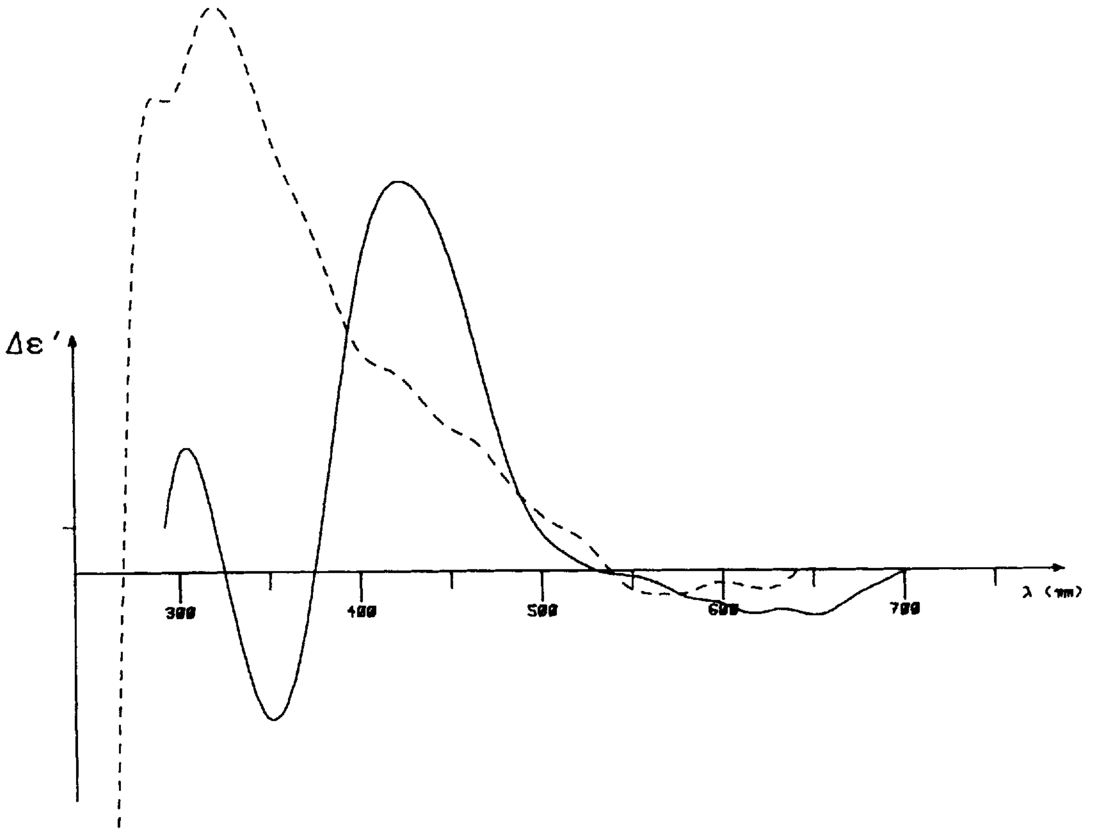

Figure 4. C.d. spectra of (-)-camphanic acid (**9**) (——, 1 Δε'-unit corresponds to 0·007), and D-phenylethyl amine (**10**) (------, 1 Δε'-unit corresponds to 0·012) in ethanol, in presence of complex (4)

wavelengths. The (apparent) negative Cotton effect between 650 and 530 nm is very small, but becomes definitely positive after addition of a droplet of HCl (Figure 4).

Typical procedure: To a stock solution of one of the complexes **1** to **4** of approximate concentration 0·7 to 1·9 mmole/l so much of the optically active compound is added that the ratio of ligand to complex is 3 ... 6 to 1. Usually 1 mg of substance is enough to obtain good signal/noise ratios within the stronger Cotton effects. DMSO, acetonitrile, pyridine, or water were used as solvents. Occasional warming up of the solution, or the addition of a drop of acid or base may be necessary. The c.d. was measured with an ISA dichrograph Mark III connected on-line to a PDP/8e. Curve smoothing was achieved with help of the Golay–Savitzky algorithm. Since the concentration(s) of the optically active complex(es) remain(s) unknown ficticious $\Delta\varepsilon'$-values are calculated on the basis of the concentration of the achiral stock complexes.

In conclusion, then, we have developed a simple, but sensitive, method for the detection of optical activity in compounds of even low rotation. This procedure should serve for the analysis and determination of absolute configuration. Its application to peptides is timely.

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