

# Induced Optical Rotation and Circular Dichroism of Some Symmetric Group IV Metal Halides<sup>1</sup>

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**Abstract:** Optical activity was induced into the tetrachlorides of tin(IV), titanium(IV), and zirconium(IV) in DMF solutions, employing *d*-tartaric and *d*- and *l*-malic acids as environment compounds. It was found that adduct formation with the solvent takes place, yielding hexacoordinate species. The possible factors contributing to these asymmetric perturbations are considered.

Recently the observation of the Pfeiffer effect<sup>2</sup> was reported for some labile hexacoordinate racemic species of the group IV elements. In the present work these studies have been extended to some *nonracemic symmetric* species of the group IV elements. According to the theory of Velluz<sup>3</sup> and Crabbé<sup>4</sup> optical rotation is inducible also in symmetric chromophores resulting, however, in smaller effects. The last point could be of considerable importance when symmetries of species are in question and the quantitative aspect of induced optical activity may become indicative of the inherent symmetries involved. An effort was made to gain more insight pertaining to the mechanism by which these asymmetric perturbations occur, especially when symmetric molecules are involved, where there can be no shift in a racemic *d* ↔ *l* equilibrium of enantiomers. To this end CD was employed.

Recent works<sup>5,6</sup> elucidated partly and, for some racemic systems showed convincingly, some of the contributing factors for induced rotation. However, these do not apply generally and each system requires its own analysis. With regard to symmetric species, for example, Kirschner and Bhatnagar<sup>7</sup> report an induced Cotton effect in the region of the *d*-*d* transition of a symmetric complex ion of cobalt(III) by inner-sphere coordination of an asymmetric ligand. Mason and Norman<sup>8</sup> have shown a Cotton effect induced into a similar symmetric species of cobalt(III) by outer-sphere coordination of the same ligand. Only a few examples<sup>9-11</sup> of induced optical rotations are cited in the literature which involve apparently symmetric molecules.

We report induced optical activity in the tetrachlorides of tin(IV), titanium(IV), and zirconium(IV) in DMF solutions employing *d*-tartaric and *d*- and *l*-malic acids as environment compounds. Table I lists the induced rotations of some of these systems.

## Results and Discussion

An investigation of the systems points toward adduct formation between the solvent (DMF) and the tetrachlorides of titanium(IV) and tin(IV) corresponding to the hexacoordinate tetrachlorobisdimethylformamidetitanium(IV) and the tetrachlorobisdimethylformamidetin(IV) species, respectively. No coordination took place between the metal chloride and the environment compound (tartaric or malic acid), as evidenced by the isolation of the same adduct regardless of whether the environment compound was present in solution or not. Identical spectra were obtained regardless of whether the adduct was formed *in situ*, *i.e.*, by the addition of TiCl<sub>4</sub> to a DMF solution containing the environment compound, or by isolating the adduct first and redissolving it in DMF solution containing the environment compound. There was no detectable change in the spectrum of the adduct when dissolved in pure DMF instead of a DMF solution containing the environment compound, though it should be pointed out that the compound does not have a visible spectrum owing to a strong uv tail, and only the uv absorption is available for comparison. Table II lists induced CD bands and absorption maxima of the [TiCl<sub>4</sub>(DMF)<sub>2</sub>] adduct.

The results obtained seem to indicate that no inner-sphere coordination of the environment compound is responsible for the induced optical activity in this system. Since both absorptions are optically active it seems that the appearance of these CD bands is essentially due to dissymmetric distortion of the molecular framework of the whole molecule by the environment compound. This distortion could be the result of outer-sphere coordination, possibly through hydrogen bonding of the hydroxyl groups on the tartrate to the halide groups on the metal and the oxygens of the tartrate through the hydrogens to the nitrogens of the coordinated DMF groups. The former probably provides the main contribution to distortion, as evident from the high value of the CD band at 285 mμ. Both tartaric and malic acid have available the hydroxyl groups and oxygens required for this type of complexation, and it is important to note that in many systems tested<sup>1,12</sup> invariably tartaric acid, which has one more hydroxyl group available than malic acid, proved to be a more effective environment compound.

(12) A paper discussing induced rotation in various new systems, employing nonaqueous solvents and new environment compounds, is currently in preparation.

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**Table I.** Induced Rotations of Symmetric Group IV Tetrachlorides in DMF Solutions

Initial sym compd, <i>M</i>	Environment compd, <i>M</i>	Obsd rotation, $\alpha(\text{obsd}),^a$ deg	$\alpha_{e+c},$ deg <sup>a</sup>	$\alpha_e,$ deg	$[M_I],^a$ deg
SnCl <sub>4</sub> , 0.03	<i>d</i> -Malic acid, 0.20	+0.059	+0.831	+0.772	+98
ZrCl <sub>4</sub> , 0.015	<i>d</i> -Tartaric acid, 0.15	+0.121	+0.652	+0.531	+510
TiCl <sub>4</sub> , 0.02	<i>d</i> -Tartaric acid, 0.16	+1.022	+1.477	+0.455	+3200

<sup>a</sup> 25°; 589 m $\mu$ ;  $\alpha(\text{obsd}) = \pm(\alpha_{e+c} - \alpha_e)$ ;  $\alpha_{e+c}$ , observed rotation of solution containing both the environment compound and the symmetric species;  $\alpha_e$ , observed rotation of environment compound in solution before addition of symmetric species;  $[M_I] =$  induced molar rotation,  $[M_I] = \alpha(\text{obsd})/[e][c]d_m$ , where  $[e]$  and  $[c]$  are the molar concentrations of environment compound and symmetric species, respectively, and  $d_m$  is the solution path length in meters.

**Table II.** Induced CD Bands and Absorption Maxima of the [TiCl<sub>4</sub>(DMF)<sub>2</sub>] Adduct in DMF Solution at Room Temperature

Absorb max, m $\mu$	Sym compd, <i>M</i>	Environment compd, <i>M</i>	Induced CD bands $\lambda_{\text{max}}$	$[\theta]_{\text{max}}$
	TiCl <sub>4</sub> (DMF) <sub>2</sub> , $1.1 \times 10^{-3}$	<i>d</i> -Tartaric acid, 0.155		
$\alpha$			353	-3,540
270			285	+99,000

<sup>a</sup> The visible absorption spectrum shows no detail owing to a strong uv tail ( $1.1 \times 10^{-3} M$ ) using a 1-cm cell. Using a 0.1-cm cell the 270-m $\mu$  peak is recorded with no tailing. In more concentrated solutions, this uv tail extends to about 550 m $\mu$ .

The [Sn(Cl<sub>4</sub>)(DMF)<sub>2</sub>] does not absorb in the visible region, only in the uv beyond the cutoff of DMF. Though the uv absorption is not observed in DMF solution, the CD spectrum shows the beginning of a shoulder around 265–275 m $\mu$  (depending on the concentration of the solution) pointing toward a negative maximum.

The high ratio of optically active environment compound to complex (see Table II) seems to be in line with other examples of outer-sphere coordination.<sup>8,10</sup>

Values obtained<sup>1,2</sup> for the molar Pfeiffer rotations of some racemic hexacoordinate tin(IV) compounds of the general formula [Sn(AA)<sub>2</sub>Cl<sub>2</sub>], in which AA is a bidentate ligand, amounted to about 600°. These compare favorably to the induced molar rotation of 100° obtained for the symmetric hexacoordinate [SnCl<sub>4</sub>(DMF)<sub>2</sub>] species studied in the present work. Not enough data are presently available for evaluating the ZrCl<sub>4</sub> and TiCl<sub>4</sub> adducts from this point of view. However, the induced molar rotation of 3200° obtained for the symmetric [TiCl<sub>4</sub>(DMF)<sub>2</sub>] is very high and caution must be used when evaluating these results. More analogous compounds with different symmetries have to be studied before these data can become meaningful.

## Experimental Section

**Materials.** Commercially available titanium tetrachloride, purified (Fisher Scientific Co.); stannic chloride, anhydrous (Matheson Coleman and Bell); zirconium tetrachloride, anhydrous (Research Organic/Inorganic Chemicals Co.); *N,N*-dimethylformamide, Spectranalyzed (Fisher Scientific Co.); and dichloromethane, Spectranalyzed (Fisher Scientific Co.) were used without further purification. Hexane (Fisher Scientific Co.) was dried over calcium hydride and redistilled. *d*-Tartaric acid (Eastman Organic Chemicals) and *d*- and *l*-malic acids (Aldrich Chemical Co.) were reagent grade.

**Spectra.** Visible and uv spectra were recorded on a Cary 14 spectrophotometer. CD measurements were taken on a Cary Model 60 with a Model 6001 CD accessory. Circular dichroism is recorded in terms of ellipticity,  $\theta$ , recorded in degrees, and  $[\theta]$ , the molecular ellipticity. Concentrations of the solutions are given in Table II.

**Polarimetry.** Optical activity was measured on a Rudolph 80 high-precision polarimeter at 589 m $\mu$  using a sodium light source. Concentrations of solutions are given in Table I.

**Preparation of Adducts. Tetrachlorobisdimethylformamidetitanium(IV).** Titanium tetrachloride (2 ml) was dissolved in 25 ml of dichloromethane; DMF was then added slowly until the reaction ceased (about 3.4 ml). The precipitate which formed was filtered and washed with solvent. Too great an excess of DMF renders it difficult to recover the precipitate, which becomes sticky and difficult to handle. The adduct was formed *in situ* by the addition of titanium tetrachloride to DMF. The analysis of [TiCl<sub>4</sub>(DMF)<sub>2</sub>] corresponds to a monomeric species, deficient in chlorine.

**Tetrachlorobisdimethylformamidetin(IV).** Stannic chloride (anhydrous, 2 ml) was dissolved in 25 ml of dichloromethane; DMF was then added slowly until the reaction ceased (about 4 ml). The precipitate was filtered and washed with solvent. *Anal.* Calcd for [SnCl<sub>4</sub>(DMF)<sub>2</sub>]: Cl, 35.00; C, 17.70; H, 3.45. Found: Cl, 34.84; C, 18.01; H, 3.07.

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