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Optical Activity Measurements on Solids. 6. Solid State Optical Activity and Circular Dichroism Measurements of Sodium Thioantimonate Nonahydrate*

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Summary. We have demonstrated that optical circular dichroism (CD) measurements can be carried out on powders suspended in a liquid medium. The refractive indices of the powder and the suspending liquid must be matched, the suspending liquid must not interact significantly with the solid to be measured and must not absorb in the region where the measurements are carried out. Sodium thioantimonate nonahydrate ($Na_3SbS_4 \cdot 9H_2O$) powders obtained by grinding of *levo-* or *dextro-*rotatory crystals were found to be excellent examples for the demonstration of this technique. Measurements of the optical rotation for *levo-* and *dextro-*rotatory crystals and powders of $Na_3SbS_4 \cdot 9H_2O$ were also carried out and provided additional characterization of this salt. In the course of developing the CD measurement technique, CD of $NaClO_3$ and $NaBrO_3$ crystals was also measured.

Keywords. Optical activity; Circular dichroism; Sodium thioantimonate nonahydrate; Suspension measurements; Isotropic compounds.

Messungen der optischen Aktivität von Festkörpern. 6. Bestimmung von optischer Aktivität und Circulardichroismus von festem Thioantimonatnonahydrat

Zusammenfassung. Wir konnten zeigen, daß Messungen des optischen Circulardichroismus an in flüssigem Medium suspendierten Pulvern durchgeführt werden können. Die Brechungsindizes von Pulver und suspendierender Flüssigkeit müssen aneinander angepaßt werden; das Suspensionsmittel darf nicht wesentlich mit dem zu messenden Feststoff in Wechselwirkung treten und darf im Meßbereich nicht absorbieren. Durch Verreiben von laevo- und dextrorotatorischen Kristallen erhaltene Natriumthioantimonatnonahydratpulver ($Na_3SbS_4 \cdot 9H_2O$) erwiesen sich als ausgezeichnete Beispiele zur Demonstration der Methode. Messungen der optischen Drehung von laevo- und dextrorotatorischen Kristallen und Pulvern von $Na_3Sb_4 \cdot 9H_2O$ wurden ebenfalls durchgeführt und trugen zur Charakterisierung des Salzes bei. Im Verlauf der Entwicklung der Meßtechnik wurden auch CD-Spektren von $NaClO_3$- und $NaBrO_3$-Kristallen aufgenommen.

* Dedicated to Prof. Dr. Karl Schlögl on the occasion of his 70th birthday with our warmest wishes

Introduction

In the past we have studied the optical activity (OA) of materials in the solid state [1–11] and have perfected our method for routine measurements of the optical rotation in suspension.

Some attempts have been made in the past to evaluate the optical activity of spherical chiral particles suspended in achiral [12, 13] and, more recently, in chiral [14, 15] fluids. The results were not related yet to measurements of particles which have irregular shapes. We have shown that chiroptical measurements can be carried out successfully and accurately in suspensions for compounds that had previously been measured in the crystal or in film form if three conditions are met: (1) The refractive indices of the solid and suspending media were matched; (2) The suspension was properly stirred to assure a constant concentration of the solid in the suspension; and (3) The solid powders were optically isotropic [7].

We were originally interested in measuring accurately the OA in the solid state because of our research on the nonracemic helicity of solid materials, especially of the helicity of insoluble polymers. For the case of non-birefringent polychloral films, we were able to show that they had high optical rotations [16–19]. Since it was known that the OA of some isotropic inorganic salts could be easily measured on crystals we had selected $NaClO_3$ (**1**) and $NaBrO_3$ (**2**) as examples for our suspension OA measurements [1, 7, 8].

In addition to simple OA measurements, two chiroptical measurements have been traditionally carried out to characterize optically active compounds; the measurements were usually done in solution. One is optical rotatory dispersion (ORD), the measurement of the optical rotation as a function of the wavelength of light [20], the second technique is circular dichroism (CD) [21, 22] which is based on the differential absorption of left and right circularly polarized light by a chiral compound.

We believed that, in principle, CD measurements in suspension should be possible but we expected to encounter some technical difficulties. In order to demonstrate the feasibility of such measurements, it was imperative, first, to find an isotropic compound that showed CD characteristics and that possessed a chromophore at the wavelength appropriate for such a measurement. Second, it was essential to find an isorefractive suspending medium that does not absorb in the critical region needed for the CD measurement.

Experimental

Materials. Sodium thioantimonate nonahydrate (Pfaltz and Bauer) was purified by recrystallization (under a nitrogen atmosphere) from water. Sodium chlorate (Allied Chemical Company) and sodium bromate (Matheson Company) were also recrystallized from water. Carbon disulfide, diiodomethane and 1-iodonaphthalene (Aldrich Chemical Company) used as media for the suspension measurements were taken from freshly opened bottles without purification.

Measurements. The optical rotation of the crystals and suspensions was measured on a Perkin–Elmer 271 Polarimeter. The CD data were acquired and processed on a computer-controlled Jasco J-710 Spectropolarimeter. The information was transferred as ASCII code and processed using a NEC computer with spreadsheet and a plotting program.

Results and Discussion

Some years ago, the CD behavior of isotropic crystals of **1** has been investigated [23]. For a crystal of *dextro*-rotatory **1** a band near 218 nm was observed; a band at about 215 nm was found for the *levo*-rotatory crystal of **1**.

We have investigated crystals of **1** with thicknesses ranging from 0.5 to 4.5 mm. **1** showed a negative CD band for the *dextro*-rotatory crystal and a positive CD band for the *levo*-rotatory crystal (Fig. 1). We found that the wavelength of the CD band depended slightly on the thickness of the crystal and consequently on the pathlength for measurements. We plotted the wavelength of the CD band as a function of the thickness of the crystals of **1** (Fig. 2). Extrapolation to zero thickness gave the values 226 nm for the *dextro*-rotatory and 223 nm for the *levo*-rotatory crystals. We have also grown large crystals of **2** [1, 7] and measured their CD spectra. We found a positive band for *dextro*-rotatory crystals at 275 nm and a negative band for *levo*-rotatory crystals of **2** at 273 nm in the thicknesses range of 0.8 to 1.2 mm (Fig. 3).

The OAs of **1** and **2** have been measured before [7]; our OA and CD measurements are summarized in Table 1.

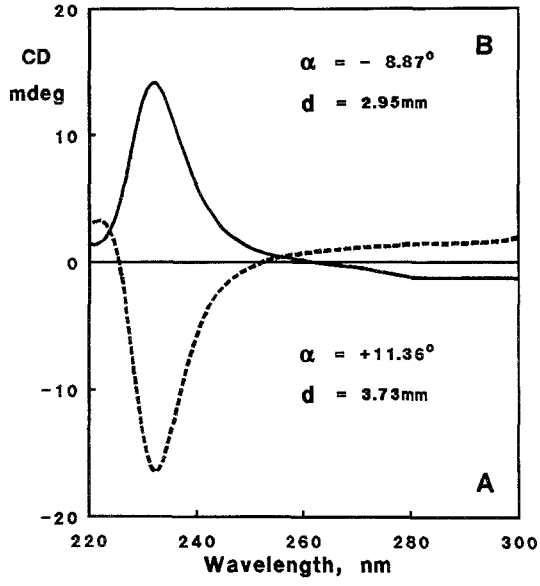

Fig. 1. Sodium chlorate crystals. Circular dichroism spectrum of **A** *dextro*-rotatory crystal; **B** *levo*-rotatory crystal

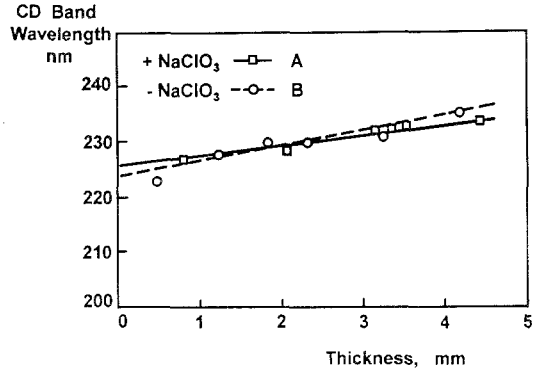

Fig. 2. Sodium chlorate crystals. Dependence of the wavelength of the CD band from the thickness of the crystals of **A** *dextro*-rotatory crystals; **B** *levo*-rotatory crystals

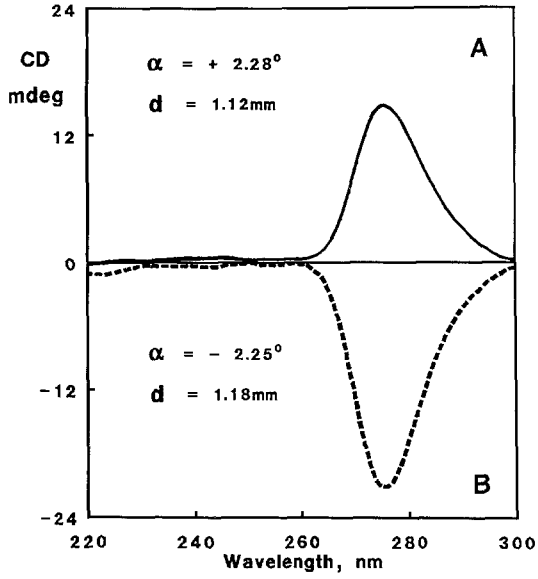

Fig. 3. Sodium bromate crystals. Circular dichroism spectrum of **A** *dextro*-rotatory crystal; **B** *levo*-rotatory crystal

Table 1. Optical activity and circular dichroism data for sodium chlorate, sodium bromate and sodium thioantimonate nonahydrate

Compound	Optical activity			Circular dichroism band		
	Crystal	Powder Susp.	Lit. value Crystal	Crystal	Powder Susp.	Lit. value Crystal
	$[\alpha]_D(^\circ)$	$[\alpha]_D(^\circ)$	$[\alpha]_D(^\circ)$	nm	nm	nm
$NaClO_3$	+122	+122	+122 [24]	226		218 [23]
	−121	−122	−122 [24]	223		215 [23]
$NaBrO_3$	+67	+62	+64 [25]	275		
	−59	−63	−64 [25]	273		
$Na_3SbS_4 \cdot 9H_2O$	+125	+120	+125 [26]	414	415	
	−122	−119	−125 [26]	417	418	

We were unable to find isorefractive suspending media suitable for CD measurements for powders of **1** and **2**. All known liquids with the appropriate refractive index had excessive absorptions at the wavelengths where the chromophores of **1** and **2** absorb. It must be remembered that our OA suspension measurements require a suspending medium whose refractive index had to be matched with that of the suspended powder. Typical concentrations of the suspended powder were 2–5%. For CD measurements even small absorptions by the suspending media can interfere significantly with the measurements because 95–98% of the suspension consists of the liquid suspending medium.

We came to the conclusion that sodium thioantimonate nonahydrate, $Na_3SbS_4 \cdot 9H_2O$ (**3**), (first prepared by Schlippe and sometimes called *Schlippe's salt* [27]), fulfilled in principle the requirement for a successful development of a CD

suspension measurements of solids. Circular polarization (as it was called at that time, in 1841) of crystals of **3** had been examined by Rammelsberg [28].

We have grown large, beautiful, bright yellow crystals of **3** from aqueous solutions (Fig. 4). These crystals showed an absorption maximum near 415 nm and are optically isotropic. They are either *dextro-* or *levo*-rotatory, the handedness of each individual crystal is caused by spontaneous and random nucleation. The optical rotation of each individual crystal of **3** was measured.

Crystals of **3** are hydrates and are stable at higher relative humidity but lose some of their water of hydration in a dry atmosphere. When loss of water of crystallization occurs, the surface of the crystals (or of the crystal powder) becomes opaque which can prevent accurate suspension measurements because of significant light scattering.

Crystals of **3** (Fig. 4) as obtained from the crystallization are not suitable for measurements and had to be polished to rectangular platelets before the optical rotation and CD could be measured.

We obtained values of the specific rotation $[\alpha]_D = -122°$ for *levo-* and $[\alpha]_D = +125°$ for *dextro*-rotatory crystals of **3** which are in excellent agreement with the literature values [26]. The suspension measurements for the optical rotation of powders of **3** were successfully carried out in carbon disulfide/1-iodonaphthalene or carbon disulfide/diiodomethane mixtures. The powders were obtained by grinding large crystals of **3**. The particle sizes of powders for suspension measurements were less than 60 microns.

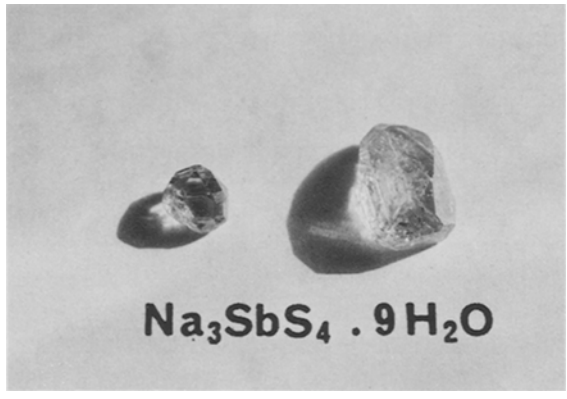

Fig. 4. Sodium thioantimonate nonahydrate crystals

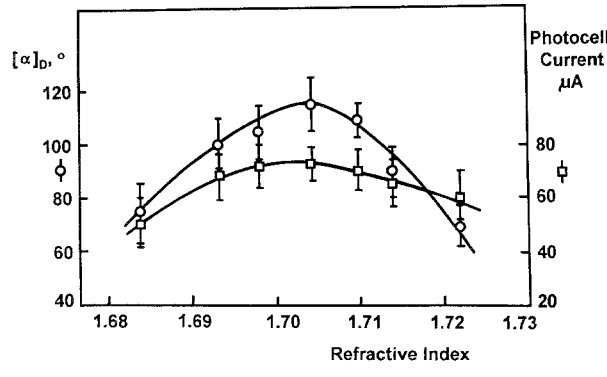

Fig. 5. Sodium thioantimonate nonahydrate powder. Specific rotation and photocell current as a function of the refractive index in carbon disulfide/diiodomethane at constant concentration of $Na_3SbS_4 \cdot 9H_2O = 0.01$ g/ml for *dextro*-rotatory powder

In Fig. 5 we show the data for the optical rotation and the photocell current as a function of the refractive index for the powder of compound **3**. The refractive index of the solid powder and the liquid [29] (carbon disulfide/diiodomethane) is matched when the photocell current (which is proportional to the transparency of the suspension) or the specific rotation as a function of the refractive index has a maximum. Our value of the refractive index $n_D = 1.704$ (Fig. 5) is close to the literature value ($n_D = 1.692$) [30]. Slightly higher deviation of the refractive index matching in the suspending medium ($n_D = 1.710$) and the literature value ($n_D = 1.742$ [31]) for the crystal was observed at the wavelength of the mercury lamp (436 nm) instead of that of the sodium lamp (589 nm). The difference is based on the "incorrect" measurement of the refractive index of the liquid medium at 589 nm instead of 436 nm.

To confirm the accuracy of our OA suspension measurements of **3**, we determined the specific rotation as a function of the concentration of **3** in the suspension. When a carbon disulfide/1-iodonaphthalene mixture was used as a suspending medium, the accuracy of the optical rotation measurement within the measuring range was better than $\pm 5\%$ (Fig. 6) for both *dextro*- and *levo*-rotatory powders. The average value of the specific rotation of the *dextro*-rotatory crystal was $[\alpha]_D = +120 \pm 4°$, that of the *levo*-rotatory crystal was $[\alpha]_D = -119 \pm 5°$. These values of the specific rotation were slightly lower than the values that had been determined for crystals of **3**. The difference may be technical – because of the adhesion of the powder to the measuring cell a slightly lower "effective" concentration was measured.

We have subsequently measured the CD spectra of **3**, first on thin crystals. The *dextro*-rotatory crystal (0.72 mm thick) showed a negative band at 414 nm and the *levo*-rotatory crystal (0.75 mm thick) a positive band at 417 nm (Fig. 7). The optical

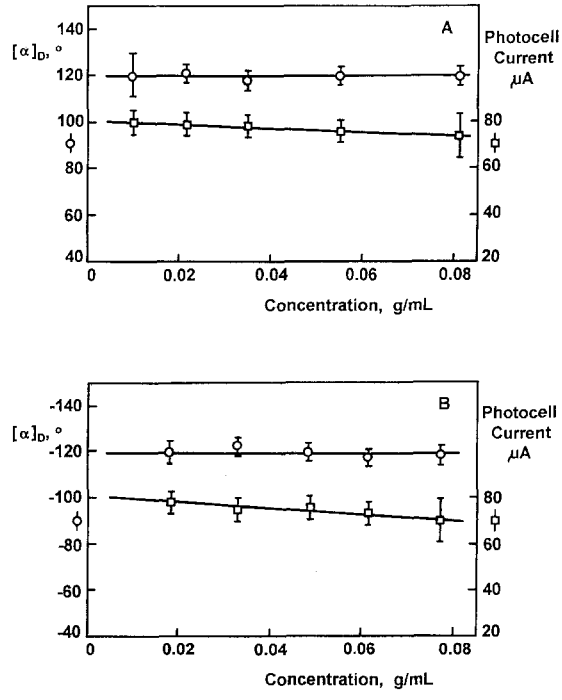

Fig. 6. Sodium thioantimonate nonahydrate powder. Specific rotation and photocell current as a function of the concentrations in carbon disulfide/1-iodonaphthalene, refractive index $n_D = 1.704$. **A** *dextro*-rotatory powder **B** *levo*-rotatory powder

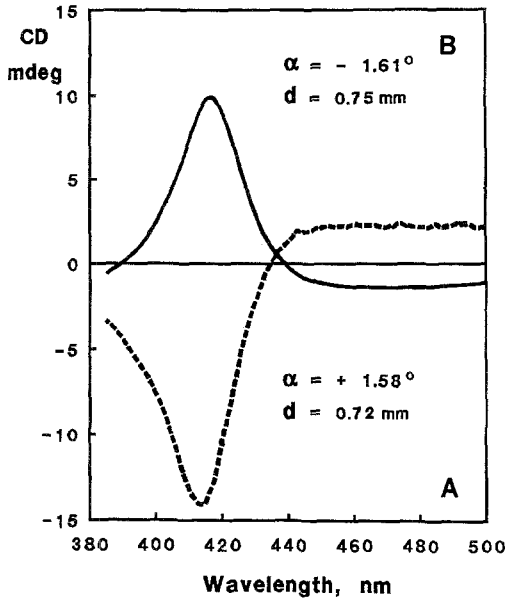

Fig. 7. Sodium thioantimonate nonahydrate crystals. Circular dichroism spectrum of **A** *dextro*-rotatory crystal; **B** *levo*-rotatory crystal

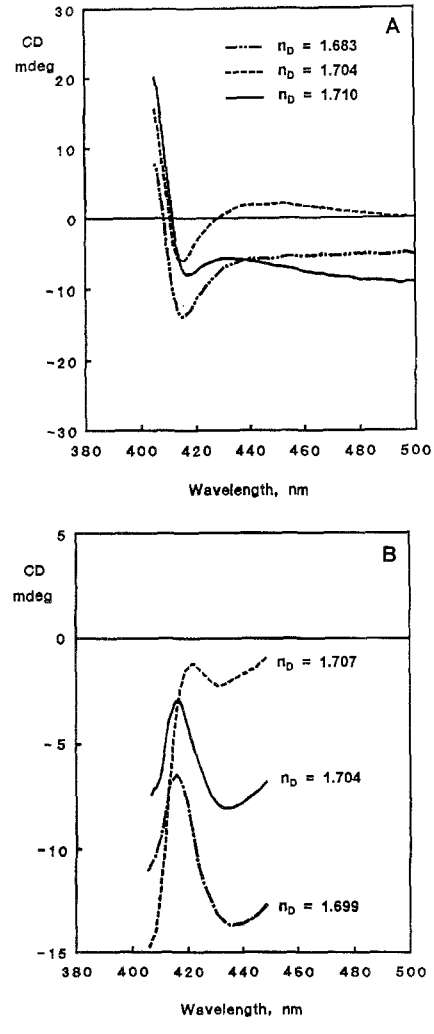

Fig. 8. Sodium thioantimonate nonahydrate powder. Circular dichroism spectrum in carbon disulfide/diiodomethane as a function of the refractive index at constant concentration of $Na_3SbS_4 \cdot 9H_2O = 0.033$ g/ml. **A** *dextro*-rotatory powder; **B** *levo*-rotatory powder

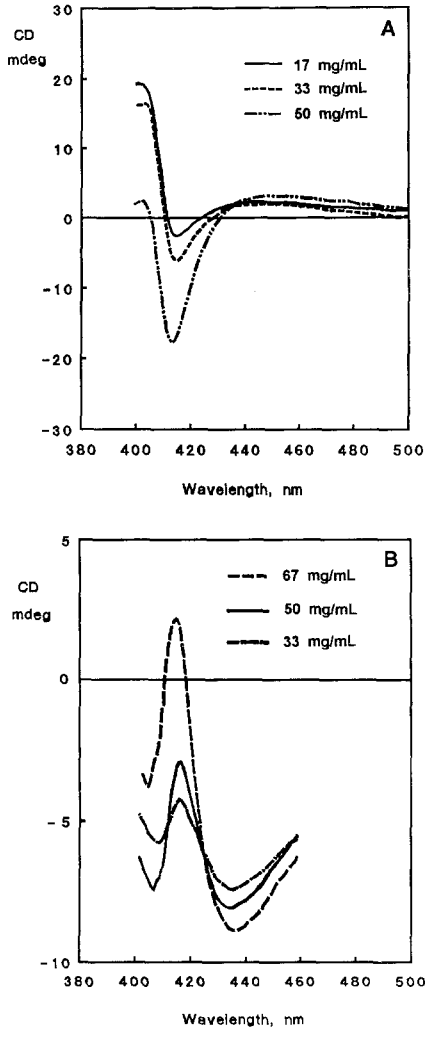

Fig. 9. Sodium thioantimonate nonahydrate powder. Circular dichroism spectrum as a function of the concentration in carbon disulfide/diiodomethane, refractive index $n_D = 1.704$. **A** *dextro*-rotatory powder; **B** *levo*-rotatory powder

rotation of powders of **3** (density: 1.806 g/ml) was originally measured in a mixture of carbon disulfide and diiodomethane as the suspending medium and gave initially values about 10% smaller than expected. We found that the density of the suspending media did not match the density of the powder sufficiently and the powder adhered to the walls of the measuring cell. Using 1-iodonaphthalene instead of diiodomethane as one of the components of the isorefractive suspending media provided a density of the mixture which was similar to that of the powder of **3** and eliminated the problem.

Unfortunately, 1-iodonaphthalene starts to absorb near 425 nm, a wavelength which is near the CD band of **3**. The CD band of **3** could, however, be observed when the powder was measured in carbon disulfide/diiodomethane suspension (Figs. 8 and 9).

We have found that small deviations of the refractive index between the powder and the suspending media do not change the main characteristics of the CD measurements, namely the wavelength of the absorption band (Fig. 8). We also found that

when the transparency of the suspension was lower and the background becomes more significant, the CD band tends to broaden.

When the concentration of the powder of **3** in the suspending medium was increased, the intensity of the CD band also increased (Fig. 9). These results are in full agreement with our observation of the CD measurements of thicker crystals.

Conclusions

In conclusion, we have demonstrated that circular dichroism measurements can be carried out successfully on optically active solid powders in suspension when optimal conditions are fulfilled. We believe that our technique of measuring of CD in suspension is a significant breakthrough in the understanding of the optical behavior of molecules and macromolecules in the solid state. When interpreted on a molecular level the results significantly advance our understanding of supermolecular arrangements in chiral solids, inorganic salts and also in polymeric materials. We have shown previously that measurements of the optical rotation can also be carried out successfully in suspension.

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