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CIRCULAR DICHROISM OF TRIGONAL SELENIUM FORMED IN A CHIRAL POLYMER MATRIX

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ABSTRACT

The circular dichroism (CD) spectrum of trigonal selenium crystallites formed in a chiral polymer film has been observed. The electronic transition polarization information obtained from the CD spectrum is consistent with the trigonal selenium single crystal reflectivity data of Tutihasi and Chen. The CD sign for the ~610 nm exciton band (polarized perpendicular to c-axis) in trigonal selenium indicates that left-handed helical crystals are formed preferentially over the right-handed crystallites in ethyl cellulose.

Since Pasteur's classic visual separation of hemihedral crystals of racemic sodium ammonium tartrate[1] in 1848, and the realization that optical activity arises from an asymmetric (chiral) grouping of atoms or molecules, the separation and observation of optical antipodes by new techniques continues to be of great scientific importance, especially as it may relate to the origin of optical activity.[2] Optical activity is often a convenient probe for obtaining detailed conformational and electronic structural information. It is known that some achiral substances, e.g. urea,[3] benzil,[4] selenium,[5] and mercuric sulfide,[6] for example, crystallize in trigonal (helical) structures which may be either left- or right-handed. Optical rotation,[7] circular dichroism,[4] the microscopic observation of the effect of a single crystal on a nematic liquid crystalline phase,[8] and the use of solid-gas reactions have been employed for the identification of chiral single crystals.[9]

Circular dichroism (CD) is an extremely useful spectroscopic technique for the investigation of chiral species provided that one can produce a chiral sample with absorption bands in a convenient spectral region. CD can determine the polarization of electronic transitions, as well as indicate the presence of hidden electronic transitions (fine structure) and yet is insensitive to absorption from achiral species.

We have employed this selectivity, for example, to provide the effective absorption of helical J-aggregate species of sensitizing dyes[10] in the presence of other light absorbing species such as monomer and achiral aggregates. In examining the CD of micro-crystalline species it is essential to extract any linear dichroic effects from the CD by the use of a polymer film as a rigid matrix. The polymers must, however, be chiral in the absence of any other dissymmetric perturbation so as to produce an enantiomeric excess of either the left or right-handed helical structure to make the CD measurement possible.

In this Note we report the observation of the CD of chiral trigonal selenium formed by the thermal decomposition[11] of bis(diphenylmethyl)diselenide (5 wt %) in a chiral ethyl cellulose polymer film. We have found it necessary to incorporate a catalyst bis(triphenylphosphine)-borohydrido copper(I) (2.5 wt %) for the thermal production of the trigonal form of selenium. The lattice of trigonal selenium consists of helical chains which have a threefold screw axis.

Figure 1 presents the absorption and circular dichroism spectrum of trigonal selenium (77°K) formed in ethyl cellulose by heating the film at 100°C for 2 hours. The absorption spectrum shows exciton bands at ∿610 nm, ∿410 nm and the beginning of a more intense electronic transition at shorter wavelength. The CD of the ∿610 nm and short wavelength (<350 nm) bands is of positive sign, indicating transitions of the same polarization, while the ∿400 nm band exhibits negative CD. The polarization information provided by the CD spectrum is totally consistent with the single crystal reflectivity data of Tutihasi and Chen[12] where the ∿610 nm exciton band was found to be polarized perpendicular to the c-axis (helix axis) of the

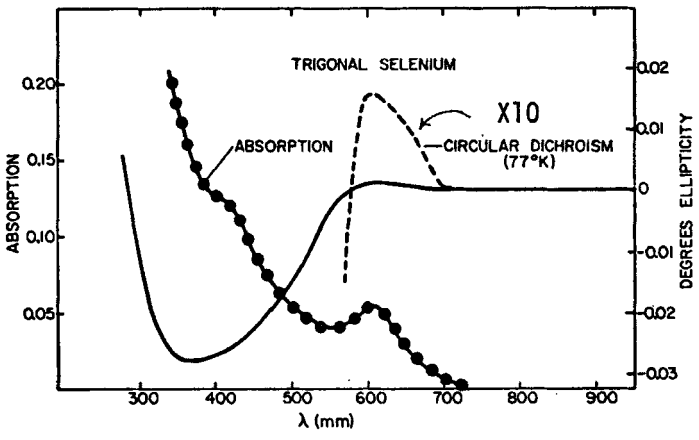
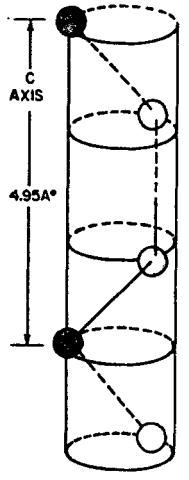


Figure 1. Absorption and circular dichroism spectra of trigonal selenium particles in ethyl cellulose at 77°K.

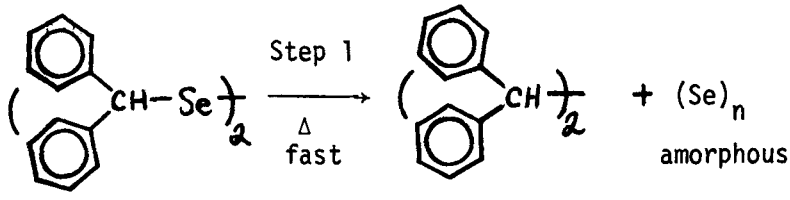
trigonal selenium single crystal[5] and the ∿400 nm band to

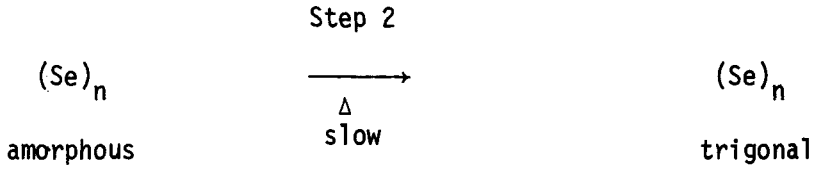


TRIGONAL SELENIUM

be polarized along the c-axis. The CD indicates that in ethyl cellulose there is a preferential formation of left-handed helical crystallites of trigonal selenium over the right-handed structure.

The production of trigonal selenium from the diselenide takes place by a two-step process as described below:[11]





The first step of the thermal decomposition produces red amorphous selenium, which then crystallizes in the chiral matrix to form trigonal selenium.

We believe this is the first report of the CD of trigonal selenium. Our polarization results are consistent with those of a classic technique and thus we feel that the chiral polymer technique can be generally applied to other enantiomeric microcrystalline species for the preferential nucleation of either D or L crystallites with the objective of probing their electronic structure.

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