

contain 7.6 % lysine, which should make them attractive from the nutritional point of view. A difference of one residue between the fraction *c* and *d* proteins may be detected for serine, glycine and, perhaps, arginine. The differences between the proteins in methionine and leucine content are of equal size but of different polarity. The same is true for the pair valine-isoleucine and suggests that these substitutions may have occurred.

Whether the rapeseed genome codes for a number of slightly different basic proteins or whether we are dealing with genetical heterogeneities within the rapeseed strain, is not known, nor is the possible biological function of these proteins. Further work characterizing the rapeseed proteins and exploring their use as human and animal food, is in progress at this laboratory.

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Circular Dichroism of Dihedral Rare Earth Carboxylates Chirally Stabilised in a Single-crystal

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This study is part of an investigation,¹ on one hand to study more generally the reliability of circular dichroism (CD) on pressed "randomised" crystalline powders and on the other to use this method to study compounds in a solid matrix, compounds which either do not exist in solution, or which are not stable towards racemisation.

The possibility to assign a certain observed CD effect to a defined environment of a chromophore will depend on a closer knowledge of the crystal structure. In a crystal the CD could originate from a *molecular configurational chirality* (e.g. due to a helical arrangement of ligands around the metal ion in a complex) but also from a *spiral crystal structure*. Examples of the latter case are circular dichroic crystals² of $[\text{Ni}(\text{H}_2\text{O})_6]\text{SO}_4 \cdot 3 \text{SiO}_2$, and NaClO_3 , etc.²

Previous CD⁴ studies on single crystals were restricted by the demand of large specimens (crystals with an area of approx 100 mm² and a thickness of approx 1 mm). Furthermore, the measurements had to be made with the incident light propagated perfectly parallel to an optic axis.

We will in the following outline a method to study CD on a pressed "randomised" powder from a single crystal. The amount of material necessary corresponds to a single crystal of the size 0.5–1 mm³. KCl was used as a matrix. By using a random orientation of the powdered dissymmetric single crystal, the CD tensors will be averaged and a CD similar to that of a random solution will be obtained. In this way it is also possible that a predominant crystal structure CD will be depressed or even averaged out; e.g. in a random sample of $[\text{Ni}(\text{H}_2\text{O})_6]\text{SO}_4$ from a ground single crystal the CD was approximately zero.

The method outlined above can be used only if *a*. the incident light is not depolarized by the sample; *b*. if the CD/absorbance ratio is approximately constant with dif-

ferent chromophor concentrations in the matrix. When these conditions are met we propose that neither birefringence nor linear dichroism is of importance.

The first point was tested by inserting a CD standard in the light path after the investigated samples and gave as a result a tolerable amount of 10 % depolarisation. The CD/absorbance ratio was also shown to be approximately constant. Hence, both the above conditions seem to be fulfilled.

The present study is a successful attempt to use the dissymmetry of $\text{Na}_3[\text{M}(\text{OCOCH}_2\text{O} \cdot \text{CH}_2\text{COO})_3] \cdot 2\text{NaClO}_4 \cdot 6\text{H}_2\text{O}$ single crystals [$\text{M} = \text{Sm}(\text{III})$ or $\text{Ho}(\text{III})$]⁵ to obtain circular dichroism in the $f-f$ transitions of rare earth chromophors. The rare earth ions are coordinated by three oxydiacetate ligands bonded along the diagonals of a slightly distorted trigonal prism.⁵ The carboxylate oxygens are situated at the corner positions of the prism and the ether oxygens, one on each of the three two-fold axes, perpendicular to a three-fold axis. The point symmetry at the metal ion site is thus D_3 . All ligands in the structure are approximately planar. This fact together with the other structural features of the solid⁵ makes it reasonable to attribute the observed CD entirely to the molecular chirality.

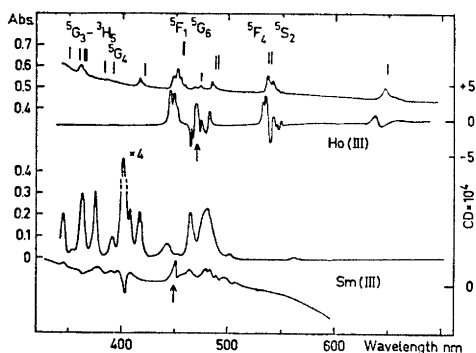


Fig. 1. From above: semi-empirical energy levels of Ho^{3+} in a doped LaCl_3 crystal (from right to left 5F_5 , 5S_2 , 5F_4 , 5F_3 , 5F_2 , 3K_8 , 5G_6 , 5F_1 , 5G_5 , 5G_4 , 3K_7 , 3H_5 , 3H_6 , 5G_3 , 5G_3 , 4L_9), absorption spectrum of one KCl disc, containing single-crystal of $\text{Na}_3\text{Ho}(\text{OCOCH}_2\text{OCH}_2\text{OCO})_3 \cdot 2\text{NaClO}_4 \cdot 6\text{H}_2\text{O}$, circular dichroism of the same disc, absorption spectrum of a 0.38 M $\text{Sm}(\text{ClO}_4)_3$ solution ($d=1$ cm), circular dichroism of a KCl disc, containing a single-crystal of $\text{Na}_3\text{Sm}(\text{OCOCH}_2\text{OCH}_2\text{OCO})_3 \cdot 2\text{NaClO}_4 \cdot 6\text{H}_2\text{O}$.

In solution, rare earths show sharp spectral transitions very similar to those in the crystalline state. These transitions can be identified with excitation of electrons from the ground state (Ho^{3+} : 5I_6 , Sm^{3+} : ${}^6H_{51/2}$) to the excited J levels of the $4f^n$ configuration (Ho^{3+} $f^{10} = f^{-4}$, $\text{Sm}^{3+} = f^5$). The energy levels of Ho^{3+} in LaCl_3 are reproduced in Fig. 1.^{6,7} A comparison with the absorption spectrum of $\text{Na}_3\text{Ho}(\text{C}_4\text{H}_4\text{O}_5)_3 \cdot 2\text{NaClO}_4 \cdot 6\text{H}_2\text{O}$ in a KCl-disc (Fig. 1) shows that the presence of the complexing agent does not shift the spectral lines very much, and they can in most cases easily be identified with the energy levels of the "free" ion.

Fig. 1 shows representative CD spectra for single-crystals of the above mentioned carboxylates with Ho and Sm. Samples taken from one single-crystal all showed the same CD spectrum. With another single-crystal a mirror-spectrum could be obtained, *i.e.* the same CD magnitudes, but with reversed signs. With a powder from many single-crystals the CD became zero.

To correlate the CD to an absolute configuration from a purely theoretical discussion seems impossible. The high number of levels that should arise when lowering the symmetry to D_3 cannot be identified with the CD bands observed though the number of CD bands can give an idea about the lifted degeneracy. The difficulty of making such an assignment is illustrated by the 5F_5 band of $\text{Ho}(\text{III})$, where a clear splitting into three CD bands appears: with $J=5$ there should arise 7 levels in D_3 , furthermore the ground state with $J=8$ could be split into 11 levels. However, one possibility may be to make an empirical rule for bands behaving similarly in a series of different $\text{Ho}(\text{III})-D_3$ chelates.

A comparison between CD and absorption spectra (after correction for a small shift to the blue of the whole CD spectrum in the Ho case, probably due to the pressed KCl disc) reveals that some absorption bands do not correspond with detectable CD bands, while other absorption bands, some of them relatively weak, give rise to strong CD bands.

Two remarkable examples of the last category are denoted by arrows in Fig. 1. In addition to electric-dipole transitions, weak magnetic-dipole transitions may contribute to the optical spectrum. A relation between a high dissymmetry factor (in principle the ratio $CD/absorption$) and magnetic dipole allowance has been discussed in other chromophores.⁸ CD studies

of $f-f$ transitions may thus be used for identification of such transitions at the side of linear dichroism measurements on crystals.⁷ The only positively identified magnetic dipole $f-f$ transition (as far as the present authors know) is the ${}^7F_0-{}^5D_1$ transition in Eu^{3+} (525 nm).⁷

An example of another metal complex with D_3 symmetry, *per se* chiral but impossible to investigate by CD in solution, is the iron(III) oxalate ion. $\text{Fe}(\text{ox})_3^{3-}$ is stable in aqueous solution, but is kinetically labile and undergoes very rapid racemisation. We have succeeded in obtaining a pressed KCl CD spectrum from an at least partly resolved crystal mass of (strychnine)₃ $\text{Fe}(\text{ox})_3$. Another study of the two enantiomers is under way by using D and L forms of α -phenylethylamine instead of strychnine as a resolving agent.

Single-crystals of $\text{Na}_3[\text{M}(\text{C}_4\text{H}_4\text{O}_6)_3] \cdot 2\text{NaClO}_4 \cdot 6\text{H}_2\text{O}$ (size 1–10 mm³) were prepared in a straight-forward way.⁵ A piece of a crystal was ground in an agate mortar together with a suitable amount of KCl, proportions 1:100 for Ho, 1:5 for Sm. (The KCl was obtained by precipitation from a saturated KCl solution with conc. HCl, rapid filtration; after air drying for 10 h it was heated at 400°C for 30 h. It was kept over P_2O_5). Pellets (diam. 13 mm) were pressed from 100–300 mg of the mixed powder *in vacuo* (1 mmHg for 10 min, then with an applied pressure of 15–20 kbar for 10 min.). The species investigated did not show any decreasing optical activity with long pressing time, *i.e.* no measurable racemisation in the solid state.

The method outlined in this study suggests the following applications of circular dichroism measurements of one pulverised single crystal:

1. Conventional analysis of absolute configuration and conformation⁸ of species, which are not stable in solution.

2. To the study of inert optically active complexes: These may in solution contain a mixture of several conformers with different CD, which makes it difficult to interpret the total CD spectrum. The number of conformers in the solid state can be determined by X-ray diffraction. In many cases one would expect only one confor-

mation of the complex, the CD spectrum of which may be determined in the solid. The data thus obtained ought to facilitate the interpretation of the corresponding solution CD spectrum.¹⁰

3. As an aid in the assignment of space groups to solids containing a suitable chromophore, *e.g.* most transition elements. The presence of CD implies dissymmetry. Hence, the lattice must belong to one of the non-centrosymmetric crystal classes indicated in *International Tables for X-Ray Crystallography*,⁹ p. 41–42.

The absence of CD does *not* imply the absence of dissymmetry: *cf.* the case of $[\text{Ni}(\text{H}_2\text{O})_6]\text{SO}_4$ mentioned above.

If the X-ray structure determination is made on a fragment of a larger single crystal, the rest of which is used for CD-measurements, it may be possible to make a spectroscopic assignment of the absolute configuration. This method might be particularly useful in the cases where the atoms have a poor anomalous scattering, or when the anomalous scatterer is a heavy atom, which forms a pattern of higher symmetry than the overall structure.

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