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# Preparation, Infrared Spectra and Differential Thermal Analyses of Rare-Earth Dithiodiacetates

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With 2 Figures

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Dithiodiacetates of the rare-earths of the general formula $M\mathrm{H}(DTDA)_2 \cdot 2\,\mathrm{H_2O}$, where $M$ = La, Ce, Pr, Nd, Sm, Ho, and Y, and $\mathrm{H_2}DTDA$ = dithiodiacetic acid, have been prepared and characterised by analyses, i.r. and differential thermal analysis. The i.r. data show that the bonding of the carboxylate group to the metal ion is bidentate. The i.r. and *DTA* studies reveal the presence of one water molecule in the coordination sphere. A coordination number of nine is suggested for the rare-earth metal ion in these compounds.

## Introduction

The metal chelates of dicarboxylic acids are of interest because they are capable of forming compounds of various stoichiometries. The rare-earth dicarboxylates that have been prepared include those of oxalic acid[1, 2], malonic acid[3] and maleic acid[4]. A survey of literature, however, shows that no metal chelates of dithiodiacetic acid, $(\mathrm{SCH_2COOH})_2$, have been prepared except those of the alkali metals which have been used in photographic developers[5]. The present paper deals with the preparation and characterisation of the dithiodiacetates of the rare-earth elements with a view to understand the nature of bonding between the metal ion and the carboxylate group.

## Experimental

### Materials

Rare-earth oxides, 99.9% purity, were obtained from American Potash and Chemical Corporation, U.S.A. Dithiodiacetic acid, obtained from Evans Chemical Inc., U.S.A., was recrystallised from ethanol. Hydrated rare-earth chlorides, except that of Ce(III) were prepared by treating the oxides with aqueous HCl and evaporating the solutions to dryness. Hydrated $CeCl_3$ was prepared by treating cerium hydroxide with aqueous HCl.

### Preparation of the Complexes

Dithiodiacetic acid (2.5 moles) was dissolved in 95% ethanol and ethanolic $NH_3$ was added drop by drop with stirring till the pH was between 6.5 and 7. If the ammonium salt separated out, a few drops of water were added to dissolve it. An aqueous solution of the rare-earth chloride was then added with stirring to precipitate out the rare-earth dithiodiacetate. The precipitated solid was filtered, washed first with water and then with ethanol. It was finally dried over anhydrous $CaCl_2$ under reduced pressure.

### Analyses

The metal content of the complexes was determined by the oxalate—oxide method. Carbon and hydrogen in a few complexes were estimated by microanalytical methods.

### Instrumentation

The i.r. spectra were taken in nujol mulls with a Carl Zeiss UR-10 automatic spectrophotometer. The spectra of dithiodiacetic acid and the lanthanum dithiodiacetate are given in figure 1. The differential thermograms were recorded on an automatic instrument fitted with a chromel-alumel thermocouple. All the samples were run at a heating rate of 2 °C/min. Calcined alumina was used as the diluent and as the reference material. The differential thermograms are presented in figure 2.

## Results and Discussion

The analytical data for the chelates conform to the general formula $M\mathrm{H}(DTDA)_2 \cdot 2\,H_2O$ where $M = $ La, Ce, Pr, Nd, Sm, Ho, and Y. The chelates are quite stable in air and are insoluble in water and common organic solvents.

No data are available in literature on the infrared spectrum of dithiodiacetic acid. Hence the spectrum of the ligand has been analysed and the frequencies assigned. The assignments are based on those for other dibasic acids such as malonic acid[3], succinic acid[6], sebacic and adipic acids[7].

The $\nu$ C=O frequency in the ligand occurs as a strong absorption at 1,700 $cm^{-1}$ with a shoulder at 1,732 $cm^{-1}$. The bands at 1,422 $cm^{-1}$ (S) and 1,275 $cm^{-1}$ (S) are probably due to the C—O stretching vibrations, which are coupled with the in-plane bending vibration of the OH groups ($\nu$ C=O+ $\delta$ OH). In the chelates all the above bands are absent and the bands due to symmetric $\nu\,COO^-$ and the asymmetric $\nu\,COO^-$ vibrational modes appear at $\approx$ 1,420 $cm^{-1}$ and $\approx$ 1,570 $cm^{-1}$ resp. The corresponding vibrations in the sodium salt appear at 1,410 $cm^{-1}$ and 1,600 $cm^{-1}$. The bonding of the carboxylate group to the rare-earth metal in these chelates cannot be monodentate, because with such a

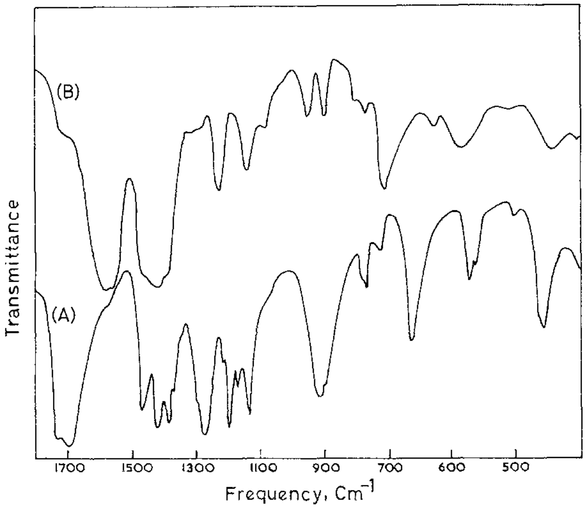

Fig. 1. Infrared Spectra of (A) Dithiodiacetic acid and (B) HLa($DTDA$)$_2$ · · 2 $H_2O$

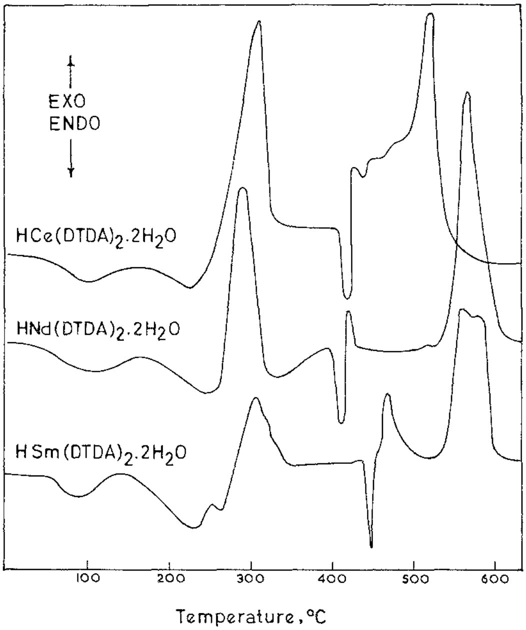

Fig. 2. $DTA$ Studies

mode of coordination, the asymmetric $\nu$ COO$^-$ frequency is expected to increase and the symmetric $\nu$ COO$^-$ frequency to decrease as the metal-oxygen bond strength increases[8]. Consequently, the difference between the symmetric and asymmetric $\nu$ COO$^-$ frequencies ($\Delta \nu$) should be more in the chelates than in the sodium salt, which is taken to be purely ionic. In the case of a bidentate mode of coordination, there are two factors influencing the symmetric and asymmetric $\nu$ COO$^-$ frequencies. The bidentate coordination of the carboxylate group to the metal results in a lowering of both the $\nu$ COO$^-$ frequencies due to the drainage of the electron density from the carboxylate group to the metal. At the same time, the O—C—O angle is expected to decrease when the metal—oxygen bond becomes stronger. The valence force-field equations for an $X Y_2$ system[9] and the calculations for the triatomic model[10, 11] have shown that a decrease in the O—C—O angle results in a decrease in the frequency separation, $\Delta \nu$, between the two $\nu$ COO$^-$ frequencies. These two factors act in the opposite direction for the symmetric $\nu$ COO$^-$ frequency but in the same direction for the asymmetric $\nu$ COO$^-$ frequency. Thus in a bidentate mode of coordination of the carboxylate group, the asymmetric $\nu$ COO$^-$ frequency decreases and the symmetric $\nu$ COO$^-$ frequency either increases or remains the same compared to that in the sodium salt. In the dithiodiacetates studied it is seen that the asymmetric $\nu$ COO$^-$ frequency decreases and the symmetric $\nu$ COO$^-$ frequency increases compared to the corresponding frequencies in the sodium salt. This suggests that the bonding of the carboxylate group to the metal is bidentate in these chelates.

The asymmetric $\nu$ COO$^-$ band in the chelates shows a slight splitting. Such a splitting of the band due to the asymmetric $\nu$ COO$^-$ is usually observed when the molecule containing more than one COO$^-$ group forms bonds of different polarity. The strong broad band observed at 910 cm$^{-1}$ in the ligand, attributed to the O—H out-of-plane deformation, is absent in the chelates due to the replacement of the acidic protons by the metal ion. The bands observed in the chelates at $\approx$ 900 cm$^{-1}$ and $\approx$ 950 cm$^{-1}$ may be due to the C—C stretching vibrations which were not seen in the ligand spectrum due to the overlap of the strong out-of-plane deformation band.

The ligand spectrum does not show any bands in the 3,000–3,600 cm$^{-1}$ region that can be assigned to the O—H stretching modes. However, bands are observed at 2,540 cm$^{-1}$ and 2,660 cm$^{-1}$ which can be attributed to the O—H stretching vibrations which have been lowered in frequency due to hydrogen bonding. As might be expected, these bands are absent in the chelates.

Two sharp peaks at 1,200 cm$^{-1}$ and 1,135 cm$^{-1}$ have been observed in the ligand spectrum. The former can be attributed to the $CH_2$ wagging mode of vibration and has been shown to be characteristic of molecules containing the $CH_2COOH$ group, the predominant contribution to which comes from the $CH_2$ wagging mode with small contributions from the C—O, C—C stretching and O—H deformation modes[6]. This band is shifted to about 1,226 $cm^{-1}$ in the chelates. The other band at 1,135 $cm^{-1}$ can be attributed to the $CH_2$ twisting frequency and is not much affected after chelation. These two bands are broader in the chelates than in the ligand. The band at 665 $cm^{-1}$ in the ligand is probably shifted to a higher frequency ($\approx$ 714 $cm^{-1}$) in the chelates.

The chelates show bands in the region 3,000–3,600 $cm^{-1}$ due to the stretching modes of the water molecules. Two bands are observed, one at $\approx$ 3,400 $cm^{-1}$ and one at $\approx$ 3,200 $cm^{-1}$ suggesting the presence of both coordinated and lattice held water, the former being due to the lattice held and the latter due to the coordinated water. The presence of coordinated water is also supported by the appearance of a new band at $\approx$ 625 $cm^{-1}$ in the spectrum of the chelates which can be attributed to the rocking mode of coordinated water. Since only two water molecules are present, one must be coordinated and the other lattice held.

Differential thermal analysis has been carried out for Ce, Nd and Sm dithiodiacetates. The differential thermograms are very similar for the three chelates studied. An endotherm is observed at $\approx$ 90 °C due to the removal of water. Isothermal heating at 100 °C for 4–5 hours showed that only one molecule of water is removed. The infrared spectrum of this heated sample showed the absence of the band around 3,400 $cm^{-1}$. The band around 3200 $cm^{-1}$ is, however, still present. This shows that at 100 °C only the lattice water is removed and the coordinated water remains intact. This mono-hydrate, when exposed to air reconverts itself to the di-hydrate, suggesting that the dihydrate is the more stable form. A weak endotherm is again observed at $\approx$ 230 °C which is immediately followed by a strong endotherm with a peak maximum around 300 °C. This may be due to the decomposition of the chelate. A fairly sharp endotherm is observed around 415 °C and finally the oxidation of the carbon formed in the decomposition reaction gives an exothermic peak in the range 500–600 °C.

From the above physico-chemical studies, the rare-earth dithiodiacetates can be represented as $H[M(DTDA)_2 \cdot H_2O] \cdot H_2O$ with a coordination number of nine for the metal ion.

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