

## Synthesis and Physicochemical Studies of Polymeric Coordination Complexes of some Lanthanides with 1,4-Dihydroxyanthraquinone

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### Abstract

Coordination polymers of lanthanum(III), praseodymium(III), neodymium(III), samarium(III), dysprosium(III) and holmium(III) with 1,4-dihydroxyanthraquinone have been synthesized and characterized. Their magnetic moments, infrared spectra and electronic spectra have been studied to establish their structure. All the polychelates are amorphous, dark coloured powders, insoluble in common organic solvents and sparingly soluble in dimethylformamide. Nephelauxetic ratio ( $\beta$ ), covalency factor ( $b^{1/2}$ ), etc. have been evaluated wherever possible. Thermogravimetric studies (TGA) indicate a higher decomposition temperature of polychelates than the parent ligand. A.c.-conductivity, dielectric constant ( $\epsilon'$ ), dielectric loss ( $\epsilon''$ ), all at various frequencies, as well as d.c.-conductivity of the prepared polychelates, are reported. The analytical data are suggestive of a 2:3 metal–ligand stoichiometry in the polychelates.

### Introduction

The synthesis and characterization of polymeric metal chelates have earlier been studied by a number of workers [1–5]. Polymers in general, and coordination polymers in particular, have good thermal stability and catalytic activity [6]. The latter have a metal–metal linkage so also possess unusual electrical properties, especially when a system of alternate single and double bonds exists. In such cases, the type and degree of polymerization as well as the nature of the metal ion to be coordinated will depend upon the structure of the ligand and its donor atoms. In fact, enough flexibility exists to prepare almost tailor-made polymeric coordination complexes in which n and p type centres can be identified. Consequently, such polymers may exhibit conductance and dielectric characteristics. With this view, complexes of lanthanides

with 1,4-dihydroxyanthraquinone, a ligand containing a symmetrically placed pair of bidentate chelating groups suitable for forming polymeric coordination chelates, have been synthesised. Thermal and electrical properties of these polychelates are reported.

### Experimental

#### Materials

Lanthanide nitrates (Indian Rare Earth Ltd.), 1,4-dihydroxyanthraquinone (Fluka) and sodium acetate (BDH) were used as received without further purification.

#### Synthesis

An aqueous solution of the metal nitrate (0.002 mol) was mixed with ethanolic solution of the ligand (0.003 mol) and the pH of the mixture was adjusted between 5.0–5.5 using sodium acetate. On refluxing the mixture for 3–4 h on a water bath, a solid separated out. It was filtered and washed several times with hot water and alcohol to remove unreacted reactants. The complex so obtained was dried *in vacuo* over  $P_4O_{10}$ .

#### Physical Measurements

Elemental analyses of the complexes were carried out using a Heraeus C, H, N Rapid instrument.

Electronic spectra of the samples in the solid state and in dimethylformamide were recorded on Perkin-Elmer UV–Vis-554 and Shimadzu-260 spectrophotometers. The infrared spectra of the ligand and the complexes were recorded in the 400–4000  $\text{cm}^{-1}$  range on a Perkin-Elmer 621 spectrophotometer. Magnetic susceptibilities were measured at room temperature by Gouy's method using mercury(II) tetrathiocyanatocobalt(II) as the calibrant. Thermogravimetric analyses (TGA) in air were carried out on a Setaram's G-70 thermobalance at a heating rate of 10  $^{\circ}\text{C}/\text{min}$ . The electrical conductivity (d.c. and a.c.) and the dielectric constant of the pellets prepared from a finely powdered sample at a pressure of  $7.03 \times 10^6 \text{ kg}/\text{m}^2$ , were measured at room tempera-

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TABLE I. Analytical and Magnetic Moment Data of 1,4-Dihydroxyanthraquinone (1,4-DHA) and its Polychelates

| Compound        | Colour | Anal. calculated (Found) (%) |                |                  | Magnetic moment (BM) |
|-----------------|--------|------------------------------|----------------|------------------|----------------------|
|                 |        | C                            | H              | M                |                      |
| 1,4-DHA         | orange | 70.00<br>(69.90)             | 3.20<br>(3.30) |                  |                      |
| La(III)-1,4-DHA | blue   | 49.13<br>(49.90)             | 2.14<br>(2.07) | 26.90<br>(27.52) |                      |
| Pr(III)-1,4-DHA | blue   | 48.84<br>(48.90)             | 2.13<br>(2.50) | 27.31<br>(27.15) | 3.28                 |
| Nd(III)-1,4-DHA | purple | 48.63<br>(48.53)             | 2.15<br>(2.11) | 27.78<br>(27.65) | 3.32                 |
| Sm(III)-1,4-DHA | red    | 47.96<br>(46.90)             | 2.93<br>(2.80) | 28.61<br>(29.11) | 1.58                 |
| Dy(III)-1,4-DHA | blue   | 46.88<br>(46.45)             | 2.04<br>(2.00) | 30.23<br>(30.40) | 10.21                |
| Ho(III)-1,4-DHA | violet | 46.67<br>(47.00)             | 2.03<br>(2.02) | 30.54<br>(30.25) | 10.10                |

TABLE II. Important IR Bands ( $\text{cm}^{-1}$ ), Thermal Decomposition and Activation Energy Data of 1,4-DHA and its Metal Complexes

| Compound   | $\nu(\text{C}=\text{O})$ | $\nu(\text{C}-\text{O})$ | $\nu(\text{OH})$ | Decomposition temperature range ( $^{\circ}\text{C}$ ) |                      | Activation energy (kcal/mol) |        |
|--|--------------------------|--------------------------|------------------|--|----------------------|------------------------------|--------|
|  |                          |                          |                  | Step 1   | Step 2               | Step 1                       | Step 2 |
| (1) 1,4-DHA  | 1620                     | 1120                     | 3300             | 240-500 <sup>a</sup>                                   |                      | 18.41                        |        |
| (2) $\text{La}_2(1,4\text{-DHA})_3 \cdot \text{H}_2\text{O}$ | 1600                     | 1140                     | 3180-3250        | 150-180 <sup>b</sup>                                   | 360-700 <sup>a</sup> |                              | 7.290  |
| (3) $\text{Pr}_2(1,4\text{-DHA})_3 \cdot \text{H}_2\text{O}$ | 1595                     | 1130                     | 3150-3250        | 160-200 <sup>b</sup>                                   | 400-710 <sup>a</sup> |                              | 7.120  |
| (4) $\text{Nd}_2(1,4\text{-DHA})_3 \cdot \text{H}_2\text{O}$ | 1590                     | 1140                     | 3100-3250        | 160-180 <sup>b</sup>                                   | 380-680 <sup>a</sup> |                              | 6.120  |
| (5) $\text{Sm}_2(1,4\text{-DHA})_3 \cdot \text{H}_2\text{O}$ | 1610                     | 1130                     | 3180-3200        | 160-200 <sup>b</sup>                                   | 400-700 <sup>a</sup> |                              | 5.856  |
| (6) $\text{Dy}_2(1,4\text{-DHA})_3 \cdot \text{H}_2\text{O}$ | 1600                     | 1145                     | 3190-3250        | 150-180 <sup>b</sup>                                   | 360-680 <sup>a</sup> |                              | 4.182  |
| (7) $\text{Ho}_2(1,4\text{-DHA})_3 \cdot \text{H}_2\text{O}$ | 1605                     | 1150                     | 3200-3400        | 150-200 <sup>b</sup>                                   | 380-720 <sup>a</sup> |                              | 4.122  |

<sup>a</sup>Order of the decomposition reaction taking place is one. reaction has not been calculated.

<sup>b</sup>This relates to elimination of a water molecule, hence order of

ture ( $25^{\circ}\text{C}$ ). d.c.-Conductivity was measured by a Keithley electrometer Model 610, while a.c.-conductivity and dielectric constant measurements were carried out on an automatic capacitance bridge (EC and G, Princeton, U.S.A.) at a frequency of 1 MHz; a CR 1615 bridge was used for measurement in the frequency range 0.1 to 100 KHz.

## Results and Discussion

All the metal chelates prepared are dark coloured, amorphous solids, insoluble in most common organic solvents but sparingly soluble in DMF and DMSO. This is suggestive of their polymeric nature. None of the complexes melted up to  $360^{\circ}\text{C}$ .

Analytical data (Table I) of the complexes suggest a 2:3 metal-ligand stoichiometry. Coordination of

one water molecule per metal atom is also inferred in each case.

### IR Spectra

The IR spectrum of the free ligand shows a broad intensity band around  $3300\text{ cm}^{-1}$  attributed to the stretching vibration of the phenolic-OH group. In polychelates this band is observed in the range  $3180-3400\text{ cm}^{-1}$ . This may be due to  $\nu(\text{OH})$  of the coordinated water molecule [7]. The spectrum of 1,4-dihydroxyanthraquinone shows a very strong band at  $1620\text{ cm}^{-1}$  which is due to the carbonyl stretching vibration, but on complexation this band is shifted to the  $1585-1605\text{ cm}^{-1}$  region, indicating that the ketonic oxygen is coordinated to the metal ion. A strong phenolic vibration band at  $1120\text{ cm}^{-1}$  in the spectrum of the ligand shifts to higher energy in all polychelates, suggesting oxygen coordi-

TABLE III. Electronic Spectral Data of Ln(III)–Polychelates of 1,4-DHA

| Complex                                | $\lambda_{\max}$ (cm <sup>-1</sup> ) | Assignment   | Spectral parameters |
|--|--------------------------------------|--|---------------------|
| Pr <sub>2</sub> (1,4-DHA) <sub>3</sub> | 17120                                | <sup>3</sup> H <sub>4</sub> → <sup>1</sup> D <sub>2</sub><br>→ <sup>3</sup> P <sub>0</sub><br>→ <sup>3</sup> P <sub>1</sub>  | $\beta$ = 0.9830    |
|  | 20500                                |  | $\delta$ = 1.729    |
|  | 21300                                |  | $b^{1/2}$ = 0.0616  |
| Nd <sub>2</sub> (1,4-DHA) <sub>3</sub> | 12422                                | <sup>4</sup> I <sub>9/2</sub> → <sup>4</sup> F <sub>5/2</sub><br>→ <sup>4</sup> F <sub>7/2</sub><br>→ <sup>4</sup> F <sub>9/2</sub><br>→ <sup>4</sup> G <sub>5/2</sub> , <sup>2</sup> G <sub>7/2</sub><br>→ <sup>4</sup> G <sub>7/2</sub><br>→ <sup>4</sup> G <sub>9/2</sub> | $\beta$ = 0.9924    |
|  | 13423                                |  | $\delta$ = 0.765    |
|  | 14600                                |  | $b^{1/2}$ = 0.0616  |
|  | 16860                                |  |                     |
|  | 19040                                |  |                     |
|  | 19250                                |  |                     |
| Sm <sub>2</sub> (1,4-DHA) <sub>3</sub> | 20700                                | <sup>6</sup> H <sub>5/2</sub> → <sup>4</sup> F <sub>3/2</sub><br>→ <sup>4</sup> I <sub>13/2</sub><br>→ <sup>4</sup> L <sub>13/2</sub>  | $\beta$ = 0.9932    |
|  | 21510                                |  | $\delta$ = 0.6846   |
|  | 25316                                |  | $b^{1/2}$ = 0.0583  |
| Ho <sub>2</sub> (1,4-DHA) <sub>3</sub> | 15450                                | <sup>5</sup> I <sub>8</sub> → <sup>5</sup> F <sub>5</sub><br>→ <sup>5</sup> S <sub>2</sub> , <sup>5</sup> F <sub>4</sub><br>→ <sup>5</sup> G <sub>6</sub> , <sup>5</sup> F <sub>1</sub>  | $\beta$ = 0.9948    |
|  | 18650                                |  | $\delta$ = 0.5227   |
|  | 22158                                |  | $b^{1/2}$ = 0.0509  |

nation of the phenolic group (C–O····M) [8]. A sharp band at 1250 cm<sup>-1</sup> in the ligand may be due to  $\delta$ (OH) vibration [9]. Polychelates also show a band in the 1240–1260 cm<sup>-1</sup> region, but this is attributed to the presence of coordinated water (Table II).

#### Magnetic Behaviour

The observed magnetic data of the polychelates are presented in Table I. Except for La(III)–polychelate, all are paramagnetic in nature. The observed magnetic moments agree closely with the Van Vleck values [10].

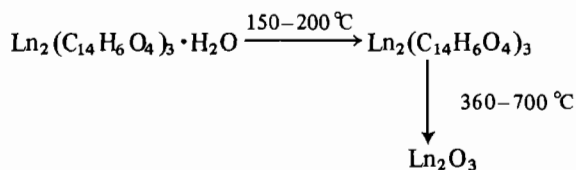
#### Electronic Spectra

Electronic spectra of polychelates and the ligand have been recorded in the solid state and in DMF. The solid state spectrum of the latter shows prominent peaks at 35 700 cm<sup>-1</sup> and 40 300 cm<sup>-1</sup>. However, in the case of the former these bands appear in the range 35 010–35 450 and 39 520–39 720 cm<sup>-1</sup> respectively. All the complexes are characterized by intense charge-transfer bands in these regions. Most of the absorption bands due to f–f transitions of the lanthanide ions in the visible region are obscured due to the broad charge-transfer bands. However, in the Pr(III), Nd(III), Sm(III) and Ho(III) polychelates, f–f bands are observed [11]. Tentative assignments for these bands are given in Table III. The red shift of the hypersensitive bands has been used to calculate the nephelauxetic effect ratio. The nephelauxetic effect ( $\beta$ ) [12], bonding parameter ( $b^{1/2}$ ) and Sinha's parameter ( $\delta$ ) [13] have also been calculated. The bonding parameter ( $b^{1/2}$ ) reflects the extent of participation of 4f orbitals in the com-

plexation. The average value of Sinha's parameter ( $\delta$ ) obtained in the presence case suggest a weak covalent character for the metal–ligand bond.

#### Thermal Studies

TGA data in air (Table II) indicate that these polychelates decompose in a gradual manner, in contrast to the sharp decomposition of 1,4-dihydroxyanthraquinone. TGA data of the present complexes show that all the complexes are stable up to ~300 °C. They undergo decomposition in two stages, as denoted by DTG peaks in the 150–200 °C and 300–700 °C range. All the complexes undergo complete decomposition at ~700 °C and above this temperature stable oxides are formed, as outlined below.



Kinetic parameters of the solid state thermal reactions involving decomposition and consequent weight loss have been calculated by Coats and Redfern's [14] method. The order of the thermal reaction and the corresponding activation energies have been evaluated from the figure obtained, using the following equation

$$-\log \left[ \frac{-\log(1-\alpha)}{T^2} \right] = A e^{-E/RT}$$

Kinetic parameters of each decomposition step have been calculated from TG curves and are present-

TABLE IV. Electrical Conductivity (a.c. and d.c.) and Relative Dielectric Constant ( $\epsilon'$ ) and Loss ( $\epsilon''$ ) of 1,4-DHA and its Polychelates

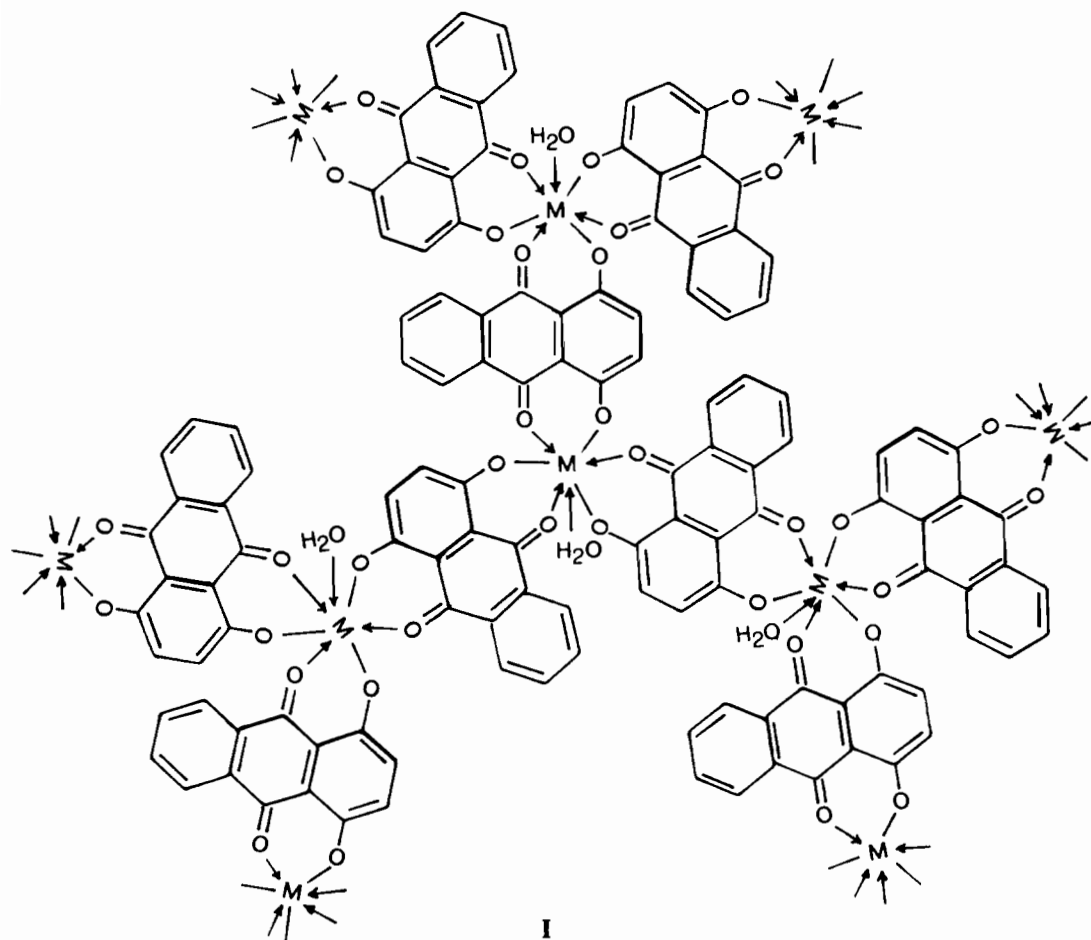
| Compound        | Frequency | $\epsilon'$ | $\epsilon''$ | a.c. $\sigma$<br>( $\Omega^{-1} \text{ cm}^{-1}$ ) | d.c. $\sigma$<br>( $\Omega^{-1} \text{ cm}^{-1}$ ) |
|-----------------|-----------|-------------|--------------|--|--|
| 1,4-DHA         | 1 MHz     | 2.68        | 0.032        | $5.06 \times 10^{-8}$                              | $7.23 \times 10^{-13}$                             |
|                 | 100 KHz   | 3.08        | 0.073        | $3.68 \times 10^{-9}$                              |  |
|                 | 10 KHz    | 3.23        | 0.141        | $8.90 \times 10^{-10}$                             |  |
|                 | 1 KHz     | 3.55        | 0.273        | $2.50 \times 10^{-10}$                             |  |
|                 | 100 Hz    | 4.00        | 7.475        | $1.60 \times 10^{-10}$                             |  |
| La(III)-1,4-DHA | 1 MHz     | 10.55       | 3.30         | $1.84 \times 10^{-6}$                              | $2.00 \times 10^{-10}$                             |
|                 | 100 KHz   | 16.22       | 3.29         | $1.83 \times 10^{-7}$                              |  |
|                 | 10 KHz    | 25.12       | 9.65         | $5.37 \times 10^{-8}$                              |  |
|                 | 1 KHz     | 58.60       | 41.25        | $2.29 \times 10^{-8}$                              |  |
|                 | 100 Hz    | 90.50       | 130.00       | $6.98 \times 10^{-9}$                              |  |
| Pr(III)-1,4-DHA | 1 MHz     | 16.52       | 5.82         | $2.63 \times 10^{-6}$                              | $4.5 \times 10^{-10}$                              |
|                 | 100 KHz   | 25.89       | 17.78        | $9.90 \times 10^{-7}$                              |  |
|                 | 10 KHz    | 62.85       | 28.09        | $1.56 \times 10^{-7}$                              |  |
|                 | 1 KHz     | 102.86      | 35.92        | $2.20 \times 10^{-8}$                              |  |
|                 | 100 Hz    | 171.88      | 89.81        | $5.21 \times 10^{-9}$                              |  |
| Nd(III)-1,4-DHA | 1 MHz     | 12.29       | 1.34         | $7.48 \times 10^{-7}$                              | $2.35 \times 10^{-10}$                             |
|                 | 100 KHz   | 18.64       | 4.68         | $2.60 \times 10^{-7}$                              |  |
|                 | 10 KHz    | 30.71       | 13.27        | $7.39 \times 10^{-8}$                              |  |
|                 | 1 KHz     | 71.97       | 53.99        | $3.00 \times 10^{-8}$                              |  |
|                 | 100 Hz    | 97.74       | 169.50       | $9.44 \times 10^{-9}$                              |  |
| Sm(III)-1,4-DHA | 1 MHz     | 11.05       | 2.78         | $1.55 \times 10^{-6}$                              | $1.90 \times 10^{-10}$                             |
|                 | 100 KHz   | 16.21       | 3.07         | $1.71 \times 10^{-7}$                              |  |
|                 | 10 KHz    | 26.77       | 8.14         | $4.53 \times 10^{-8}$                              |  |
|                 | 1 KHz     | 57.53       | 34.81        | $1.94 \times 10^{-8}$                              |  |
|                 | 100 Hz    | 85.84       | 108.90       | $6.65 \times 10^{-9}$                              |  |
| Dy(III)-1,4-DHA | 1 MHz     | 7.82        | 1.57         | $8.74 \times 10^{-7}$                              | $1.26 \times 10^{-10}$                             |
|                 | 100 KHz   | 9.88        | 2.84         | $1.58 \times 10^{-7}$                              |  |
|                 | 10 KHz    | 13.20       | 4.80         | $2.68 \times 10^{-8}$                              |  |
|                 | 1 KHz     | 31.99       | 21.88        | $1.21 \times 10^{-8}$                              |  |
|                 | 100 Hz    | 53.61       | 59.63        | $3.32 \times 10^{-9}$                              |  |
| Ho(III)-1,4-DHA | 1 MHz     | 6.74        | 1.57         | $8.77 \times 10^{-7}$                              | $8.46 \times 10^{-10}$                             |
|                 | 100 KHz   | 9.08        | 1.82         | $1.01 \times 10^{-8}$                              |  |
|                 | 10 KHz    | 12.34       | 5.01         | $2.79 \times 10^{-8}$                              |  |
|                 | 1 KHz     | 30.24       | 19.78        | $1.09 \times 10^{-8}$                              |  |
|                 | 100 Hz    | 50.62       | 64.48        | $3.59 \times 10^{-9}$                              |  |

ed in Table II. A plot of  $-\log(-\log(1-\alpha)/T^2)$  versus  $1/T$  results in a straight line of slope  $-E/2.303R$ . The order of reaction has been found to be one in each case. Since each molecule of the ligand contains two bidentate groups symmetrically attached on either side of the central framework the two metal atoms can be coordinated to one molecule of such a ligand. A situation like this results in a complex containing coordinatively unsaturated metal atom. Such complexes are unstable and react with a donor ligand or solvent to produce a coordinatively saturated complex.

The observed solubility pattern suggests the polymeric nature of the complexes under study. The tentative structure I for the polychelates is suggested.

#### Conductivity Studies

a.c.-Conductivity and the relative dielectric constant of 1,4-dihydroxyanthraquinone and its polychelates have been studied at various frequencies between 100 Hz to 1 MHz. The results are given in Table IV. d.c.-Conductivity at room temperature has also been measured. It is observed that d.c.-conductivity of



the ligand is low and close to that of a good insulator. However, its magnitude increases on chelation. No noticeable change in the d.c.-current with time has been observed. This indicates that electronic conduction is mainly responsible for the observed conductivity of these materials. Since a.c.-conductivity at higher frequencies, both of the ligand as well as its metal complexes, is found to be more than the corresponding d.c.-conductivity, this suggests that the mechanism of conduction is 'hopping', as short-range motion of electrons under applied a.c. field gives rise to a higher value.

**Dielectric Constant Measurements**

The dielectric constant ( $\epsilon'$ ) of these chelates shows a dispersion in the frequency region studied. The magnitude of dielectric loss ( $\epsilon''$ ) is much higher than that expected from d.c.-conductivity. This indicates the dipolar nature of these materials. The dielectric constant variation as a function of frequency shows that in the low frequency region it increases slowly, indicating a static dielectric constant value of the bulk material. However, in the lower frequency region (10 KHz–100 Hz), the dielectric constant

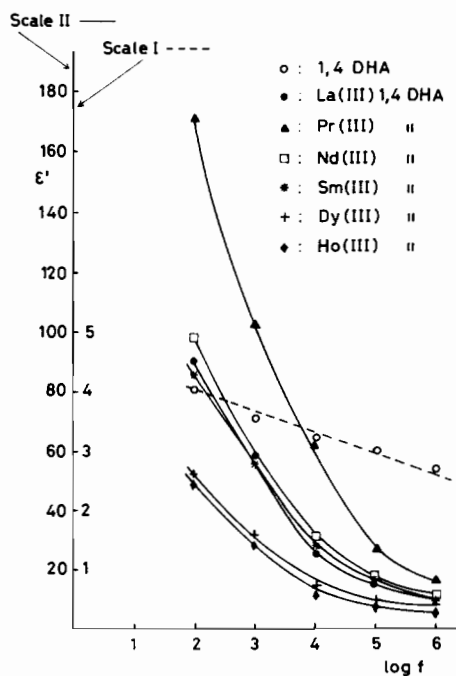


Fig. 1. Plot of  $\log f$  vs.  $\epsilon'$ .

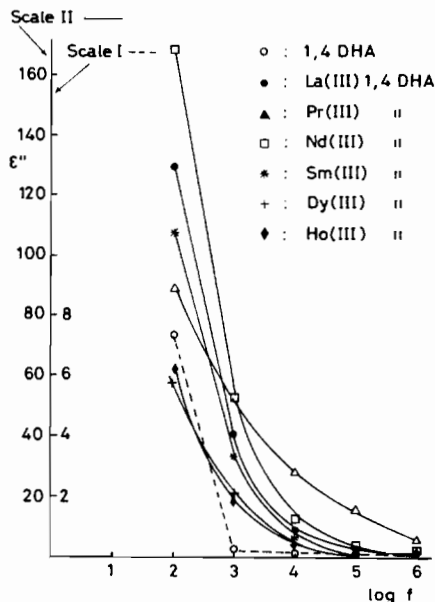


Fig. 2. Plot of  $\log f$  vs.  $\epsilon''$ .

increases sharply and linearly (Fig. 1). This is attributed to an intercrystalline or electrode barrier caused by strong overlap of the two dispersion regions. Consequently, no distinct peak in the dielectric loss *versus* frequency curve is observed (Fig. 2). However, from the data it is evident that up to 1 MHz the dielectric constant shows a decrease and the limiting high value due to electronic and ionic polarization is not achieved.

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