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# Synthesis and Spectral Studies of Dichloroacetates of Lanthanoids

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**Synopsis.** Dichloroacetates of lanthanoids (Pr, Nd, Sm, Ho, and Er) have been synthesized and characterized by elemental analysis, absorption and IR spectral data, and the X-ray power patterns. Magnetic moments of these derivatives have been measured. Molecular weights determined ebullioscopically in acetic acid showed them to be dimeric.

The halogen substituted acetates of d transition elements have been extentively studied.[1,2,6,7] However, there has been only a very limited effort made in the study of halogen substituted acetates of lanthanoids.[3,4] The trihydrated dichloroacetates (DCA) separate out from the reaction of lanthanoids carbonates and dichloroacetic acid. These can be made anhydrous by keeping in a vacuum desiccator over $P_2O_5$ for 4 days or heating at 60 °C for 6 h at 0.01 Torr pressure.

## Experimental

Crystalline lanthanoids dichloroacetates were prepared by adding slight excess lanthanoids carbonates to dichloroacetic acid (Fluka).

Absorption spectra were measured on Carl Zeiss VSU-2 Spectrophotometer in water and infrared spectra of the KBr pellets were run on a Perkin-Elmer 521 Spectrophotometer.

X-Ray diffraction patterns were obtained using a Phillips diffractometer with nickel filtered Cu*Kα* radiation. Magnetic properties of the compounds were measured by Gouy method at 295 K. The molar susceptibilities were corrected for the diamagnetism of the constituent atoms by means of Pascal's constant.[5] Molecular weights were determined in acetic acid by Gallenkemp semimicro ebulliometer with thermistor ensing.

## Results and Discussion

Stretching frequencies $\gamma_s$COO$^-$ in acetates have been found to be sensitive to both coordination to a metal and substitution in acetate group.[6,7] During the complex formation $\gamma_s$COO$^-$ shifts to higher frequency, while $\gamma_a$COO$^-$ shifts in opposite direction. Comparing the values of $\gamma_a$COO$^-$ in sodium dichloroacetate,[8] Cu(II)[2] and lanthanoids dichloroacetates we have observed that the $\gamma_a$COO$^-$ values lie inbetween highly ionic sodium dichloroacetate and covalent Cu(II) dichloroacetate. In the lower lanthanoids (Pr and Nd) the values are closer to sodium analogue, while in the higher lanthanoids (Ho and Er) dichloroacetates the values lie closer to copper analogue. This appears well in the conformity of lanthanoids contraction. The $\gamma_a$COO$^-$ of lanthanoids dichloroacetates, a strong band occuring at 1615—1622 cm$^{-1}$ shows a decrease as compared to sodium analogue, which can be interpreted in terms of dimeric COO$^-$ group, as parallel behavior was observed in the case of Cu(II) dichloroacetate[2]. The existence of dimeric nature of dichloroacetate group is also supported by our mol wt data which point toward dimeric units for dichloroacetate thus involving both bidentate and dimeric dichloroacetate grouping.

*C–Halogen Stretching.* In lanthanoids dichloroacetates we find high C–halogen and weak low C–halogen stretching frequencies pointing towards the existence of both trans and gauche conformation on the line suggested by Spinner.[8] In general, we find high C–halogen stretching frequencies generally increase with

TABLE 1. ANALYTICAL, MAGNETIC SUSCEPTIBILITY AND MOLECULAR WEIGHT DATA FOR DICHLOROACETATES OF LANTHANOIDS

| Compound | Elementary analysis[a] | | | | Molar susceptibility $\chi'^{\mathrm{coor}}_{\mathrm{m}} \times 10^6$ cgs units | Magnetic moment $\mu_{\mathrm{eff}}$ in B.M. | Mol wt (Found) |
|---|---|---|---|---|---|---|---|
| | Metal (%) | Cl (%) | C (%) | H (%) | | | |
| $Pr(CHCl_2COO)_3 \cdot 3H_2O$ | 24.23 | 36.71 | 12.49 | 1.51 | 5069 | 3.47 | — |
| | (24.34 | 36.75 | 12.45 | 1.56) | | | |
| $Nd(CHCl_2COO)_3 \cdot 3H_2O$ | 24.59 | 36.43 | 12.31 | 1.43 | 5548 | 3.63 | — |
| | (24.78 | 36.54 | 12.38 | 1.55) | | | |
| $Sm(CHCl_2COO)_3 \cdot 3H_2O$ | 25.62 | 36.12 | 12.16 | 1.52 | 1766 | 2.04 | — |
| | (25.58 | 36.15 | 12.24 | 1.54) | | | |
| $Ho(CHCl_2COO)_3 \cdot 3H_2O$ | 27.17 | 35.14 | 11.75 | 1.50 | 45264 | 10.37 | — |
| | (27.36 | 35.28 | 11.95 | 1.50) | | | |
| $Er(CHCl_2COO)_3 \cdot 3H_2O$ | 27.73 | 35.03 | 11.96 | 1.41 | 38134 | 9.52 | — |
| | (27.64 | 35.15 | 11.90 | 1.49) | | | |
| $Pr(CHCl_2COO)_3$ | 26.81 | 40.43 | 13.60 | 0.51 | — | — | 1007 |
| | (26.85 | 40.53 | 13.73 | 0.57) | | | (524.73) |
| $Nd(CHCl_2COO)_3$ | 27.14 | 40.21 | 13.51 | 0.43 | — | — | 1002 |
| | (27.31 | 40.28 | 13.64 | 0.57) | | | (528.06) |
| $Er(CHCl_2COO)_3$ | 30.42 | 38.50 | 12.89 | 0.46 | — | — | 1087 |
| | (30.35 | 38.59 | 13.07 | 0.54) | | | (551.08) |

a) Figures in parentheses indicate the calculated values.

Table 2. Characteristic COO$^-$, C–halogen stretchings frequencies and low frequency IR absorption of dichloroacetates (DCA)

| Sodium[8] DCA | Cu[10] DCA | Pr DCA | Nd DCA | Sm DCA | Ho DCA | Er DCA | Assignments |
|---|---|---|---|---|---|---|---|
| 1660 m | 1689 s | 1515 s | 1615 s | 1615 s | 1622 s | 1625 s | $\nu_{asym}$ COO$^-$ |
| 1640 vs | 1582 s | 1580 s | 1580 s | 1580 s | 1595 ms | 1595 s | |
| 1399 s | 1435 sh | 1410 ms | 1410 ms | 1415 m | 1416 ms | 1416 m | $\nu_{sym}$ COO$^-$ |
| | 1415 vs | 1380 m | 1375 ms | 1380 s | 1386 s | 1380 s | |
| 821 | 835 sh | 830 w | 829 w | 827 sh | 840 w | 834 w | |
| 807 R | 825 vs | 822 s | 817 s | 820 s | 822 s | 827 s | $\nu_{asym}$ C–Cl$_2$ |
| 779 | 807 w | 792 m | 794 m | 794 m | 802 m | 794 w | |
| 738 | 761 w | 726 w | 759 w | 755 w | 747 w | 742 w | $\nu_{sym}$ C–Cl$_2$ |
| | 502 w | 462 w | 456 w | 456 w | 456 w | 457 w | |
| | 482 vw | 433 w | 436 w | 433 w | 428 w | 430 w | $\beta_{asym}$ C–Cl$_2$ |
| | 463 sh | 425 w | 421 w | 416 w | 408 w | 412 w | |
| | 442 w | | | | | | |
| | 408 w | 398 w | 396 w | 392 w | 379 w | 384 w | $\beta_{sym}$ C–Cl$_2$ |

R=Raman, $\beta$=deformation.

the rise of atomic number of lanthanoids, again in conformity with the lanthanoids contraction. Absorption in 500—350 cm$^{-1}$ of dichloroacetates probably arises from C–halogen bending vibrations. Faniran and Patel[2] reported four bands for Cu(II) dichloroacetate, while in lanthanoids dichloroacetates we observe three bands. The higher frequency band in dichloroacetates can be identified with antisymmetric motion, while those at lower frequencies are attributed to the symmetrical deformations.

Table 3. Nephelauxetic ratio ($\beta$), covelency parameter ($\delta$) and bonding parameter ($b^{1/2}$) of the DCA of lanthanoids

| Compound | $\beta$ | $\delta$ (%) | $b^{1/2}$ |
|---|---|---|---|
| Pr DCA | 0.99230 | +0.7761 | 0.06205 |
| Nd DCA | 0.99467 | +0.5358 | 0.05162 |
| Sm DCA | 0.99887 | +0.1131 | 0.02377 |
| Ho DCA | 1.0052 | −0.5174 | — |
| Er DCA | 1.0051 | −0.5173 | — |

Karraker[9] showed that the symmetry coordination number of a lanthanoids could be predicted from the shape, intensity and wavelength of its hypersensitive transitions in the visible absorption spectrum. The shape of the hypersensitive transition of Nd dichloroacetate ($^4I_{9/2} \rightarrow {}^4G_{5/2}$, $^2G_{7/2}$) in water is quite identical with the bands of the nonacoordinated $Nd(BrO_3)_3 \cdot 9H_2O$ in water as well as in solid.[9] The similarlity among the spectra indicate that in these solutions at least the dichloroacetates are most likely nonaccordinated. It is, of course, risky to transfer conclusions from solution measurement to solid compounds, but we feel that the evidence in hand suggests that these compounds are most likely nonacoordinated in solid state as well.

The values of nephelauxetic ratio ($\beta$) which are less than one, and covalency parameters ($\delta$) which are positive indicate thereby that the nature of bonding between metal and ligand is covalent as compared to lanthanoids aqua ions. Like Sinha[10] we find negative values for $\delta$ in case of Ho and Er, which he interpreted in terms of ionic characters in the complexes as compared to respective aqua ions. This behavior is quite surprising in view of the highly coordinated nature of the dichloroacetate grouping. The smaller values of bonding parameter $b^{1/2}$ [11] suggests that 4f orbitals are very slightly involved in bonding in lanthanoids dichloroacetates. The magnetic susceptibilities of Pr, Nd, Sm, Ho, and Er dichloroacetates have been measured and the values of magnetic moments of these derivatives have been found to be quite closer to the values reported by earlier workers.[12–15] X-Ray diffraction studies indicate the compounds to be isomorphous within a group by virtue of similar interplanar spacing $d$ and the line intensities.

Table 4. Power X-ray diffraction data of DCA of lanthanoids

| Pr | | Nd | | Sm | | Ho | | Er | |
|---|---|---|---|---|---|---|---|---|---|
| $d$(Å) | $I/I_0$ | $d$(Å) | $I/I_0$ | $d$(Å) | $I/I_0$ | $d$(Å) | $I/I_0$ | $d$(Å) | $I/I_0$ |
| 11.8565 | 100 | 11.4710 | 100 | 11.7770 | 100 | 11.6220 | 100 | 11.7770 | 100 |
| 3.7909 | 20 | 3.7509 | 12 | 3.7660 | 26 | 3.8968 | 18 | 5.7860 | 5 |
| 2.9377 | 24 | 2.9144 | 28 | 2.9330 | 17 | 2.9190 | 38 | 3.8801 | 37 |
| 2.6724 | 8 | 2.7040 | 3 | 2.6649 | 6 | 2.3362 | 3 | 2.9190 | 60 |
| 2.3010 | 19 | 2.3421 | 21 | 2.3480 | 12 | | | 2.3962 | 8 |
| 1.9632 | 13 | 1.9513 | 13 | 1.9938 | 7 | | | 1.9473 | 6 |
| | | | | | | | | 1.9012 | 1 |

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