April, 1983] © *1983 The Chemical Society of Japan* NOTES *Bull. Chem. Soc. Jpn.*, **56**, *1237—1238 (1983)* 1237

Syntheses and Characterization of Lanthanoid(III) Propoxyacetate

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(Received September 30, 1982)

Synopsis. New lanthanoid(III) complexes with the formula of $ML_3 \cdot H_2O$, where M=La, Ce, Pr, Nd, Eu, Dy, or Er, and HL=propoxyacetic acid, have been synthesized; they are isostructural with each other. From the shift direction of the ^1H-NMR peaks of L^- in an aqueous solution upon adding Eu(III) or Pr(III) salt, the ligand is likely to be coordinated to the metal by both the ether and carboxyl oxygen atoms.

The interesting structures of some lanthanoid(III) carboxylate complexes in their crystals have already been revealed by the single crystal X-ray diffraction technique.[1–5] The structure of lanthanoid(III) alkylthioacetates has also been elucidated, and it has been found that the ligand is coordinated to the metal only by the carboxylate oxygen atoms, not by the sulfide sulfur atom.[6] On the other hand, in the case of tris(diglycolato)lanthanoid(III) complexes, the ligand acts as a terdentate where the central metal is coordinated to both the ether and carboxylate oxygen atoms.[7] Therefore, it was thought to be interesting to synthesize the lanthanoid(III) alkoxyacetates and to check whether or not the ether oxygen atom of the ligand in them is coordinated to the metal. The complexes obtained were found to be stable to moisture, even in open air.

Experimental

Synthesis of Lanthanum(III) Propoxyacetate Monohydrate, $La(C_3H_7OCH_2CO_2)_3 \cdot H_2O$. The ligand, propoxyacetic acid, was obtained by Rule's method.[8] Propoxyacetic acid (2.13 g, 18 mmol) and sodium hydrogencarbonate (1.43 g, 17 mmol) were dissolved in about 7 cm^3 of water, and lanthanum(III) chloride heptahydrate (1.86 g, 5 mmol) dissolved in 3 cm^3 of water was added to the former solution. The mixture was then stirred and heated, and the complex was precipitated. It was filtered off, dissolved in about 40 cm^3 of hot water, concentrated by means of a rotary vacuum evaporator to about 10 cm^3, and left standing at room temperature overnight. The crystals thus obtained were filtered off, washed with a little water, and dried in open air. Although the yield of the first crop obtained was only 21%, crystals of almost the same purity were also obtained when the filtrate in a beaker was kept longer in a silica-gel desiccator; the total yield was about 66%.

The propoxyacetates of Ce, Pr, Nd, Eu, and Dy were obtained in almost the same way, and their yields were comparable. In the case of the Er complex, the product appeared as an oily layer when the starting materials were mixed and heated: it gradually turned into a solid precipitate within a few minutes while it was being stirred and cooled.

These complexes have the formula of $M(C_3H_7OCH_2CO_2)_3 \cdot H_2O$. Analyses (Calcd values were obtained from the formula of $C_{15}H_{29}O_{10}M$): M=La, Found: La, 27.16; C, 35.35; H, 5.76%. Calcd: La, 27.33; C, 35.45; H, 5.75%. M=Ce, Found: Ce, 27.61; C, 35.42; H, 5.74%. Calcd: Ce, 27.50; C, 35.36; H, 5.74%. M=Pr, Found: Pr, 27.49; C, 35.25; H, 5.88%. Calcd: Pr, 27.61; C, 35.31; H, 5.73%. M=Nd, Found: Nd, 27.94; C, 35.13; H, 5.71%. Calcd: Nd, 28.08;; C, 35.08; H, 5.69%. M=Eu, Found: Eu, 29.18; C, 34.52 H, 5.74%. Calcd: Eu, 29.15; C, 34.56; H, 5.61%. M=Dy, Found: Dy, 30.58; C, 33.73; H, 5.63%. Calcd: Dy, 30.55; C, 33.87; H, 5.50%. M=Er, Found: Er, 31.14; C, 33.48; H, 5.60%. Calcd: Er, 31.17; C, 33.57; H, 5.45%.

Magnetic Moments, X-Ray, Infrared Spectra, and ^1H-NMR Measurements. Their X-ray powder patterns were obtained by the use of a diffractometer, model DX-GO-F JEOL, using Cu *Kα* radiation from 3 to 60° in 2θ.

The infrared spectra of the samples were obtained by means of a JASCO A202 infrared spectrophotometer, using Nujol and hexachloro-1,3-butadiene mull. The ^1H-NMR was measured by means of a Varian EM-390 spectrometer, using D_2O as the solvent and sodium 3-(trimethylsilyl)-1-propanesulfonate (DSS) as the internal standard.

The magnetic moments of the complexes at room tempeature were measured by the use of a Gouy balance.

Results and Discussion

From the analyses and from their X-ray powder patterns, all of these seven complexes are isostructural. Their single crystals have a layer structure, consisting of mica-like thin films. As there is a tendency found extreme cleavage, the single-crystal diffraction study has not yet been completed. The magnetic moments of $ML_3 \cdot H_2O$, where HL=propoxyacetic acid are; M=La, diamagnetic; M=Ce, 2.4_9; M=Pr, 3.5_0; M=Nd, 3.5_5; M=Eu, 3.2_8; M=Dy, 10.6_8; M=Er, 9.6_1 BM,** respectively. They mean that no significant metal-metal interaction exists.[9]

Both the $\nu_{as}(COO)$ and $\nu_s(COO)$ absorptions of the IR spectra split into several peaks. The main $\nu_{as}(COO)$ peak of each complex appears between 1596 (La complex) and 1608 (Er complex) cm^{-1}, and the wave number increases depending on the atomic number of the central metal. The wave number of the maximum of the $\nu_{as}(COO)$ peak is higher than that of the corresponding lanthanoid(III) alkylthioacetates (about 1590—1580 and 1540 cm^{-1}).[6]

In Fig. 1 are shown the shifts of ^1H-NMR peaks of sodium butyrate, propylthioacetate, and propoxyacetate in a D_2O solution upon the addition of europium(III) chloride or of praseodymium(III) chloride. In all cases, the shift direction of the peaks upon the addition of Eu(III) is the opposite of that upon the addition of Pr(III): the ratio of the two shifts is about 1 : 2 for the same proton of the same acid salt. This means that the shifts occur mainly because of the dipole effect.[10] In the case of butyrate, where the central metal atom is coordinated only to the carboxyl oxygen atoms, all the proton peaks shift in the same direction—downfield by Pr(III) and upfield by Eu(III). Also, in the case of propylthioacetate, where the lanthanoid metal atom is coordinated only to the carboxyl oxygen atoms,[6] the shift direction of all the proton signals is the same as

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** 1 BM=9.274078(36)·10^{-24} J T^{-1}.

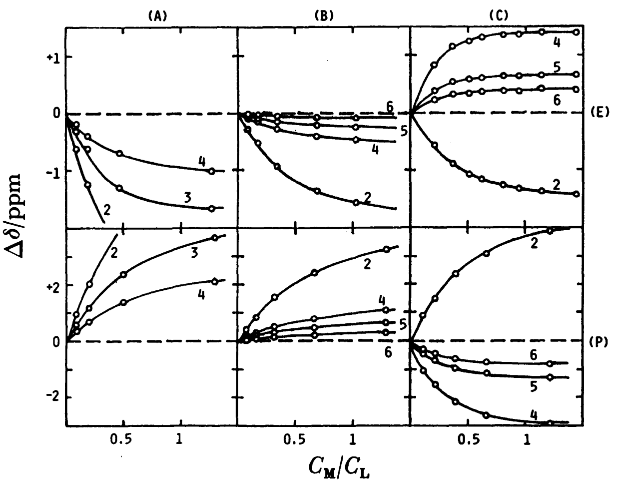

Fig. 1. The shifts of ^{1}H-NMR peaks by the addition of europium(III) chloride (E: the upper ones), or praseodymium(III) chloride (P: the lower ones), in D_2O solution. C_M/C_L = mol/mol. C_M: Concentration of Eu(III) or Pr(III). C_L: Concentration of propoxyacetate. Downfield $\Delta\delta$ was shown positive. Original chemical shifts for (A) $CH_3(4)$–$CH_2(3)$–$CH_2(2)$–CO_2Na, (B) $CH_3(6)$–$CH_2(5)$–$CH_2(4)$–S–$CH_2(2)$–CO_2Na, (C) $CH_3(6)$–$CH_2(5)$–$CH_2(4)$–O–$CH_2(2)$–CO_2Na: (A) (4) 0.87(t), (3) 1.53(m), (2) 2.15(t); (B) (6) 0.94(t), (5) 1.58(m), (4) 2.52 (t), (2) 3.15(s); (C) (6) 0.88(t), (5) 1.59(m), (4) 3.46(t), (2) 3.88(s) ppm (in δ, DSS=0; s: singlet, t: triplet, and m: multiplet). The concentration of the original sodium salts are, (A) 0.069; (B) 0.068; (C) 0.20 mol dm^{-3} for (E)s, and (A) 0.067; (B) 0.068; (C) 0.19 mol dm^{-3} for (P)s. Used $EuCl_3$ or $PrCl_3$ solutions: (A), (B), 0.13 mol dm^{-3}; (C) 0.37 mol dm^{-3} containing 0.19 mol dm^{-3} of sodium propoxyacetate.

that of butyrate. Thus, all the ligand protons of butyrate or of propylthioacetate can be expected to be out of the axial cone of the central lanthanoid atom.

On the other hand, in the case of propoxyacetate, as is shown in Fig. 1, only the signal of the protons of the methylene group which is next to the carboxyl group shifts in the same direction as those of the butyrate or of propylthioacetate. The signals of propoxyl protons, on the contrary, shift in the opposite direction, and the shift decreases rapidly depending on the increase in the distance between the proton and the ether oxygen atom.[11] This seems to be because the ether oxygen atom moves in the axial direction, while the propoxyl group shifts into the axial cone. Therefore, from this ^{1}H-NMR result, the propoxyacetate ion is found to be coordinated to the lanthanoid(III) metal atom by both carboxyl and ether oxygen atoms.

The authors are greatly obliged to the Shin-Etsu Chemical Co., Ltd., for aiding this study by presenting the highly pure lanthanoid(III) oxides.

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