The Structure and Properties of the Triaquahexakis(methylthioacetato)-dineodymium(III) Polymer, $[Nd_2(C_3H_5SO_2)_6(H_2O)_3]_n$, and the Same-ligand Complexes of Lanthanoid Elements

Satoshi KONDO, Mamoru SHIMOI, Akira OUCHI,* and Toshio TAKEUCHI†

Department of Chemistry, College of General Education, The University of Tokyo, Komaba 3-8-1, Meguro-ku, Tokyo 153

† *Department of General Sciences, Faculty of Science and Technology, Sophia University, Kioi-cho 7, Chiyoda-ku, Tokyo 102*

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The crystal and molecular structure of the title complex has been determined by the X-ray diffraction method. The crystal was triclinic, space group $P\bar{1}$, $a=12.80(1)$, $b=16.65(1)$, $c=8.659(9)$ Å, $\alpha=104.6(1)$, $\beta=93.7(2)$, $\gamma=107.5(1)°$, $Z=2$, $D_x=1.892(3)$, $D_m=1.91(2)$ Mg m^{-3}, μ(Mo $K\alpha$)$=3.45$ mm^{-1}, and the final R value was 0.051 for 3577 reflections. The coordination number of both neodymium atoms is nine, although the coordinated atoms around one neodymium atom are arrayed in a tri-capped trigonal prism, and those around the other neodymium atom, in a mono-capped tetragonal antiprism. The neodymium atoms are arrayed on a linear chain bridged by the ligand; however, no metal-metal interaction is observed. The corresponding complexes of cerium(III), praseodymium(III), and europium(III) form isomorphous crystals with the title complex, but the complex of lanthanum(III) has the formula of $ML_3\cdot 4.5H_2O$ (HL=(methylthio)acetic acid), and the complexes of dysprosium(III) and ytterbium(III), $ML_3\cdot 2H_2O$.

Many synthetic works were already published about the (alkylthio)acetato** complexes of 3d elements,[1–11] and we have already reported about these structures.[12–15] According to our results, in general, one oxygen atom as well as a sulfur atom are coordinated with the central metal atom, thus forming a five-membered chelate ring. However, in the case of bis(isopropylthioacetato)copper(II) dihydrate, two oxygen atoms of a carboxyl group of the ligand are coordinated to separate metal atoms.[14] In the case of the bis(propylthioacetato)cobalt(II) hexamer, there are two kinds of ligands acting in different modes of coordination.[15] Although no structural analysis was done, in the case of bis(alkylthioacetato)triphenylantimony(III) the ligand is expected to be coordinated to the metal atom by only one oxygen atom.[11]

The methylthioacetato complexes of lanthanoid elements now obtained were found to have the formula of $ML_3\cdot nH_2O$ (where HL=methylthioacetic acid, and $n=4.5$, 1.5, or 2 for their hydrated complexes). The lanthanoid elements generally show a high coordination number, and the sulfur atom of a ligand is hardly coordinated at all to the metal because of its "hard" character. Consequently, it is not probable that the five-membered chelate ring found in the 3d element complexes exists also in the lanthanoid complexes. On the other hand, a linear polymer structure has been reported for some carboxylato complexes of 4f and 5f metals, such as cerium(III) acetate[16] and uranium(IV) acetate.[17] Therefore, for the alkylthioacetato complexes of lanthanoid elements, too, such a type of interesting polymerized structure was expected. Thus, we have attempted to determine their crystal and molecular structure by means of X-ray diffraction. The methylthioacetato complexes of other lanthanoid elements were also obtained and were compared with the titled complex with regard to their analytical, spectral, and thermochemical properties, as well as their X-ray powder patterns in order to classify them.

** The parentheses in the name of the ligand are neglected hereafter.

Experimental

Synthesis of Triaquahexakis(methylthioacetato)dineodymium(III), $[Nd_2(CH_3SCH_2CO_2)_6(H_2O)_3]_n$. The ligand was obtained by means of a slight modification of the method of Larsson:[18] a condensation reaction between dimethyl sulfate (in place of methyl iodide) and mercaptoacetic acid in the presence of sodium hydroxide in an aqueous solution. The aqueous solutions of sodium methylthioacetate (2.4 g (19 mmol) in 5 cm^3 of water) and of neodymium(III) chloride hexahydrate (2.0 g (5.5 mmol) in 5 cm^3 of water) were mixed and the mixture was left standing for one day or more at 6 °C. The first crop of the product was thus obtained; the yield was 1.1 g (41%). The filtered mother liquor was concentrated to 5 cm^3 and then left standing; a second crop which was almost as pure as the first one was also obtained; the total yield was 1.8 g (66%). The complex could be recrystallized from water, although the crystal appeared slowly, and the yield was low because of its fairly high solubility. The crystals thus obtained were submitted to the X-ray diffraction after being checked by means of their Weissenberg photograph. Found: Nd, 29.76; C, 22.08; H, 3.69%. Calcd for $Nd_2C_{18}H_{36}S_6O_{15}$: Nd, 29.64; C, 22.21; H, 3.73%.

Syntheses and Analyses of the Methylthioacetato Complexes of Lanthanoid Elements. These complexes were obtained in almost the same way as the neodymium complex. Among them, the cerium(III), praseodymium(III), and europium(III) complexes have the same type of chemical formula, $ML_3\cdot 1.5H_2O$ (HL=methylthioacetic acid). 1) Cerium(III) complex, Found: Ce, 28.78; C, 22.30; H, 3.67%. Calcd for $CeC_9H_{18}O_{7.5}S_3$: Ce, 29.04; C, 22.42; H, 3.76%. 2) Praseodymium(III) complex, Found: Pr, 29.15; C, 22.24; H, 3.70%. Calcd for $PrC_9H_{18}O_{7.5}S_3$: Pr, 29.15; C, 22.37; H, 3.75%. 3) Europium(III) complex, Found: Eu, 30.73; C, 21.80; H, 3.63%. Calcd for $EuC_9H_{18}O_{7.5}S_3$: Eu, 30.74; C, 21.87; H, 3.67%. The lanthanum(III) complex of the ligand has the chemical formula of $ML_3\cdot 4.5H_2O$. Found: La, 25.67; C, 19.81; H, 4.17%. Calcd for $LaC_9H_{24}O_{10.5}S_3$: La, 25.95; C, 20.19; H, 4.52%. The dysprosium(III) and ytterbium(III) complexes have the chemical formula of $ML_3\cdot$

$2H_2O$. 1) Dysprosium(III) complex, Found: Dy, 31.61; C, 21.02; H, 3.68%. Calcd for $DyC_9H_{18}O_8S_3$: Dy, 31.62; C, 21.03; H, 3.73%. 2) Ytterbium(III) complex, Found: Yb, 33.01; C, 20.54; H, 3.57%. Calcd for $YbC_9H_{18}O_8S_3$: Yb, 32.99; C, 20.61; H, 3.65%.

X-Ray Measurements. *X-Ray Powder Pattern*: Their X-ray powder patterns were obtained by the use of the diffractometer, Model DX-GO-F JEOL, using Cu $K\alpha$ radiation, in the range from 6° to 30° in 2θ.

Single-crystal X-Ray Analysis: Almost all single crystals of the title complex obtained were thin-plate ones; the crystal grew poorly in the a axis direction. As it was brittle, a crystal of 0.3 mm × 0.2 mm × 0.3 mm was used for the measurement, without any reshaping process.

The crystallographic data are: $Nd_2C_{18}H_{36}O_{15}S_6$, F.W.= 973.34, triclinic, space group $P\bar{1}$, $Z=2$, $a=12.80(1)$, $b=16.65(1)$, $c=8.659(9)$ Å $\alpha=104.6(1)$, $\beta=93.7(2)$, $\gamma=107.5(1)°$, $D_x=1.892(3)$, $D_m=1.91(2)$ Mg m^{-3}, μ(Mo $K\alpha$)=3.45 mm^{-1}.

The reflections with 2θ less than 55° were collected on a Philips PW 1100 automated four-circle diffractometer with Mo $K\alpha$ radiation, the θ-2θ scan technique being employed. We used 3577 independent reflections with $|F_o|>3\sigma(|F_o|)$ for the structure refinement. The intensities were corrected for Lorentz and polarization factors, but no correction was made for absorption and extinction.

All the calculations were carried out on a HITAC M-200H computer at The Computer Center of The University of Tokyo, using the local version of the UNICS program.[19] The atomic-scattering factors were taken from the tables.[20]

Structure Determination. The structure was solved by the heavy-atom method. The positions of neodymium atoms were deduced from a three-dimensional Patterson map, while all the other non-hydrogen atoms were located by means of successive Fourier syntheses. Their positional and thermal parameters were refined by the block-diagonal least-squares method. The positions of 20 hydrogen atoms were obtained from a difference Fourier synthesis and were also refined. The position of a sulfur atom, S(4), was divided into two, and the probability of the occupancy of each position was approximately assigned from the Fourier map and refined by the full-matrix procedure with regard to the positions of the atoms of the ligand. The final values are 46.7 and 53.3% respectively. Although it is not necessary to divide the position of the methyl carbon atom of each ligand, it has a relatively large amplitude of thermal vibration, just as in the case of some ligands in the hexamer of the propylthioacetato complex of cobalt(II).[15] In the last cycle of the refinement with anisotropic temperature factors for all non-hydrogen atoms, all the parameter shifts were less than one-third of the corresponding standard deviations. The final R value obtained was 0.051.[21]

Other Measurements. The magnetic moments of the solid samples were measured using a Gouy balance at 25 °C.

The simultaneous thermogravimetric (TG) and differential thermal analysis (DTA) were carried out with a Rigaku Denki "Thermoflex" M-8075 using a sample weighing about 10 mg in each operation, at the heating rate of 10 °C min^{-1} in air, using α-alumina as the reference.

The infrared spectra of the samples were obtained by means of a JASCO 403G infrared spectrophotometer, using Nujol and hexachloro-1,3-butadiene mull.

Results and Discussion

The crystal structure of the triaquahexakis(methylthioacetato)dineodymium(III) polymer will now be summarized. The final atomic parameters are listed in Table 1,[22] while the interatomic distances as well as the bond angles are tabulated in Table 2. A projection of the structure along the c axis is shown in Fig. 1, and a perspective drawing of the complex around Nd(1) and Nd(2), together with the numbering scheme of neodymium, oxygen, and carbon atoms, is presented in Fig. 2.

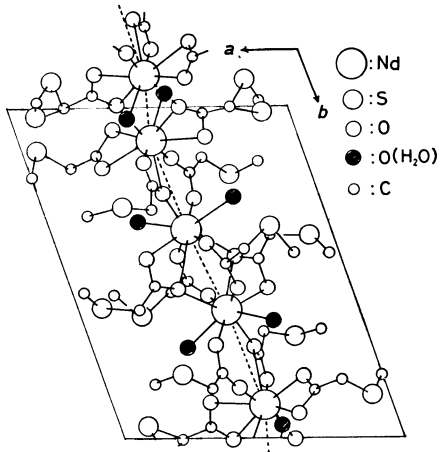

Fig. 1. Crystal packing diagram of $[Nd_2(CH_3SCH_2CO_2)_6(H_2O)_3]_n$ projected along c.

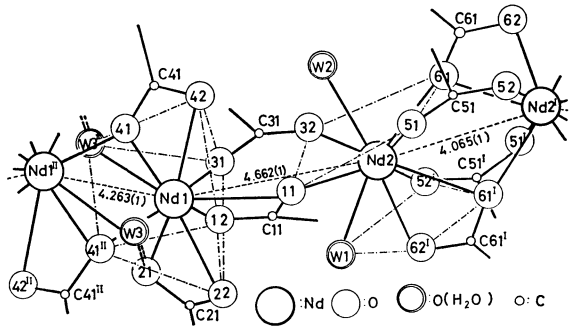

Fig. 2. A perspective drawing of $[Nd_2(CH_3SCH_2CO_2)_6(H_2O)_3]_n$, and the numbering scheme of neodymium, oxygen, and carboxyl carbon atoms. Each coordination polyhedron around neodymium atom is shown by —·—.

The crystal consists of the linear polymer of $[Nd(CH_3SCH_2CO_2)_3(H_2O)$–$Nd(CH_3SCH_2CO_2)_3(H_2O)_2]_n$, nearly parallel to the b axis. Each chain is connected with a hydrogen bond between O(W3) atom and the O(21) atom of the neighbouring chain in the c axis direction. No other bonds were observed between chains except for van der Waals interactions. As is shown in Fig. 1, the coordination number of both the neodymium atoms in the complex is nine. Their coordination polyhedrons are, however, different from each other; that around Nd(1) is a distorted tri-capped trigonal prism, while that around Nd(2) is, rather, a mono-capped tetragonal antiprism, as is shown by the —·— line in Fig. 2. Each water molecule is coordinated to one of the neodymium atoms, and, as is shown above, one of them forms a hydrogen bond with the carboxyl oxygen atom of a neighbouring chain. Each methylthioacetato ligand is coordinated to neodymium atoms through the oxygen

Table 1. Final atomic coordinates ($\times 10^4$ for non-hydrogen atoms, and $\times 10^3$ for hydrogen atoms), equivalent isotropic (for non-hydrogen atoms), and isotropic temperature factors (for hydrogen atoms), with estimated standard deviations in parentheses

Atom	x	y	z	B_{eq}/Å^2 a)
Nd (1)	5352.0 (4)	967.4 (3)	3724.1 (6)	2.2
Nd (2)	5203.7 (4)	3800.4 (3)	4435.4 (6)	2.0
S (1)	7308 (3)	3046 (2)	9564 (3)	5.0
S (2)	9466 (3)	1355 (3)	2249 (5)	6.7
S (3)	2918 (3)	1949 (2)	−1449 (4)	4.9
S (4A)****	1013 (8)	187 (8)	4163 (15)	9.4
S (4B)****	1246 (5)	−745 (4)	3142 (8)	4.9
S (5)	2169 (2)	3611 (2)	7939 (4)	3.8
S (6)	942 (3)	3960 (2)	1506 (4)	4.4
O (11)	5594 (5)	2618 (4)	5456 (7)	2.3
O (12)	5888 (6)	1671 (4)	6639 (8)	3.3
O (21)	6619 (6)	751 (4)	1638 (8)	3.5
O (22)	7277 (5)	1926 (4)	3676 (8)	3.1
O (31)	4822 (7)	1555 (6)	1775 (10)	5.2
O (32)	4408 (7)	2742 (5)	1774 (8)	4.1
O (41)	3918 (5)	23 (4)	5241 (7)	2.7
O (42)	3496 (6)	1000 (4)	4360 (10)	3.7
O (51)	4676 (6)	4200 (4)	7077 (8)	3.0
O (52)	4288 (6)	5438 (4)	7613 (8)	3.5
O (61)	3836 (5)	4503 (4)	4193 (7)	2.8
O (62)	3006 (5)	5375 (4)	3536 (8)	3.0
O (W1)	6879 (6)	3491 (5)	3338 (9)	4.1
O (W2)	3330 (6)	2687 (4)	4626 (8)	3.4
O (W3)	5838 (6)	412 (4)	8248 (8)	3.4
C (11)	6872 (8)	2421 (6)	6709 (11)	2.6
C (12)	6188 (8)	3155 (6)	8315 (11)	2.7
C (13)	8368 (13)	3288 (13)	8340 (23)	8.1
C (21)	7351 (9)	1465 (6)	2266 (13)	3.6
C (22)	8387 (11)	1792 (9)	1565 (17)	5.8
C (23)	9959 (13)	2044 (11)	4316 (19)	6.6
C (31)	4349 (8)	1997 (6)	1156 (12)	2.9
C (32)	3810 (10)	1514 (7)	−594 (13)	4.0
C (33)	1784 (13)	1654 (10)	−393 (27)	8.0
C (41)	3204 (8)	355 (6)	4939 (11)	2.4
C (42)	2015 (10)	−24 (8)	5115 (14)	4.1
C (43)	1247 (16)	−108 (17)	2036 (25)	10.7
C (51)	4199 (8)	4707 (7)	7806 (11)	3.1
C (52)	3478 (8)	4378 (6)	9036 (10)	2.6
C (53)	1507 (12)	4380 (11)	7487 (21)	7.1
C (61)	3033 (7)	4626 (6)	3414 (10)	2.1
C (62)	2139 (9)	3810 (6)	2392 (12)	3.0
C (63)	383 (12)	4417 (10)	3243 (18)	5.9

Atom	x	y	z	B_{iso}/Å^2
H (W11)	716 (8)	300 (6)	368 (11)	3.01 (1)
H (W21)	386 (8)	220 (6)	465 (12)	3.01 (1)
H (W31)	615 (8)	89 (6)	818 (12)	3.01 (1)
H (W32)	605 (8)	66 (6)	947 (12)	3.01 (1)
H (11)	557 (8)	289 (6)	872 (12)	3.01 (1)
H (12)	610 (8)	390 (6)	863 (11)	3.01 (1)
H (13)	851 (8)	404 (6)	780 (12)	2.94 (1)
H (14)	771 (8)	288 (6)	728 (12)	2.93 (1)
H (21)	845 (8)	228 (6)	142 (12)	3.01 (1)
H (22)	800 (8)	173 (6)	27 (11)	3.01 (1)
H (31)	336 (7)	106 (6)	−42 (11)	3.01 (1)
H (33)	187 (8)	103 (6)	−10 (12)	2.93 (1)
H (41)	160 (8)	−14 (6)	594 (12)	3.01 (1)
H (43)	196 (8)	12 (6)	168 (11)	2.93 (1)
H (44)	60 (8)	9 (6)	186 (12)	2.93 (1)
H (51)	337 (8)	480 (6)	1017 (12)	3.01 (1)
H (52)	411 (8)	404 (6)	940 (12)	3.01 (1)
H (53)	206 (8)	491 (6)	692 (11)	2.93 (1)
H (61)	226 (8)	412 (6)	123 (12)	3.01 (1)
H (62)	191 (8)	353 (6)	313 (11)	3.01 (1)

a) The equivalent isotropic temperature factors for non-hydrogen atoms were computed using the following expression: $B_{eq}=(4/3)(B_{11}a^2+B_{22}b^2+B_{33}c^2+B_{12}ab\cos\gamma+B_{13}ac\cos\beta+B_{23}bc\cos\alpha)$. The B_{ij}'s are defined by: $\exp[-(h^2B_{11}+k^2B_{22}+l^2B_{33}+2klB_{23}+2hlB_{13}+2hkB_{12})]$.

**** The probability of the occupancy of each position was 46.7% for S(4A) and 53.3% for S(4B).

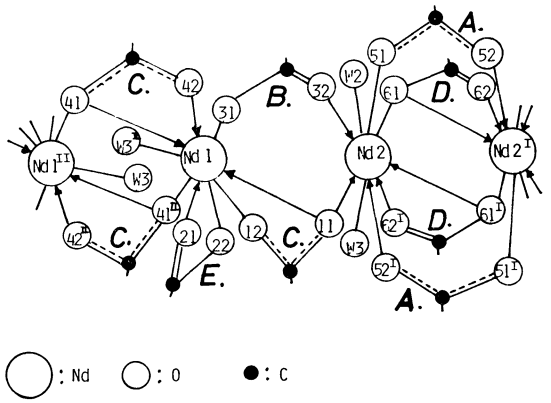

Fig. 3. Schematic presentation of the bonding modes of ligands. The mode of each carboxyl group is presented by *A*—*E*. The Nd–O bond without arrow mark is the shortest one of those from the carboxyl group.

atoms, not through its sulfur atom. As is shown in Fig. 3, there are five kinds of ligands, as considered in terms of their coordination modes; they are tentatively named *A*—*E*-mode ligands.

The *A* and *B* ligands span two neodymium atoms through both the oxygen atoms of a carboxyl group. The C–O distances of *A* ligand are almost the same (C(51)–O(51)=1.256(14), C(51)–O(52)=1.258(14) Å), and the corresponding Nd–O distances are not much different (Nd(2)–O(51)=2.415(7), Nd(2)–O(52^{I})=2.456(9) Å). In the case of the *B* ligand, one C–O is longer than the other one (C(31)–O(31)=1.272(16), C(31)–O(32)=1.198(13) Å), while the Nd–O from the oxygen atom of the shorter C–O is longer than the other one (Nd(2)–O(32)=2.454(8), Nd(1)–O(31)=2.312(10) Å). The *C* and *D* ligands bridge two neodymium atoms by one oxygen atom, and, at the same time, the other oxygen atom of the ligand is coordinated to one of the bridged neodymium at-

TABLE 2. INTERATOMIC DISTANCES AND BOND ANGLES WITH ESTIMATED STANDARD DEVIATIONS IN PARENTHESES

Interatomic distance	l/Å		l/Å
Nd(1)···Nd(2)	4.662(1)	O(22)-C(21)	1.294(13)
Nd(2)···Nd(2^{I})	4.065(1)	C(21)-C(22)	1.503(19)
Nd(1)···Nd(1^{II})	4.263(1)	C(22)-S(2)	1.850(18)
Nd(1)-O(11)	2.691(7)	S(2)-C(23)	1.818(15)
Nd(1)-O(12)	2.452(7)	O(31)-C(31)	1.272(16)
Nd(1)-O(21)	2.536(9)	O(32)-C(31)	1.198(13)
Nd(1)-O(22)	2.512(7)	C(31)-C(32)	1.528(14)
Nd(1)-O(31)	2.312(10)	C(32)-S(3)	1.744(15)
Nd(1)-O(41)	2.681(8)	S(3)-C(33)	1.777(21)
Nd(1)-O(42)	2.488(8)	O(41)-C(41)	1.247(14)
Nd(1)-O(41^{II})	2.441(8)	O(42)-C(41)	1.265(13)
Nd(1)-O($W3^{II}$)	2.468(8)	C(41)-C(42)	1.497(15)
Nd(2)-O(61)	2.405(8)	C(42)-S(4A)	1.651(19)
Nd(2)-O(32)	2.454(8)	C(42)-S(4B)	1.835(12)
Nd(2)-O(11)	2.513(8)	S(4A)-C(43)	1.851(25)
Nd(2)-O(W1)	2.541(9)	S(4B)-C(43)	1.598(30)
Nd(2)-O(51)	2.415(7)	O(51)-C(51)	1.256(14)
Nd(2)-O(W2)	2.599(8)	O(52)-C(51)	1.258(14)
Nd(2)-O(52^{I})	2.456(9)	C(51)-C(52)	1.552(15)
Nd(2)-O(61^{I})	2.633(8)	C(52)-S(5)	1.799(10)
Nd(2)-O(62^{I})	2.568(9)	S(5)-C(53)	1.838(20)
O(11)-C(11)	1.269(13)	O(61)-C(61)	1.289(13)
O(12)-C(11)	1.241(13)	O(62)-C(61)	1.236(12)
C(11)-C(12)	1.538(12)	C(61)-C(62)	1.505(11)
C(12)-S(1)	1.820(12)	C(62)-S(6)	1.782(13)
S(1)-C(13)	1.789(19)	S(6)-C(63)	1.800(16)
O(21)-C(21)	1.236(11)	O(W3)···O(21^{III})	2.894(11)

Bond angle	θ/°		θ/°
Nd(1)···Nd(2)···Nd(2^{I})	171.58(2)	O(W2)-Nd(2)-O(W1)	128.6(2)
Nd(1^{II})···Nd(1)···Nd(2)	137.38(2)	O(W2)-Nd(2)-O(62^{I})	132.1(2)
O(11)-Nd(1)-O(21)	118.3(2)	O(W2)-Nd(2)-O(61^{I})	132.9(2)
O(11)-Nd(1)-O(41)	101.4(2)	O(W2)-Nd(2)-O(52^{I})	131.6(2)
O(21)-Nd(1)-O(41)	139.5(2)	O(11)-Nd(2)-O(51)	82.2(2)
O(11)-Nd(1)-O(12)	50.2(2)	O(51)-Nd(2)-O(61)	73.2(3)
O(11)-Nd(1)-O(22)	72.0(2)	O(61)-Nd(2)-O(32)	90.5(2)
O(11)-Nd(1)-O(31)	77.8(3)	O(32)-Nd(2)-O(11)	90.3(2)
O(11)-Nd(1)-O(42)	72.5(2)	O(W1)-Nd(2)-O(62^{I})	67.8(2)
O(21)-Nd(1)-O(22)	51.0(2)	O(62^{I})-Nd(2)-O(61^{I})	97.1(2)
O(21)-Nd(1)-O(41^{II})	83.1(2)	O(61^{I})-Nd(2)-O(52^{I})	69.6(2)
O(21)-Nd(1)-O(31)	75.8(3)	O(52^{I})-Nd(2)-O(W1)	68.8(3)
O(21)-Nd(1)-O($W3^{II}$)	79.0(2)	O(11)-Nd(2)-O(W1)	70.4(3)
O(41)-Nd(1)-O(12)	71.9(2)	O(11)-Nd(2)-O(62^{I})	76.4(2)
O(41)-Nd(1)-O(41^{II})	67.4(2)	O(51)-Nd(2)-O(62^{I})	72.7(2)
O(41)-Nd(1)-O($W3^{II}$)	70.7(2)	O(51)-Nd(2)-O(61^{I})	70.4(2)
O(41)-Nd(1)-O(42)	49.0(2)	O(61)-Nd(2)-O(61^{I})	72.5(2)
O(12)-Nd(1)-O(42)	82.3(2)	O(61)-Nd(2)-O(52^{I})	76.4(3)
O(41^{II})-Nd(1)-O($W3^{II}$)	83.2(2)	O(32)-Nd(2)-O(52^{I})	72.4(2)
O(22)-Nd(1)-O(31)	84.9(3)	O(32)-Nd(2)-O(W1)	76.8(2)
O(12)-Nd(1)-O(41^{II})	74.7(2)	Nd(1)-O(11)-C(11)	88.1(6)
O(12)-Nd(1)-O(22)	83.0(2)	Nd(1)-O(11)-Nd(2)	127.2(2)
O(22)-Nd(1)-O(41^{II})	91.0(2)	Nd(1)-O(12)-C(11)	100.2(6)
O(42)-Nd(1)-O(31)	79.0(3)	Nd(2)-O(11)-C(11)	144.5(7)
O(42)-Nd(1)-O($W3^{II}$)	79.9(2)	O(11)-C(11)-O(12)	121.5(8)
O(31)-Nd(1)-O($W3^{II}$)	81.4(3)	O(11)-C(11)-C(12)	116.8(9)
O(W2)-Nd(2)-O(11)	71.4(2)	O(12)-C(11)-C(12)	126.6(9)
O(W2)-Nd(2)-O(51)	68.7(2)	C(11)-C(12)-S(1)	109.4(7)
O(W2)-Nd(2)-O(61)	74.1(2)	C(12)-S(1)-C(13)	98.4(7)
O(W2)-Nd(2)-O(32)	70.4(2)	Nd(1)-O(21)-C(21)	95.1(6)

Table 2. Continued

Bond angle	θ/°		θ/°
Nd(1)-O(22)-C(21)	94.7(6)	S(4A)-C(43)-S(4B)	58.6(9)
O(21)-C(21)-O(22)	118.4(10)	S(4A)-C(42)-S(4B)	58.2(6)
O(21)-C(21)-C(22)	123.7(10)	Nd(1)-O(41)-Nd(1^{III})	112.6(3)
O(22)-C(21)-C(22)	117.5(9)	Nd(1^{III})-O(41)-C(41)	155.6(7)
C(21)-C(22)-S(2)	109.4(11)	Nd(2)-O(51)-C(51)	137.5(7)
C(22)-S(2)-C(23)	103.2(7)	Nd(2^{I})-O(52)-C(51)	96.7(6)
Nd(1)-O(31)-C(31)	157.4(8)	O(51)-C(51)-O(52)	126.8(10)
Nd(2)-O(32)-C(31)	134.7(7)	O(51)-C(51)-C(52)	115.8(9)
O(31)-C(31)-O(32)	125.4(10)	O(52)-C(51)-C(52)	117.4(9)
O(31)-C(31)-C(32)	112.1(9)	C(51)-C(52)-S(5)	108.3(6)
O(32)-C(31)-C(32)	122.0(10)	C(52)-S(5)-C(53)	99.8(7)
C(31)-C(32)-S(3)	116.4(8)	Nd(2)-O(61)-C(61)	153.4(7)
C(32)-S(3)-C(33)	99.5(8)	Nd(2^{I})-O(61)-C(61)	92.3(6)
Nd(1)-O(41)-C(41)	91.7(6)	Nd(2^{I})-O(62)-C(61)	96.7(6)
Nd(1)-O(42)-C(41)	100.6(6)	Nd(2)-O(61)-Nd(2^{I})	107.5(2)
O(41)-C(41)-O(42)	117.7(9)	O(61)-C(61)-O(62)	121.0(7)
O(41)-C(41)-C(42)	122.6(9)	O(61)-C(61)-C(62)	116.8(8)
O(42)-C(41)-C(42)	119.6(10)	O(62)-C(61)-C(62)	123.0(8)
C(41)-C(42)-S(4A)	122.0(11)	C(61)-C(62)-S(6)	116.7(8)
C(41)-C(42)-S(4B)	108.6(8)	C(62)-S(6)-C(63)	102.7(7)
C(42)-S(4A)-C(43)	90.9(24)	O(12)···O(W3)···O(21^{III})	126.2(3)
C(42)-S(4B)-C(43)	97.9(28)		

Key to symmetry operations: I. $1.0-x$, $1.0-y$, $1.0-z$; II. $1.0-x$, $-y$, $1.0-z$; III. x, y, $1.0+z$

oms. The two C–O distances of the *D* ligand are different from each other (C(61)–O(61)=1.289(13), C(61)–O(62)=1.236(12) Å); the difference is a little larger than those of *C* ligands (C(11)–O(11)=1.269(13), C(11)–O(12)=1.241(13) Å; C(41)–O(41)=1.247(14), C(41)–O(42)=1.265(13) Å). In the *D* ligand, the oxygen atom of the longer C–O, O(61), forms the bridge, and both the bridging Nd–O distances are a little shorter than the one-oxygen-atom-bridging Nd–O distances of the *C* ligands (Nd(2)–O(61)=2.405(8), and Nd(2^{I})–O(61)=2.633(8) Å, *vs.* Nd(2)–O(11)=2.513(8), Nd(1)–O(11)=2.691(7); Nd(1^{II})–O(41)=2.441(8), Nd(1)–O(41)=2.681(8) Å). The Nd–O distance of the non-bridged oxygen atom of the *D* ligand (Nd(2)–O(62^{I})=2.568(9) Å) is longer than the corresponding Nd–O distance of the *C* ligands (Nd(1)–O(12)=2.452(7), Nd(1)–O(42)=2.488(8) Å). The *E* ligand forms a four-membered chelate ring by being coordinated its two oxygen atoms to the same neodymium atom. Its two C–O distances are different from each other (C(21)–O(21)=1.236(11), C(21)–O(22)=1.294(13) Å).

Consequently, as is shown in Fig. 3, there are three kinds of bridging modes between neodymium atoms in a polymer chain; *i.e.* Nd(1^{II})···Nd(1) (4.236(1) Å), where two *C* bridges exist; Nd(1)···Nd(2) (4.662(1) Å), connected with one each of the *B* and *C* bridges, and Nd(2)···Nd(2^{I}) (4.065(1) Å), with two each of the *A* and *D* bridges. From these Nd···Nd distances, the *B* bridge is found to be weaker than the *C* one in the ability of bridging neodymium atoms, while Nd(2)···Nd(2^{I}) is the shortest because of the existence of four bridges between them. This type of complicated polymeric linear-chain structure, including many types of coordination modes of the ligands, has not previously known.

Each complex has a normal magnetic moment as the metal salt of each elements,[23] and no metal-metal interaction was found. The found magnetic moments of the methylthioacetato complexes of lanthanum(III), diamagnetic; and cerium(III) was 2.4_2; praseodymium(III), 3.5_8; neodymium(III), 3.5_4; europium(III), 3.3_8; dysprosium(III), 10.6_5; ytterbium(III), 4.4_4 BM,*** at 25 °C.

The powder X-ray diffraction patterns of synthesized methylthioacetato complexes of lanthanoid elements are shown in Fig. 4. They are divided into three groups according to their patterns; the grouping is the same as that when they are divided by their chemical composition: *i.e.*, Group 1 (lanthanum(III) complex $ML_3 \cdot 4.5H_2O$), Group 2 (cerium(III), praseodymium(III), neodymium(III) and europium(III) complexes; $ML_3 \cdot 1.5H_2O$), and Group 3 (dysprosium(III) and ytterbium(III) complexes; $ML_3 \cdot 2H_2O$). The same grouping was also observed with regard to their infrared absorption spectra, as well as with regard to TG and DTA, as will be shown later. The complexes belonging to the same group give similar powder X-ray diffraction patterns, and the intensity ratios of their main peaks are nearly the same. Therefore, they are found to be isomorphous with each other, and the structure given to the neodymium(III) complex can be expected to be the same as those of light lanthanoid elements, although exceptionally, lanthanum(III) makes a different type of hydrate. On the other hand, as Group 3 elements make the $ML_3 \cdot 2H_2O$ type of hydrated complexes, they are likely to be like those of heavy lanthanoid elements. In fact, this kind of difference in hydration number and this type of difference in structure between the complexes of light

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

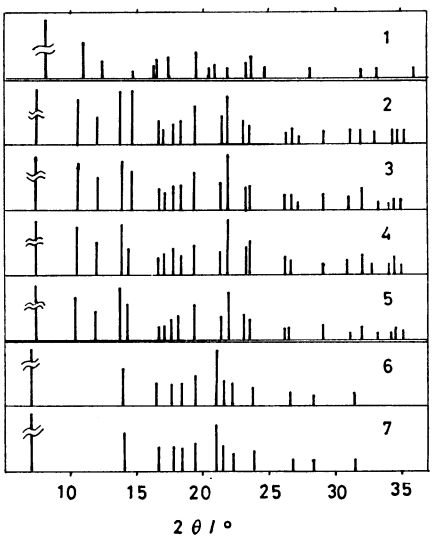

Fig. 4. X-Ray powder patterns of methylthioacetato complexes of lanthanoid elements (Cu $K\alpha$).
1: $LaL_3 \cdot 4.5\ H_2O$, 2: $CeL_3 \cdot 1.5\ H_2O$, 3: $PrL_3 \cdot 1.5\ H_2O$, 4: $NdL_3 \cdot 1.5\ H_2O$, 5: $EuL_3 \cdot 1.5\ H_2O$, 6: $DyL_3 \cdot 2\ H_2O$, 7: $YbL_3 \cdot 2\ H_2O$ (HL=methylthioacetic acid).

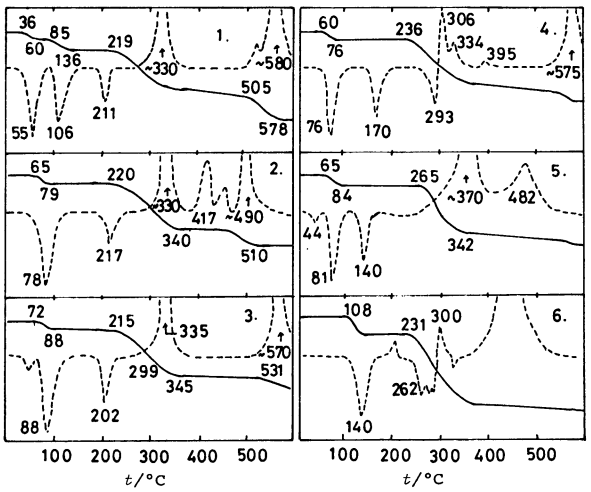

Fig. 5. TG(——) and DTA(- - -) curves of the methylthioacetato complexes.
1: $LaL_3 \cdot 4.5\ H_2O$, 2: $CeL_3 \cdot 1.5\ H_2O$, 3: $NdL_3 \cdot 1.5\ H_2O$, 4: $DyL_3 \cdot 2\ H_2O$, 5: $YbL_3 \cdot 2\ H_2O$, 6: $CoL_2 \cdot 2\ H_2O$. (HL = methylthioacetic acid) (10 °C min^{-1})
Mass loss of TG was taken downwards, and the exothermal change of DTA was taken upwards.

and heavy lanthanoid elements are often observed; for example, the hydrated oxalates of the light lanthanoid metals are commonly decahydrates, while the heavy lanthanoid metals make stable hexa- or heptahydrates.[23]

The results of the simultaneous TG and DTA of these complexes, together with that of diaquabis(methylthioacetato)cobalt(II), are shown in Fig. 5. As is shown by Pattern 3 of the figure, the dehydration of the neodymium(III) complex is in one step, even in the each coordination mode of O(W1) and O(W2) is different from that of O(W3). It is characteristic that the dehydration occurs at a low temperature;

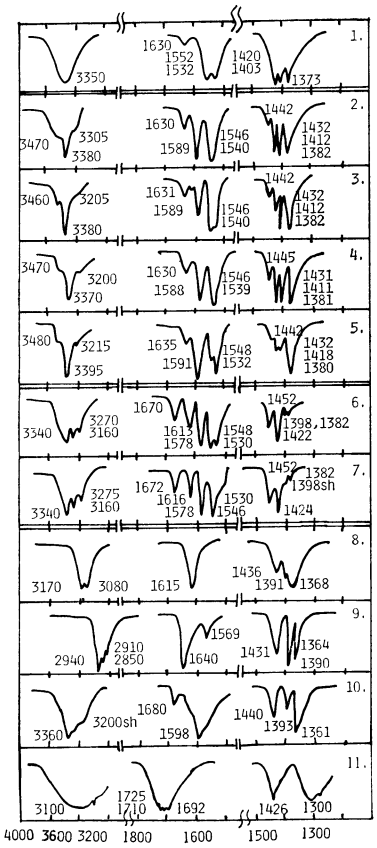

Fig. 6. Infrared absorption spectra of the methylthioacetato complexes and the related compounds.
1: $LaL_3 \cdot 4.5\ H_2O$, 2: $CeL_3 \cdot 1.5\ H_2O$, 3: $PrL_3 \cdot 1.5\ H_2O$, 4: $NdL_3 \cdot 1.5\ H_2O$, 5: $EuL_3 \cdot 1.5\ H_2O$, 6: $DyL_3 \cdot 2\ H_2O$, 7: $YbL_3 \cdot 2\ H_2O$, 8: $CoL_2 \cdot 2\ H_2O$, 9: bis(propylthioacetato)cobalt(II) hexamer-xylene, 10: bis(isopropylthioacetato)copper(II) dihydrate (violet isomer), 11: HL (HL=methylthioacetic acid).

lower than that of the corresponding hydrated complexes of cobalt(II) and of other 3d elements (*cf.* Pattern 6). A drastic mass loss due to the decomposition of the ligand occurs at about 200—300 °C, and the temperature is about the same as that of 3d-complexes.

The hydrated methylthioacetato complexes of the other Group 2 elements show almost the same TG and DTA patterns as are shown by Patterns 2 and 3 in the figure.

Although the general features of the TG and DTA curves of the other-group complexes are nearly the same, and although the low dehydration temperature is characteristic of all of them, there are some differences between them, as will be shown below. The lanthanum(III) complex (Group 1) gives two steps of dehydration, as is shown in Pattern 1 of the figure, and the Group 3 complexes give an endothermic peak of DTA, due to the isomerization and not the melting, between the dehydration and the ligand degradation temperatures, when the complexes are kept in the solid state (see Patterns 4 and 5).

Their infrared absorption spectra of the ν(OH), ν_{as}(COO), and ν_s(COO) regions are shown in Fig. 6, together with the maximum wave numbers of the peaks. The corresponding charts of some related com-

plexes and of methylthioacetic acid are also shown. These spectra, too, are divided into Groups 1, 2, and 3 in terms of their general features, as well as in terms of the wave numbers of the split peaks in the range, as is shown in the figure. This splitting of the peak of ν_{as}(COO) and of ν_{s}(COO) is probably due to the existence of multi-modes of the coordination of the carboxyl groups, although the assignment of each splitting peak is difficult. The ν_{as}(COO) peak of the methylthioacetato complexes of lanthanoid elements appears in rather a little lower wave number region than that of the common 3d-metal complexes.[24] This is probably due to the "hard" character of lanthanoid elements, which makes the coordination bond more ionic. The bridging of the carboxyl group in these complexes may be another reason.

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