Lanthanide(III) Methylsquarates: Synthesis and X-ray Structures

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Reaction of 3-methyl-4-hydroxycyclobut-3-ene-1,2-dione (methylsquarate) with $LaCl_3{\cdot}7H_2O$ and $M(NO_3)_3{\cdot}xH_2O$ (M = Eu, Gd, and Tb) in alcoholic solutions afforded the polymeric complexes $\{La[\mu_3\text{-}(CH_3C_4O_3)][(H_2O)_6][Cl_2]{\cdot}H_2O\}_n$ (**1**), $\{Eu[\mu\text{-}(CH_3C_4O_3)_3][(H_2O)_2]\}_n$ (**3**), $\{Gd[\mu\text{-}(CH_3C_4O_3)_2][(H_2O)_4][NO_3]{\cdot}H_2O\}_n$ (**4**), and $\{Tb[\mu\text{-}(CH_3C_4O_3)_2][(H_2O)_4][NO_3]{\cdot}H_2O\}_n$ (**5**), respectively and with $La(NO_3)_3{\cdot}6H_2O$, the monomer $La(CH_3C_4O_3)_3(H_2O)_6{\cdot}H_2O$ (**2**). Complex **1** crystallizes in the orthorhombic space group $Pca2_1$, with $a = 13.239(2)$ Å, $b = 7.836(1)$ Å, $c = 14.209(2)$ Å, and $Z = 4$. The lanthanum atom is nine-coordinate adopting a monocapped square antiprismatic geometry, being bonded to three μ_3-bridging methylsquarate and six pendant aqua ligands and forming cationic polymer sheets which are intercalated by chloride ions and water of crystallization. Complex **3** is a 3-dimensional neutral network polymer in which the methylsquarate ligands are μ-1,3-bridging and the europium atoms adopt a bicapped trigonal prismatic geometry. **3** crystallizes in the orthorhombic space group *Pbna* with $a = 8.713(1)$ Å, $b = 13.115(1)$ Å, $c = 15.253(1)$ Å, and Z = 4. The gadolinium and terbium complexes, **4** and **5,** are isomorphous cationic sheet polymers with the methylsquarate ligand again adopting a μ-1,3-bridging role and with the metal having square antiprismatic geometry. Adjacent sheets are arranged so as to form channels within which the nitrate anions and water molecules are located. Complex **4** crystallizes in the monoclinic space group $P2_1/c$, with $a = 14.543(2)$ Å, $b = 8.396(1)$ Å, $c = 15.251(2)$ Å, $\beta = 109.37(1)°$, and $Z = 4$. The monomer **2** crystallizes in the space group $P2_1/c$ with $a = 10.438(2)$ Å, $b = 14.813(2)$ Å, $c = 15.151(2)$ Å, $\beta = 108.21(1)°$, and $Z = 4$. The lanthanum atom is nine-coordinate adopting a monocapped square antiprismatic geometry with each metal atom being coordinated to three methylsquarate and six aqua ligands. In all of the polymeric species there is a pattern of delocalization which extends to include adjacent metal centers.

Introduction

As part of our continuing research exploring the potential for forming polymeric complexes with high coordination number transition metals and lanthanides, possessing structural characteristics similar to those of the lead(II) dialkylaminosquarates,[1] we have attempted the syntheses of Ln complexes (Ln = La, Eu, Gd, and Tb) with similar monosubstituted squarate ligands.[2] We rationalized that in such complexes the diffuse nature of the d and f orbitals in the transition and lanthanide metals, together with the delocalized bridging ligands functioning as suitable conduits, would facilitate electron transfer along the polymer chains. However, when dialkylaminosquarates[2] were used, these syntheses resulted in the hydrolysis of the substituents, whereas diphenylaminosquarate produced a mononuclear lanthanum species and isomorphous dimers with europium, gadolinium, and terbium.[3] Since no polymers were obtained with either the dialkylaminosquarates or diphenylaminosquarate, we decided to use an alternative monosubstituted ligand with a less bulky substituent (methylsquarate) in order to minimize any steric effects that may have inhibited polymer formation with the lanthanides. It should be noted, however, that several polymeric diphenylaminosquarate complexes of first-row transition metals, with coordination number six and consequently less steric hindrance (ligand−metal−ligand angles ca. 90° vs ligand−metal−ligand ca. 70° for the eight-coordinate lanthanides), have been synthesized.[4] Here we describe the syntheses of four polymeric lanthanide methylsquarates.

Experimental Section

Preparation of the Ligand. The 3-methyl-4-hydroxycyclobut-3-ene-1,2-dione (methylsquarate) ligand was prepared according to the method of Liebeskind et al.[5]

Preparation of the Complexes. $\{\mathbf{La[\mu_3\text{-}(CH_3C_4O_3)][(H_2O)_6][Cl_2]{\cdot}H_2O\}_n}$ **(1).** Twenty milliliters of a solution of methylsquarate (0.10 g, 7.8×10^{-4} mol) in propan-1-ol was added to an equimolar solution of $LaCl_3{\cdot}7H_2O$ (0.30 g, 7.8×10^{-4} mol) in the same solvent and the mixture allowed to stand at ambient temperature until crystallization was complete.

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$\{La[\mu_3\text{-}(CH_3C_4O_3)][(H_2O)_6][Cl_2]\cdot H_2O\}_n$: colorless blocks. Yield: 0.18 g, 50%. Anal. Calcd for $C_5H_{17}Cl_2LaO_{10}$: C, 13.4; H, 3.8; Cl, 15.9; La, 31.1. Found: C, 13.4; H, 3.9, Cl, 15.9; La, 31.1.

$La(CH_3C_4O_3)_3(H_2O)_6\cdot H_2O$ (2). This complex was synthesized using a procedure similar to that of **1** except that an equimolar amount of $La(NO_3)_3\cdot 6H_2O$ was used in place of $LaCl_3\cdot 7H_2O$.

$La(CH_3C_4O_3)_3(H_2O)_6\cdot H_2O$: colorless blocks. Yield: 0.050 g, 13%†.[11] Anal. Calcd for $C_{15}H_{23}LaO_{16}$: C, 30.1; H, 3.9; La, 23.2. Found: C, 29.6; H, 3.7; La, 23.1.

$\{Eu[\mu\text{-}(CH_3C_4O_3)_3][(H_2O)_2]\}_n$ (3). Fifty milliliters of an ethanolic solution of methylsquarate (0.10 g, 8.92×10^{-4} mol) was added to an equal volume of an equimolar solution of $Eu(NO_3)_3\cdot 5H_2O$ (0.40 g, 8.92×10^{-4} mol) in the same solvent. The mixture was then filtered and left to evaporate slowly at room temperature until crystallization was complete.

$\{Eu[\mu\text{-}(CH_3C_4O_3)_3][(H_2O)_2]\}_n$: colorless plates. Yield: 0.042 g, 18%†.[11] Anal. Calcd for $C_{15}H_{13}EuO_{11}$: C, 34.6; H, 2.5; Eu, 29.2. Found: C, 34.2; H, 2.6; Eu, 27.6.

$\{Gd[\mu\text{-}(CH_3C_4O_3)_2][(H_2O)_4][NO_3]\cdot H_2O\}_n$ (4). This complex was prepared using the same conditions as for $\{Eu[\mu\text{-}(CH_3C_4O_3)_3(H_2O)_2]\}_n$.

$\{Gd[\mu\text{-}(CH_3C_4O_3)_2][(H_2O)_4][NO_3]\cdot H_2O\}_n$: yield 0.10 g, 22%†.[11] Colorless platy needles. Anal. Calcd for $C_{10}H_{16}NGdO_{14}$: C, 22.6; H, 3.0; N, 2.6; Gd, 29.6. Found: C, 22.4; H, 2.9; N, 2.5; Gd, 29.4.

$\{Tb[\mu\text{-}(CH_3C_4O_3)_2][(H_2O)_4][NO_3]\cdot H_2O\}_n$ (5). A solution of methylsquarate (0.03 g, 2.94×10^{-4} mol) in 60 mL of propan-1-ol was mixed with an equal volume of a solution of $Tb(NO_3)_3\cdot 5H_2O$ (0.18 g, 4.02×10^{-4} mol) in the same solvent. The mixture was then left to evaporate slowly until crystal formation was complete: colorless plates. Yield: 0.089 g, 18%†.[11] Anal. Calcd for $C_{10}H_{16}NTbO_{14}$: C, 21.1; H, 2.5; N, 2.4; Tb, 27.9. Found: C, 20.0; H, 2.9; N, 2.9; Tb, 28.8.

Elemental Analyses. C, H, N, Cl and metal analyses were performed by MEDAC Limited, Brunel Science Centre, Egham, Surrey, U.K.

Crystallographic Analyses. Table 1 provides a summary of the crystallographic data for compounds **1**−**5**. Data were collected on Siemens P4/PC diffractometers using graphite-monochromated Mo Kα (for compounds **1**, **2**, **4**, and **5**) and Cu Kα (for compound **3**) radiation. In each case the data were corrected for Lorentz and polarization factors and for absorption. The structures were solved by direct methods, and the non-hydrogen atoms were refined anisotropically using full matrix least-squares based on F^2. In all five structures the C−H hydrogen atoms were placed in calculated positions, assigned isotropic thermal parameters, $U(H) = 1.2U_{eq}(C)$ [$U(H) = 1.5U_{eq}(C{-}Me)$], and allowed to ride on their parent atoms. The O−H hydrogen atoms for compounds **2**, **4**, and **5** were located from ΔF maps and refined isotropically subject to an O−H distance constraint (for compounds **1** and **3** the O−H hydrogen atoms could not be located). Due to instabilities in the anisotropic refinement of **1**, some of the light atoms had their relative thermal vibrations lightly restrained. In **3**, where there is disorder of one of the methylsquarate ligands about an inversion center, the bond lengths of the consequently "overlapping" methyl and carbonyl-oxygen atoms were constrained to ideal values. The polarity of **1** was determined by a combination of R-factor tests [$R_1^+ = 0.0382$, $R_1^- = 0.0395$] and by use of the Flack parameter [$x^+ = -0.03(6)$]. All computations were carried out using the SHELXTL PC program system.[6] CCDC 156772, 156773, 147244, 156774, and 156775 for **1**−**5**, respectively.

Results and Discussion

Lanthanum Methylsquarate Chloride $\{La[\mu_3\text{-}(CH_3C_4O_3)][(H_2O)_6][Cl_2]\cdot H_2O\}_n$ (1). The X-ray analysis of the complex formed by the reaction of $LaCl_3\cdot 7H_2O$ with methylsquarate reveals the formation of an ionic sheet polymer of constitution $\{La[\mu_3\text{-}(CH_3C_4O_3)][(H_2O)_6][Cl_2]\cdot H_2O\}_n$ (Figure 1). The geometry at lanthanum is distorted monocapped square antiprismatic (Figure 2) with each lanthanum atom being coordinated to six aqua ligands and to a different oxygen atom from each of the three symmetry-related methylsquarate ligands (Figure 3); the capping atom is one of the methylsquarate oxygens, O(3A). The La−O distances are in the range 2.486(11) to 2.595(11) Å, and there is no obvious differentiation between the La−O(aqua) and La−O(methylsquarate) bond lengths (Table 2). The methylsquarate ligands are trismonodentate and serve to bridge adjacent lanthanum centers to form the sheet network depicted in Figure 1. The pattern of bonding within the methylsquarate ligands, which is very similar to that observed in the related

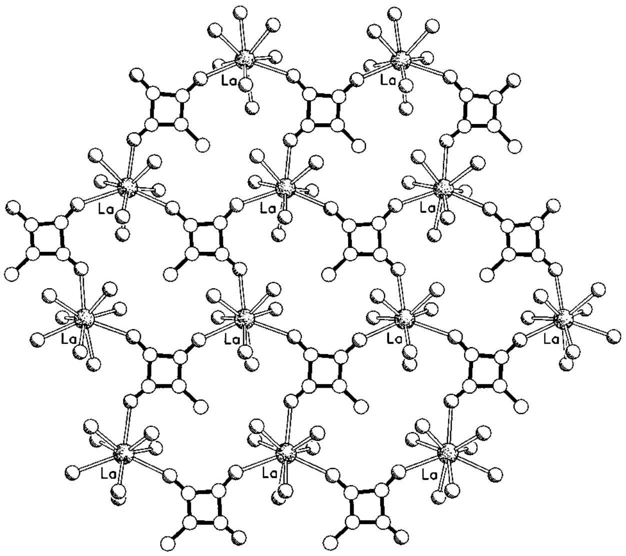

Figure 1. Part of one of the polymeric cationic sheets present in the structure of $\{La[\mu_3\text{-}(CH_3C_4O_3)][(H_2O)_6][Cl_2]\cdot H_2O\}_n$ (**1**).

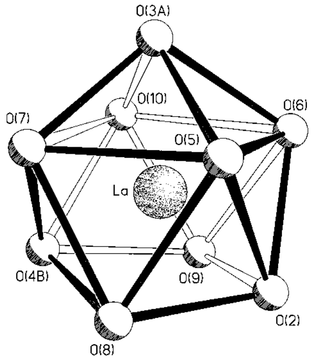

Figure 2. The monocapped square antiprismatic geometry of the lanthanum coordination sphere of **1**.

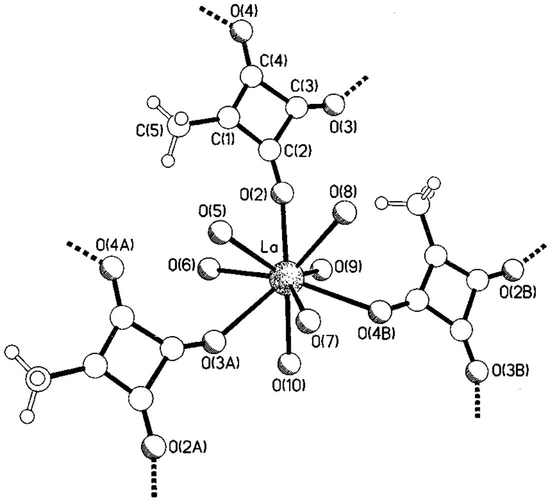

Figure 3. The lanthanum environment in **1** showing the atomic numbering scheme.

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(6) *SHELXTL PC*, version 5.03; Siemens Analytical X-Ray Instruments, Inc.: Madison, WI, 1994.

Table 1. Crystallographic Data for Compounds **1**−**5**

data	**1**	**2**	**3**	**4**	**5**
chem form	$C_5H_{17}O_{10}Cl_2La$	$C_{15}H_{23}O_{16}La$	$C_{15}H_{13}O_{11}Eu$	$C_{10}H_{16}NO_{14}Gd$	$C_{10}H_{16}NO_{14}Tb$
fw	447.0	598.24	521.2	531.5	533.2
space group	$Pca2_1$ (No. 29)	$P2_1/c$ (No. 14)	$Pbna$ (No. 60)	$P2_1/c$ (No. 14)	$P2_1/c$ (No. 14)
T (°C)	−100	20	20	20	20
a (Å)	13.239(2)	10.438(2)	8.713(1)	14.543(2)	14.574(2)
b (Å)	7.836(1)	14.813(2)	13.115(1)	8.396(1)	8.397(1)
c (Å)	14.209(2)	15.151(2)	15.253(1)	15.251(2)	15.272(2)
β (deg)		108.21(1)		109.37(1)	109.43(1)
V (Å^3)	1474.0(3)	2225.1(6)	1742.9(2)	1756.9(4)	1762.4(4)
Z	4	4	4[a]	4	4
ρ_{calcd} (g cm^{-3})	2.014	1.786	1.986	2.009	2.009
λ (Å)	0.71073	0.71073	1.54178	0.71073	0.71073
μ (cm^{-1})	33.0	20.0	263	38.5	40.9
$R1$[b]	0.038	0.042	0.047	0.033	0.033
$wR2$[c]	0.092	0.090	0.095	0.073	0.074

[a] The molecule has crystallographic C_2 symmetry. [b] $R1 = \sum||F_o| - |F_c||/\sum|F_o|$. [c] $wR2 = \{\sum[w(F_o^2 - F_c^2)^2]/\sum[w(F_o^2)^2]\}^{1/2}$; $w^{-1} = \sigma^2(F_o^2) + (aP)^2 + bP$.

Table 2. Selected Bond Lengths (Å) and Angles (deg) for **1**

La−O(2)	2.486(11)	La−O(3A)	2.595(11)
La−O(4B)	2.568(9)	La−O(5)	2.536(10)
La−O(6)	2.522(11)	La−O(7)	2.551(10)
La−O(8)	2.566(11)	La−O(9)	2.582(12)
La−O(10)	2.573(12)		
O(2)−La−O(6)	69.6(3)	O(2)−La−O(5)	78.1(3)
O(6)−La−O(5)	76.1(4)	O(2)−La−O(7)	138.0(4)
O(6)−La−O(7)	134.8(3)	O(5)−La−O(7)	77.6(3)
O(2)−La−O(8)	68.2(4)	O(6)−La−O(8)	133.3(4)
O(5)−La−O(8)	76.5(4)	O(7)−La−O(8)	73.1(4)
O(2)−La−O(4B)	111.0(3)	O(6)−La−O(4B)	143.7(4)
O(5)−La−O(4B)	140.2(3)	O(7)−La−O(4B)	70.4(3)
O(8)−La−O(4B)	72.0(3)	O(2)−La−O(10)	130.4(4)
O(6)−La−O(10)	82.0(4)	O(5)−La−O(10)	134.0(3)
O(7)−La−O(10)	90.7(4)	O(8)−La−O(10)	142.3(4)
O(4B)−La−O(10)	70.5(3)	O(2)−La−O(9)	64.6(3)
O(6)−La−O(9)	77.2(4)	O(5)−La−O(9)	139.7(4)
O(7)−La−O(9)	141.2(3)	O(8)−La−O(9)	101.5(4)
O(4B)−La−O(9)	71.5(3)	O(10)−La−O(9)	70.1(4)
O(2)−La−O(3A)	132.1(3)	O(6)−La−O(3A)	69.7(3)
O(5)−La−O(3A)	68.6(3)	O(7)−La−O(3A)	66.7(3)
O(8)−La−O(3A)	131.0(4)	O(4B)−La−O(3A)	116.7(3)
O(10)−La−O(3A)	65.9(3)	O(9)−La−O(3A)	127.4(4)
C(2)−O(2)−La	158.2(10)	C(3)−O(3)−La′	147.2(9)
C(4)−O(4)−La″	132.4(9)		

ionic polymers $\{M[\mu\text{-}(CH_3C_4O_3)][(H_2O)_4]^+\}_n$ (M = Co, Ni),[7a] indicates delocalization that extends from O(2) to O(4) via C(1), though in the present structure (due to the dominance of the lanthanum atom) the error margins are very much higher. There is no clear-cut evidence for the extension of this delocalization to include the M−O bond as was apparent in the related cobalt and nickel polymers[7a] (vide supra). It is interesting to note, however, that there is a retention of formal single bond character for C(2)−C(3) and C(3)−C(4) despite the adoption of a trismonodentate coordination mode. There are marked departures from trigonal geometry at each of the coordinated oxygen atoms, the La−O−C angles being 158.2(10)°, 147.2(9)°, and 132.4(9)° at O(2), O(3), and O(4), respectively.

The two chloride anions and the included solvent water molecule form a hydrogen-bonded intercalated layer between the cationic polymer sheets. The anionic and cationic components are linked via hydrogen bonds between the aqua ligands and the included water molecule (Figure 4). Although the positions of the O−H hydrogen atoms could not be located, the internuclear distances, which for the O···Cl contacts range between 3.09 and 3.31 Å and for the O···O contacts between 2.78 and 2.81 Å, are clearly indicative of hydrogen-bonding interactions.

Lanthanum Methylsquarate $La(CH_3C_4O_3)_3(H_2O)_6{\cdot}H_2O$ (2). In contrast to the polymeric structure formed when the complex was synthesized using $LaCl_3{\cdot}7H_2O$, that formed using $La(NO_3)_3{\cdot}6H_2O$ results in a hydrated monomer (Figure 5). The lanthanum center is coordinated to three independent methylsquarate and six aqua ligands in a slightly distorted monocapped square antiprismatic geometry, the aqua ligand O(10) occupying the capping position. The La−O distances are in the range 2.517(5)−2.629(5) Å showing no differentiation in the bond lengths to aqua compared to methylsquarate (Table 3). A notable difference between the monomeric and polymeric structures is that, in the monomer, all three methylsquarate ligands are coordinated via the oxygen atom oriented cis to their methyl substituents cf. two cis and one trans. The pattern of bonding in all three methylsquarate ligands is, within statistical significance, the same, comprising two short and two long C−C bonds, the two short bonds being those immediately adjacent to the methyl substituents. The Δ(C−C) [ca.0.09 Å] is the same as in the polymer and comparable with that observed in the first row transition metal methylsquarate complexes.[7a]

The conformation of the complex is to some degree controlled by a pair of intramolecular O−H···O hydrogen bonds (**a** and **b**) between the aqua ligands O(9) and O(10) and the ketonic oxygen atoms O(2) and O(2″), respectively. The monomers are assembled via a complex pattern of O−H···O hydrogen bonds involving not only the aqua ligands but also the ketonic oxygen atoms and the included water molecule, forming a 3-dimensional network. Within this network, there are also π−π stacking interactions involving the C_4-cycles of all three methylsquarate ligands. Ring **A** of one molecule (Figure 5) is stacked with ring **C** of another (mean-interplanar and centroid···centroid separations 3.41and 3.66 Å, rings inclined by 1°), which in turn is stacked with ring **B** of a third molecule (centroid···centroid separation, 3.71 Å, rings inclined by 18°).

Europium(III) Methylsquarate $\{Eu[\mu\text{-}(CH_3C_4O_3)_3][(H_2O)_2]\}_n$ (3). Single-crystal X-ray analysis revealed that **3**, the product of the reaction between $Eu(NO_3)_3{\cdot}5H_2O$ and methylsquarate, is a neutral network polymer, the repeat unit of which is depicted in Figure 6. In this network each europium atom is coordinated to six methylsquarate groups and two aqua

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(7) (a) Alleyne, B. D.; Hosein, H.-A.; Jaggernauth, H.; Hall, L. A.; White, A. J. P.; Williams, D. J. *Inorg. Chem.* **1999**, *38*, 2416. (b) Hosein, H.-A.; Jaggernauth, H.; Alleyne, B. D.; Hall, L. A.; White, A. J. P.; Williams, D. J. *Inorg. Chem.* **1999**, *38*, 3716. (c) Alleyne, B. D.; Williams, A.; Hosein, H.-A.; Jaggernauth, H.; Hall, L. A.; Foxman, B. *Inorg. Chim. Acta*, in press.

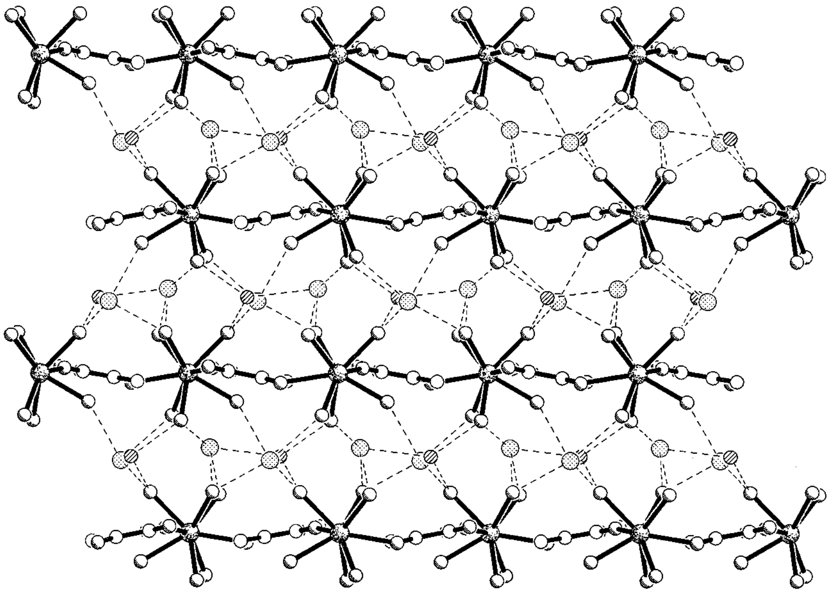

Figure 4. View down the crystallographic *b* direction of the cross-linking of the polymeric sheets via the intercalated chloride anions and included water molecules in **1**. The broken bonds indicate potential hydrogen-bonding interactions.

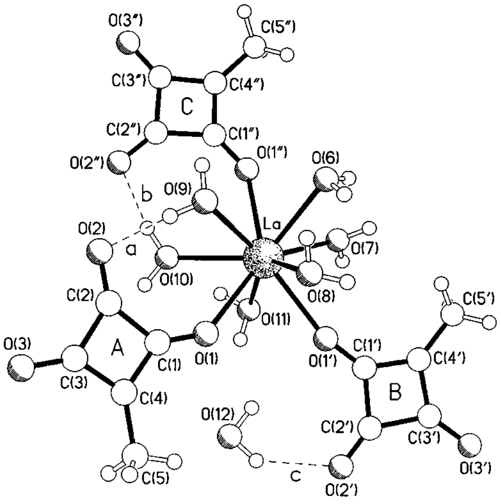

Figure 5. The coordination environment of the La center in the structure of **2**. The hydrogen-bonding geometries are O···O, H···O (Å), O−H···O (deg) (**a**) 2.76, 1.86, 175; (**b**) 2.74, 1.85, 168; (**c**) 2.88, 2.11, 142.

ligands (Figure 7) in a severely distorted bicapped trigonal prismatic geometry (Figure 8) with O(1) and O(1A) as the capping atoms. The Eu−O(methylsquarate) distances, which are in the range 2.340(6)−2.389(6) Å (Table 4), are all significantly shorter than those to the aqua ligands [2.493(6) Å]. We speculate that the marked difference in the Eu−O bond distances to the aqua ligand cf. those to the methylsquarate units may reflect an extension of the pattern of delocalization within the methylsquarate ligand to include the lanthanide center, a feature that we have observed in some first row transition metal complexes with the same ligand.[7a] The europium atom is positioned on a crystallographic C_2 axis; one of the independent methylsquarate ligands **A** [C(1) to C(5)] lies in a general position whereas the other **B** [C(6) to C(8)] is positioned about an inversion center and hence is disordered. The relative positions of the C(8)-methyl and O(8)-carbonyl oxygen atoms are thus indeterminate (i.e., they virtually overlap by symmetry). Each methylsquarate ligand is coordinated μ-1,3 and bridges the adjacent europium centers of the contiguous 3-dimensional network (Figure 6). The bonding in the unique ordered methylsquarate ligand again shows a pattern of delocalization that extends from O(2) via C(1) to O(4), the C(2)−C(3) and C(3)−C(4) bonds both retaining their formal single-bond character. All three unique Eu−O−C angles are obtuse and range between 137.6(5)° at O(2) and 146.0(7)° at O(7).

Table 3. Selected Bond Lengths (Å) and Angles (deg) for **2**

La−O(1)	2.587(5)	La−O(6)	2.550(5)
La−O(7)	2.544(5)	La−O(8)	2.629(5)
La−O(9)	2.530(5)	La−O(10)	2.564(5)
La−O(11)	2.522(6)	La−O(1′)	2.517(5)
La−O(1″)	2.593(4)		
O(1′)−La−O(11)	71.6(2)	O(1′)−La−O(9)	137.1(2)
O(11)−La−O(9)	137.8(2)	O(1′)−La−O(7)	73.1(2)
O(11)−La−O(7)	72.1(2)	O(9)−La−O(7)	136.4(2)
O(1′)−La−O(10)	125.9(2)	O(11)−La−O(10)	66.4(2)
O(9)−La−O(10)	71.5(2)	O(7)−La−O(10)	121.1(2)
O(1′)−La−O(6)	103.6(2)	O(11)−La−O(6)	138.8(2)
O(9)−La−O(6)	73.7(2)	O(7)−La−O(6)	67.6(2)
O(10)−La−O(6)	130.4(2)	O(1′)−La−O(1)	75.5(2)
O(11)−La−O(1)	86.0(2)	O(9)−La−O(1)	76.9(2)
O(7)−La−O(1)	146.0(2)	O(10)−La−O(1)	69.3(2)
O(6)−La−O(1)	133.6(2)	O(1′)−La−O(1″)	144.5(2)
O(11)−La−O(1″)	95.3(2)	O(9)−La−O(1″)	74.3(2)
O(7)−La−O(1″)	71.5(2)	O(10)−La−O(1″)	72.8(2)
O(6)−La−O(1″)	64.4(2)	O(1)−La−O(1″)	137.87(14)
O(1′)−La−O(8)	68.2(2)	O(11)−La−O(8)	137.5(2)
O(9)−La−O(8)	72.3(2)	O(7)−La−O(8)	107.7(2)
O(10)−La−O(8)	131.2(2)	O(6)−La−O(8)	65.8(2)
O(1)−La−O(8)	71.5(2)	O(1″)−La−O(8)	125.7(2)
C(1)−O(1)−La	141.2(5)	C(1′)−O(1′)−La	157.7(5)
C(1″)−O(1″)−La	143.5(5)		

In contrast to the “cubic” structures formed between the squarate ion and the first-row transition metals Mn, Cu, and Zn[7b,8−10] where the metals are located at the centers of the edges of the “cubes”, here the europium atoms are positioned at the vertices (which are on C_2 axes). Within the 3-dimensional network illustrated in Figure 6 the Eu···Eu separations along the three rhomboid edges are 8.78, 8.78, and 8.85 Å with interaxial angles of 110°, 110°, and 121°. The Eu···Eu separa-

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(8) Weiss, A.; Riegler, E.; Robl, C. *Z. Naturforsch.* **1986**, *41b*, 1329.
(9) Weiss, A.; Riegler, E.; Robl, C. *Z. Naturforsch.* **1986**, *41b*, 1333.
(10) Lee, C.-A.; Wang, C.-C, Wang, Y. *Acta Crystallogr.* **1996**, *B52*, 966.
(11) Note: These quoted yields are not optimal since they were calculated on the initial set of good-quality crystals harvested.

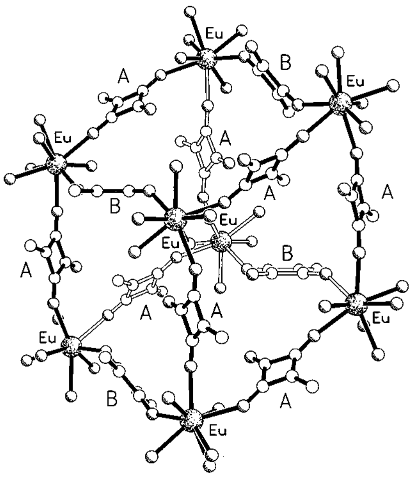

Figure 6. Part of the 3-dimensional contiguous network present in the structure of **3**.

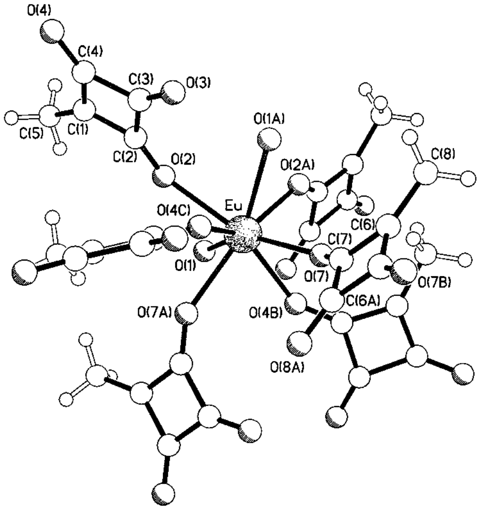

Figure 7. The coordination environment of the Eu atom in complex **3**.

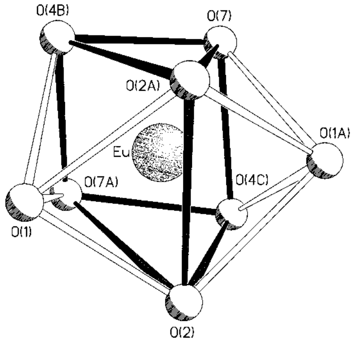

Figure 8. The severely distorted bicapped trigonal prismatic coordination polyhedron in **3**.

tion along the short body diagonal is 7.12 Å whereas that along the long body diagonal is 17.64 Å thus emphasizing the severe flattening and effective self-filling of the central voids within each rhomboidal unit. Indeed there is an O−H···O hydrogen bond (2.82 Å) that links pairs of inwardly directed aqua ligands across the short diagonal. The rhomboids pack to form a contiguous chevron-like lattice (Figure 9).

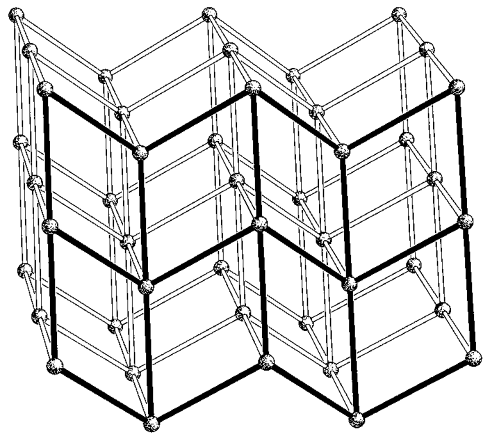

Figure 9. The chevron-like 3-dimensional network formed by the europium atoms in **3**.

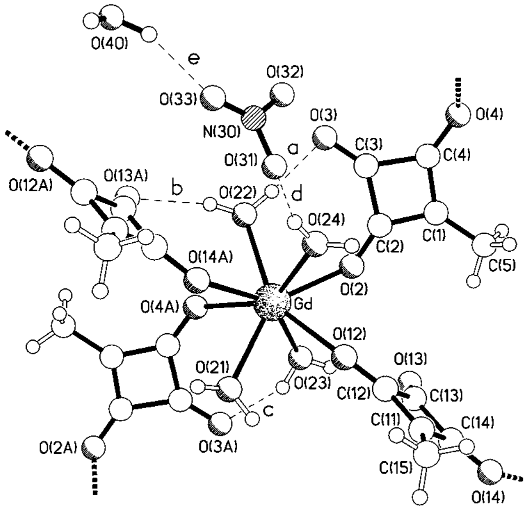

Figure 10. The coordination environment of the Gd center in the structure of **4** showing also the nitrate anion and included water molecule. The hydrogen-bonding geometries are O···O, H···O (Å), O−H···O (deg) (**a**) 2.73, 1.87, 159; (**b**) 2.87, 2.00, 163; (**c**) 2.78, 1.95, 152; (**d**) 2.76, 1.89, 162; (**e**) 2.76, 1.91, 157.

Table 4. Selected Bond Lengths (Å) and Angles (deg) for **3**

Eu−O(1)	2.493(6)	Eu−O(1A)	2.493(6)
Eu−O(2)	2.389(6)	Eu−O(2A)	2.389(6)
Eu−O(4C)	2.370(6)	Eu−O(4B)	2.370(6)
Eu−O(7)	2.340(6)	Eu−O(7A)	2.340(6)
O(7A)−Eu−O(7)	100.5(4)	O(7A)−Eu−O(4C)	72.6(2)
O(7)−Eu−O(4C)	77.0(3)	O(7A)−Eu−O(4B)	77.0(3)
O(7)−Eu−O(4B)	72.6(2)	O(4C)−Eu−O(4B)	131.6(3)
O(4C)−Eu−O(2)	78.0(2)	O(7)−Eu−O(2)	146.4(2)
O(4C)−Eu−O(2A)	140.8(2)	O(4B)−Eu−O(2)	140.8(2)
O(2)−Eu−O(2A)	92.2(3)	O(7)−Eu−O(2A)	93.1(3)
O(7)−Eu−O(1)	144.1(2)	O(4B)−Eu−O(2A)	78.0(2)
O(4B)−Eu−O(1)	71.9(2)	O(4C)−Eu−O(1)	132.9(2)
O(7)−Eu−O(1A)	76.5(3)	O(2)−Eu−O(1)	69.0(2)
O(4B)−Eu−O(1A)	132.9(2)	O(4C)−Eu−O(1A)	71.9(2)
O(1)−Eu−O(1A)	126.5(4)	O(2)−Eu−O(1A)	74.6(2)

M Methylsquarate {M[μ-($CH_3C_4O_3$)$_2$][(H_2O)$_4$][NO_3]·H_2O}$_n$ [M = Gd(4), Tb(5)]. In contrast to the neutral polymer **3** that was the product of the reaction between Eu(NO_3)·5H_2O and methylsquarate, when the same reaction was carried out with Gd(NO_3)$_3$·6H_2O, a single-crystal X-ray analysis revealed the formation of an ionic sheet polymer that is distinctly different from that seen for **3**. Here the gadolinium is eight-coordinate with a square antiprismatic geometry (cf. the severely distorted bicapped trigonal prismatic geometry present in **3**), being bound to the oxygen atoms of four methylsquarate units and to four aqua ligands (Figure 10). The relative orientations of the four methylsquarate ligands are to some extent controlled by intramolecular O−H···O hydrogen bonds between the aqua

Table 5. Selected Bond Lengths (Å) and Angles (deg) for **4** and **5**

	4 (M = Gd)	**5** (M = Tb)		**4** (M = Gd)	**5** (M = Tb)
M−O(14A)	2.354(5)	2.346(5)	M−O(12)	2.358(5)	2.348(5)
M−O(4A)	2.381(5)	2.383(5)	M−O(21)	2.381(5)	2.374(5)
M−O(2)	2.388(5)	2.383(5)	M−O(23)	2.393(6)	2.395(5)
M−O(24)	2.394(5)	2.388(5)	M−O(22)	2.398(5)	2.389(5)
O(14A)−M−O(12)	111.1(2)	111.0(2)	O(14A)−M−O(4A)	79.6(2)	80.0(2)
O(12)−M−O(4A)	143.3(2)	143.0(2)	O(14A)−M−O(21)	73.4(2)	73.4(2)
O(12)−M−O(21)	73.6(2)	73.8(2)	O(4A)−M−O(21)	76.6(2)	76.2(2)
O(14A)−M−O(2)	142.8(2)	143.0(2)	O(12)−M−O(2)	79.1(2)	78.5(2)
O(4A)−M−O(2)	114.2(2)	114.6(2)	O(21)−M−O(2)	141.8(2)	141.5(2)
O(14A)−M−O(23)	146.1(2)	146.3(2)	O(12)−M−O(23)	78.3(2)	78.8(2)
O(4A)−M−O(23)	75.3(2)	74.8(2)	O(21)−M−O(23)	78.8(2)	79.2(2)
O(2)−M−O(23)	69.7(2)	69.4(2)	O(14A)−M−O(24)	73.7(2)	73.5(2)
O(12)−M−O(24)	72.8(2)	72.8(2)	O(4A)−M−O(24)	142.1(2)	142.5(2)
O(21)−M−O(24)	119.3(2)	119.2(2)	O(2)−M−O(24)	75.9(2)	75.9(2)
O(23)−M−O(24)	138.5(2)	138.6(2)	O(14A)−M−O(22)	78.6(2)	78.6(2)
O(12)−M−O(22)	146.9(2)	146.7(2)	O(4A)−M−O(22)	68.2(2)	68.7(2)
O(21)−M−O(22)	138.2(2)	138.2(2)	O(2)−M−O(22)	75.7(2)	76.1(2)
O(23)−M−O(22)	111.8(2)	111.5(2)	O(24)−M−O(22)	80.4(2)	80.2(2)

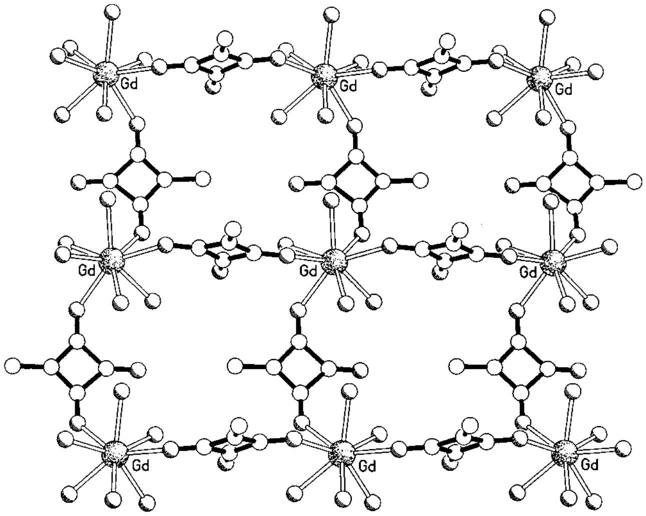

Figure 11. Part of the 2-dimensional ridged network present in the structures of **4** and **5**.

ligands and their proximal methylsquarate ketonic oxygen atoms (interactions **a**, **b**, and **c** in Figure 10). The Gd−O distances fall into two ranges with those to the methylsquarate oxygens lying between 2.354(5) and 2.388(5) Å whereas those to the aqua ligands are between 2.381(5) and 2.398(5) Å (Table 5). The polymer contains two independent methylsquarate ligands, each of which is coordinated μ-1,3 linking adjacent gadolinium centers to form the ridged sheet polymer depicted in Figure 11; the planes of the independent methylsquarate ligands are essentially orthogonal (88°) to each other. The bonding in the two independent methylsquarate ligands is the same, retaining in each case a pattern of delocalization that extends between two coordinated oxygen atoms via the methyl-bearing carbon; the single-bond nature of the C(2)−C(3), C(3)−C(4) and C(12)−C(13), C(13)−C(14) linkages is still pronounced. In this complex the Gd−O−C angles range betweeen 130.8(5)° and 143.0(6)°.

The cationic polymer sheets pack back-to-back and face-to-face, the face-to-face arrangement creating large channels within which (extending along the crystallographic *b* direction) the nitrate anions and the included water molecules are located (Figure 12). Adjacent sheets are stepped with respect to each other in the *b* direction, the inwardly directed methyl groups

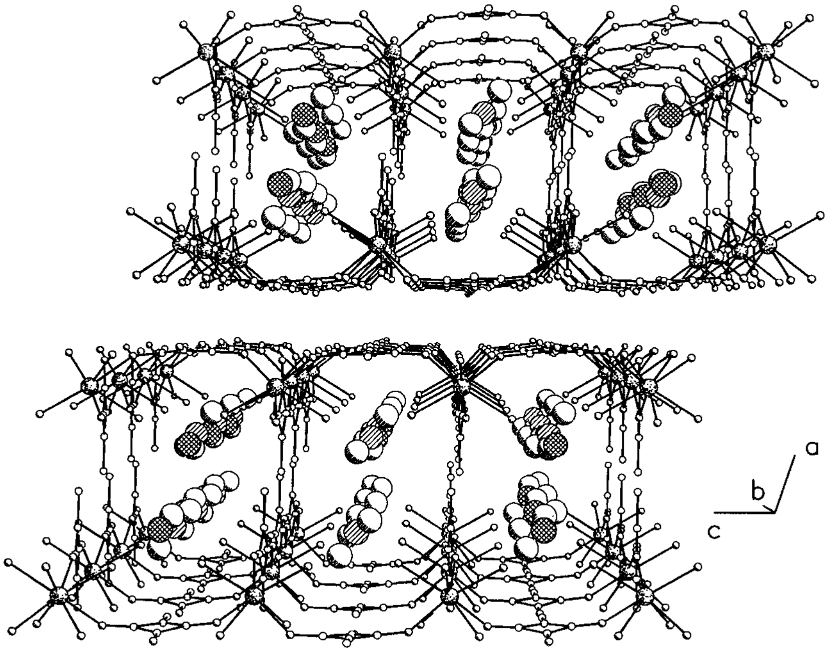

Figure 12. The channels formed by the face-to-face stacking of the ridged 2-D sheets in **4** and **5** showing the location of the nitrate anion, the included water molecules, and the back-to-back stacking of these motifs.

(which form the ridges in each sheet) interdigitating with each other. This face-to-face arrangement is stabilized via intermolecular anion···cation hydrogen-bonding interactions involving the aqua ligands of the cation and the oxygen atoms of the anion; the included water molecules also play a linking role. Although the planes of the back-to-back arranged sheets are separated by only 3.05 Å, there is no overlap of the methylsquarate ligands. The only dominant intersheet interaction is an electrostatic attraction between orthogonally oriented carbonyl groups, the carbonyl group [O(13)] trans to the methyl group, which forms the ridges in the sheets in one layer, being directed orthogonally into the C atom [C(13)] of its counterpart in the next; the O···C distance is 3.24 Å, and the associated C═O···C angle is 170°.

The terbium complex **5** is isomorphous with the gadolinium structure **4**, there being no significant differences in either the molecular or supramolecular arrangements.

Conclusions

The ability in most instances to form polymeric lanthanide complexes with the methylsquarate ligand, while with the diphenylaminosquarate ligand only monomers and dimers are formed, strongly suggests that the steric requirement of the substituent is a determining factor in polymer formation. We have demonstrated that on going from first-row transition metals to lanthanides, polymer formation can still be achieved provided there is a reduction in the steric bulk of the squarate ring substituent. The nature of the network formed (chain, sheet, or 3-dimensional network) is to a large extent determined by the number of ligands that can be simultaneously accommodated about the metal center. Exceptions to this paradigm do exist, however, as evidenced by the formation of a monomer in the case of the lanthanide complex **2**, but we still believe that a basic principle has been established for polymer formation in these systems.

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Supporting Information Available: Ellipsoid representations of the complexes (5 figures). Ring stacking in **2**. Five X-ray crystallographic files, in CIF format. This material is available free of charge via the Internet at http://pubs.acs.org.

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