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Article

Attempted Syntheses of Lanthanide(III) Complexes of the Anisole- and Anilinosquarate Ligands

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The polymeric lanthanide complexes $\{Ln(\mu\text{-}CH_3OC_6H_5C_4O_3)(CH_3OC_6H_5C_4O_3)_2 (H_2O)_4 \cdot xH_2O\}_n$ [Ln = La (**1**), Eu (**2**), Gd (**3**)], formed from the reaction of aqueous solutions of anisolesquarate and $Ln(NO_3)_3 \cdot xH_2O$, are all structurally similar with only subtle differences between the lanthanum complex and the isomorphous pair of europium and gadolinium analogues. The lanthanum atom in **1** has a square antiprismatic coordination geometry comprising two pendant and two μ-1,3-bridging anisolesquarate groups and four aqua ligands. Complexes **2** and **3** have two independent metal atoms in their asymmetric units compared to one for the lanthanum complex. However, the gross structures of **1**–**3** are essentially the same. The asymmetric unit of the terbium complex $\{(CH_3OC_6H_5C_4O_3)_3\text{-}Tb(H_2O)_4(\mu\text{-}CH_3OC_6H_5C_4O_3)(CH_3OC_6H_5C_4O_3)_2Tb(H_2O)_5\} \cdot H_2O$ (**4**) contains two independent binuclear units which hydrogen bond to form an extended structure very similar to those of **1**–**3**. The ionic polymers $\{[Ln(\mu_2\text{-}C_4O_4)\text{-}(H_2O)_6][C_6H_5NHC_4O_3] \cdot 4H_2O\}_n$ [Ln = Eu (**5**), Gd (**6**), Tb (**7**)] result from the incomplete hydrolysis of the anilinosquarate ion during the attempted synthesis of Eu(III), Gd(III), and Tb(III) anilinosquarate complexes. However, complete hydrolysis of the substituent is accomplished by La(III) ions, and the neutral polymer $\{La_2(\mu_2\text{-}C_4O_4)_2(\mu_3\text{-}C_4O_4)\text{-}(H_2O)_{11} \cdot 2H_2O\}_n$ (**8**) is formed. In complexes **5**–**7**, the central lanthanide atom has a square antiprismatic geometry, being bonded to two μ-1,2-bridging squarate and six aqua ligands. Two anilinosquarate counteranions participate in second-sphere coordination via direct hydrogen bonding to aqua ligands on each metal center. These counteranions, and the included waters of crystallization, serve to link neighboring cationic polymer chains via an extensive array of O–H···O hydrogen bonds to form a 3-dimensional network. The polymeric lanthanum complex **8** contains two different metal environments, each having distorted monocapped square antiprismatic geometry. For one lanthanum atom the coordination polyhedron comprises five aqua and four squarate ligands, while for the other the polyhedron consists of six aqua and three squarate ligands; in each case one of the aqua ligands occupies the capping position. The squarate ligand exhibits two coordination modes in **8** (μ-1,2- and μ-1,3-bridging), and neighboring polymer chains are cross-linked by hydrogen bonds to form a 3-dimensional network.

Introduction

Our interest in the synthesis of polymeric lanthanide complexes of monosubstituted squarate ligands is their perceived potential for exhibiting interesting electronic properties, such as semiconductivity, which could be tuned by the appropriate alteration of the ligand substituent.[1] For example, analysis of several series of such complexes that

we have synthesized so far has revealed that the steric bulk of the substituent is a particularly important factor in influencing not only whether polymer formation would be realized but also the structural characteristics of the polymers.[2–6] We have reported previously that the bulky diphenylamino substituent in the (diphenylamino)squarate ligand suppresses polymer formation[3] while the less sterically demanding methyl substituent in methylsquarate facilitates the formation of polymers of diverse structures.[4] We have

also observed that the orientation of the substituent to the C_4-cycle is an important consideration especially with substituents that are attached to it via atoms containing lone pairs of electrons. In particular, for dialkylamino substituents, the coplanarity of the NR_2 units and the C_4-rings seems to enhance the susceptibility of these amino groups to hydrolysis, resulting in the formation of products without monosubstituted squarate ligands, thereby defeating the object of the exercise.[2] By contrast, when the (diphenylamino)squarate ligand was used, the steric effect of the out-of-plane phenyl rings prevented the hydrolysis, allowing the formation of monosubstituted squarate complexes.[3,7] This coplanarity assumes less importance in the case of the anilinosquarate ligand, where complexes with both coplanar [Ru(II) anilinosquarate] and twisted [M(II) anilinosquarate; M = Mn, Co, Ni, Cu, Zn] relative orientations of the C_4- and C_6-rings, respectively, have been observed.[8,9] The electron delocalization on the C_4-ring and the extent of electron transfer from the monosubstituted squarate ligand to the coordinated metal center are also considered to be important factors in polymer formation and have been shown to be significantly effected by the availability of lone pairs on the substituents on the C_4-ring.[2,3,10−13] To date, however, only cases where the atom

with the lone pairs is directly bonded to the C_4-ring have been studied.

We decided therefore to investigate the following:

(1) the effect of a small change in steric demand (compared to the larger changes previously investigated) of the ligand substituent ($MeOC_6H_4$ compared to C_6H_5) on the structures of the complexes formed;

(2) whether the inclusion of a group with mobile electron density (viz. OMe) on the phenyl substituent (anisolesquarate) would alter the delocalization on the C_4-ring and the complexing properties of the phenylsquarate ligand;

(3) whether the anilinosquarate ligand would undergo hydrolysis (as in the case of the dialkylaminosquarates) or resist it (as in the case of the diphenylaminosquarates and in ruthenium(II) anilinosquarate) (note that, on the basis of theoretical considerations, we expected that the anilino substituent would be always coplanar with the C_4-ring due to extended conjugation involving the π-systems on the phenyl and C_4-rings and one of the p orbitals on the intervening N atom);

(4) the effect of the location of the mobile electron density on the substituent in lanthanide complexes of monosubstituted squarate ligands.

We also hoped that further investigations of the complexing properties of the anilinosquarate ligand would provide more information on the factors affecting the orbital energies of monosubstituted squarate ligands and thus improve our ability to design metal complexes in which the metal and ligand orbital energies are compatible.[11,14] This compatibility is, we believe, important if polymeric metal complexes are to show properties that are dependent on electron migration along the polymer chains.[1a,c,e,g,k,15]

Here, we report on the eight compounds resulting from attempted syntheses of lanthanide anisole- and anilinosquarates.

Experimental Section

Preparation of the Ligands. Anisolesquarate. 3-(4-Methoxyphenyl)-4-hydroxycyclobut-3-ene-1,2-dione (anisolesquarate) was prepared according to the method of Bellus[16,17] as modified by Law and Bailey.[18]

Sodium Anilinosquarate. 3-Anilino-4-hydroxycyclobut-3-ene-1,2-dione (anilinosquarate) was first prepared according to the method of Gauger and Manecke[19] as revised by Neuse and Green.[20] However, the best results were obtained using the following

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Table 1. Crystallographic Data for Compounds **1−8**[a]

data	1	2	3	4
chem formula	$C_{33}H_{29}O_{16}La$	$C_{33}H_{29}O_{16}Eu$	$C_{33}H_{29}O_{16}Gd$	$C_{66}H_{60}O_{33}Tb_2$
solvent	3 H_2O	2.75 H_2O	2.75 H_2O	H_2O
fw	874.52	883.07	888.36	1717.00
space group	$C2/c$ (No. 15)	$P2/c$ (No. 13)	$P2/c$ (No. 13)	$P\bar{1}$ (No. 2)
a (Å)	27.6785(5)	27.9447(4)	27.9313(5)	9.9302(2)
b (Å)	13.6572(3)	13.5745(2)	13.5738(3)	26.3743(5)
c (Å)	19.7535(4)	19.5747(2)	19.5825(3)	28.5376(5)
α (deg)				62.9737(9)
β (deg)	105.8280(10)	108.6297(6)	108.6525(9)	81.5369(7)
γ (deg)				87.1893(7)
V (Å^3)	7183.9(3)	7036.3(2)	7034.4(2)	6584.0(2)
Z	8	8	8	4[b]
ρ_{calcd} (g cm^{-3})	1.617	1.667	1.678	1.732
μ (mm^{-1})	1.272	1.866	1.969	2.230
R_1[c]	0.036	0.043	0.065	0.054
wR_2[d]	0.071	0.103	0.126	0.108

data	5	6	7	8
chem formula	$C_{14}H_{18}NO_{13}Eu$	$C_{14}H_{18}NO_{13}Gd$	$C_{14}H_{18}NO_{13}Tb$	$C_{12}H_{22}O_{23}La_2$
solvent	4 H_2O	4 H_2O	4 H_2O	2 H_2O
fw	632.32	637.61	639.28	848.15
space group	$I2/a$ (No. 15)	$I2/a$ (No. 15)	$I2/a$ (No. 15)	$P2_1/c$ (No. 14)
a (Å)	16.5920(8)	16.5761(2)	16.5424(6)	9.66820(10)
b (Å)	7.6238(2)	7.60560(10)	7.5852(3)	15.3770(3)
c (Å)	35.4976(13)	35.4890(5)	35.4632(14)	16.4646(3)
α (deg)				
β (deg)	96.540(2)	96.5620(10)	96.457(2)	90.1073(7)
γ (deg)				
V (Å^3)	4461.0(3)	4444.83(10)	4421.6(3)	2447.75(7)
Z	8	8	8	4
ρ_{calcd} (g cm^{-3})	1.883	1.906	1.921	2.302
μ (mm^{-1})	2.896	3.069	3.284	3.557
R_1[c]	0.049	0.033	0.039	0.030
wR_2[d]	0.121	0.082	0.093	0.075

[a] Details in common: Nonius Kappa CCD diffractometer, graphite-monochromated Mo Kα radiation (λ = 0.710 73 Å), −123 °C, refinement based on F^2. [b] There are two crystallographically independent molecules in the asymmetric unit. [c] $R_1 = \sum||F_o| - |F_c||/\sum|F_o|$. [d] $wR_2 = \{\sum[w(F_o^2 - F_c^2)^2]/\sum[w(F_o^2)^2]\}^{1/2}$; $w^{-1} = \sigma^2(F_o^2) + (aP)^2 + bP$.

modified procedure. A total of 116 mL of a solution of aniline (37.20 g, 0.40 mol) in DMF was added to 120 mL of a solution of 3,4-dihydroxycyclobut-3-ene-1,2-dione (22.80 g, 0.20 mol) in the same solvent. The mixture was allowed to cool in a dry ice/acetone bath for 10 min, followed by the addition of 250 mL ether that was previously cooled in a similar manner. This mixture was allowed to stand in the cold bath for a further 10 min. The solids were then removed by suction filtration, washed with ether, and dried on a rotary evaporator. The dried solids were then heated for 20 min at 200 °C to give 37.85 g (100%) of crude anilinosquarate.

The sodium salt of the anilinosquarate ligand was then prepared by dissolving the crude compound (37.85 g, 0.20 mol) in 100 mL of 2 M NaOH. The resulting yellow-brown mixture was then stirred for 45 min. The suspension was filtered, the filtrate pumped down, and the crude sodium salt of the anilinosquarate ligand recrystallized from hot water. Yield: 25.75 g (61%). ^{1}H NMR (400 MHz; DMSO-d_6): δ 6.82 (t, J = 12 Hz, 1H), 7.19 (m, 2H), 7.66 (d, J = 12 Hz, 2H), 9.28 (s, 1H).

Preparation of the Complexes. (a) {Ln(μ-CH$_3$OC$_6$H$_5$C$_4$O$_3$)-(CH$_3$OC$_6$H$_5$C$_4$O$_3$)$_2$(H$_2$O)$_4$·xH$_2$O}$_n$ [Ln = La (1), Eu (2), Gd (3)] and {(CH$_3$OC$_6$H$_5$C$_4$O$_3$)$_3$Tb(H$_2$O)$_4$(μ-CH$_3$OC$_6$H$_5$C$_4$O$_3$)-(CH$_3$OC$_6$H$_5$C$_4$O$_3$)$_2$Tb(H$_2$O)$_5$}·H$_2$O (4). A 15 mL volume of an aqueous solution of Ln(NO$_3$)$_3$·xH$_2$O (4.90 × 10^{-4} mol) (Ln = La, Eu, Gd, Tb) was added to 35 mL of an aqueous solution of anisolesquarate (0.10 g, 4.90 × 10^{-4} mol). The mixture was filtered and left to stand at about 28 °C until crystallization was complete.

{La(μ-CH$_3$OC$_6$H$_5$C$_4$O$_3$)(CH$_3$OC$_6$H$_5$C$_4$O$_3$)$_2$(H$_2$O)$_4$·3H$_2$O}$_n$ (1): pale yellow needles. Yield: 20%. Anal. Calcd for C$_{33}$H$_{35}$-LaO$_{19}$: C, 45.3; H, 4.0; La, 15.9. Found: C, 45.9; H, 3.4; La, 16.1.

{Eu(μ-CH$_3$OC$_6$H$_5$C$_4$O$_3$)(CH$_3$OC$_6$H$_5$C$_4$O$_3$)$_2$(H$_2$O)$_4$·2.75H$_2$O}$_n$ (2): pale yellow needles. Yield: 22%. Anal. Calcd for C$_{33}$H$_{34.5}$EuO$_{18.8}$: C, 44.8; H, 3.9; Eu, 17.2. Found: C, 44.8; H, 3.4; Eu, 17.7.

{Gd(μ-CH$_3$OC$_6$H$_5$C$_4$O$_3$)(CH$_3$OC$_6$H$_5$C$_4$O$_3$)$_2$(H$_2$O)$_4$·2.75H$_2$O}$_n$ (3): colorless needles. Yield: 30%. Anal. Calcd for C$_{33}$H$_{34.5}$GdO$_{18.8}$: C, 44.6; H, 3.9; Gd, 17.7. Found: C, 46.1; H, 3.6; Gd, 18.5.

{(CH$_3$OC$_6$H$_5$C$_4$O$_3$)$_3$Tb(H$_2$O)$_4$(μ-CH$_3$OC$_6$H$_5$C$_4$O$_3$)-(CH$_3$OC$_6$H$_5$C$_4$O$_3$)$_2$Tb(H$_2$O)$_5$}·H$_2$O (4): tiny colorless needles. Yield: 36%. Anal. Calcd for C$_{66}$H$_{62}$O$_{34}$Tb$_2$: C, 46.2; H, 3.6; Tb, 18.5. Found: C, 46.3; H, 3.6; Tb, 18.3.

(b) {[Ln(μ$_2$-C$_4$O$_4$)(H$_2$O)$_6$][C$_6$H$_5$NHC$_4$O$_3$]·4H$_2$O}$_n$ [Ln = Eu (5), Gd (6), Tb (7)] and {La$_2$(μ$_2$-C$_4$O$_4$)$_2$(μ$_3$-C$_4$O$_4$)(H$_2$O)$_{11}$·2H$_2$O}$_n$ (8). A 15 mL aliquot of an aqueous solution of Ln(NO$_3$)$_3$·xH$_2$O (1.58 × 10^{-4} mol) (Ln = La, Eu, Gd, Tb) was added to 25 mL of an aqueous solution of sodium anilinosquarate (0.10 g, 4.74 × 10^{-4} mol). The solution was filtered, and THF was added until the first signs of turbidity. The resulting mixture was filtered and allowed to evaporate slowly at 5 °C until crystallization was complete.

{[Eu(μ$_2$-C$_4$O$_4$)(H$_2$O)$_6$][C$_6$H$_5$NHC$_4$O$_3$]·4H$_2$O}$_n$ (5): colorless plates. Yield: 40%. Anal. Calcd for C$_{14}$H$_{26}$EuNO$_{17}$: C, 26.6; H, 4.1; Eu, 24.1; N, 2.2. Found: C, 27.0; H, 3.4; Eu, 24.3; N, 2.2.

{[Gd(μ$_2$-C$_4$O$_4$)(H$_2$O)$_6$][C$_6$H$_5$NHC$_4$O$_3$]·4H$_2$O}$_n$ (6): pale yellow plates. Yield: 11%. Anal. Calcd for C$_{14}$H$_{26}$GdNO$_{17}$: C, 26.4; H, 4.1; Gd, 24.7; N, 2.2. Found: C, 26.6; H, 3.8; Gd, 24.7; N, 2.2.

{[Tb(μ$_2$-C$_4$O$_4$)(H$_2$O)$_6$][C$_6$H$_5$NHC$_4$O$_3$]·4H$_2$O}$_n$ (7): colorless plates. Yield: 20%. Anal. Calcd for C$_{14}$H$_{26}$NO$_{17}$Tb: C, 26.3; H, 4.1; N, 2.2; Tb, 24.9. Found: C, 24.9; H, 3.1; N, 1.7; Tb, 25.9.

{**La$_2$(μ_2-C$_4$O$_4$)$_2$(μ_3-C$_4$O$_4$)(H$_2$O)$_{11}$·2H$_2$O**}$_n$ (**8**): colorless plates. Yield: 15%. Anal. Calcd for C$_{12}$H$_{26}$La$_2$O$_{25}$: C, 17.0; H, 3.1; La, 32.8. Found: C, 18.0; H, 3.1; La, 32.0.

pH Study. Materials and Methods. All pH measurements were taken using a Hanna Instruments HI 9025 microcomputer pH meter calibrated using Hanna Instruments buffer solutions pH 4.01 and 7.01. The buffer solutions utilized in pH adjustments were prepared using a 0.05 M solution of anhydrous disodium hydrogen ortho-phosphate and dilute HCl.[21]

The pH of 15 mL aqueous solutions of each Ln(NO$_3$)$_3$·xH$_2$O (1.58 × 10^{-4} mol) (Ln = La, Eu, Gd, Tb) and a 25 mL aliquot of sodium anilinosquarate (0.10 g, 4.74 × 10^{-4} mol) were taken separately. Each 15 mL aliquot of the Ln(NO$_3$)$_3$·xH$_2$O solution was then mixed thoroughly with a 25 mL aliquot of sodium anilinosquarate, the mixture filtered, and the pH of the resulting solution determined. THF was then added to each mixture until first turbidity (to mimic the conditions used in the preparations of the complexes) and the volume of THF was noted.

The pH values of the mixtures of aqueous solutions of Ln(NO$_3$)$_3$·xH$_2$O (Ln = La, Eu, Gd, Tb) and Na anilinosquarate separately were 4.24, 4.14, 4.11, and 4.14, respectively.

The pH of four 25 mL aliquots of aqueous solutions of sodium anilinosquarate (0.10 g, 4.74 × 10^{-4} mol) were adjusted using buffer to pH 2.10, 4.05, 6.01, and 7.44, respectively. (These values were selected to include the range of pH's observed when the Ln(NO$_3$)$_3$·xH$_2$O and anilinosquarate solutions were mixed.) A 0.65 mL volume of THF was then added to each solution, and the resulting mixtures were filtered and allowed to stand at 5 °C for 3 days. These solutions were then left to evaporate to dryness at 28 °C. ^{1}H NMR spectra of the residue obtained in each case were measured. ^{1}H NMR (400 MHz; DMSO): δ 6.82 (t, J = 12 Hz, 1H), 7.19 (m, 2H), 7.66 (d, J = 12 Hz, 2H), 9.28 (s, 1H).
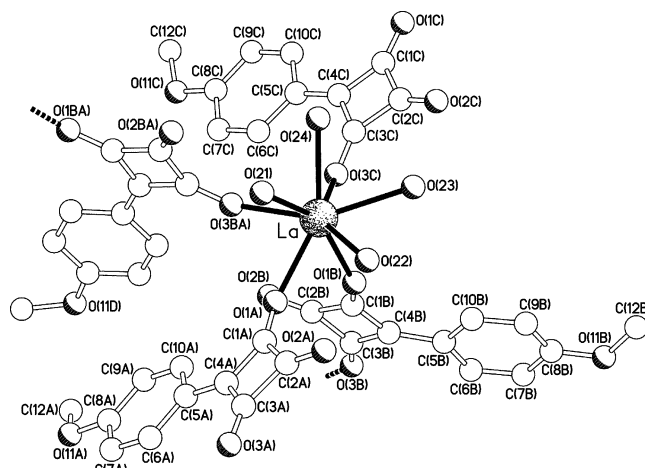
X-ray Crystallography. Table 1 provides a summary of the crystallographic data for compounds **1** − **8**. The somewhat high anisotropy seen for the methoxy oxygen atom O(11E) in compound **2** (see Figure S2) is a consequence of (i) a small angular disorder in the position of this anisole ligand and (ii) the presence of two discrete 50% occupancy positions for the terminal carbon atom. X-ray data are reported in CCDC 222338 to 222345.

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

Results and Discussion

For all the lanthanide anisolesquarate complexes, crystalline samples were prepared by evaporation of the filtered reaction mixture of anisolesquarate and the corresponding lanthanide nitrate.

{**La(μ-CH$_3$OC$_6$H$_5$C$_4$O$_3$)(CH$_3$OC$_6$H$_5$C$_4$O$_3$)$_2$(H$_2$O)$_4$· 3H$_2$O**}$_n$ (**1**). Single crystal analysis of **1** showed the complex to be polymeric with the metal atom coordinated to the oxygen atoms of four anisolesquarate and four aqua ligands in a slightly distorted square antiprismatic arrangement, the four aqua ligands occupying one of the square faces. Two of the anisolesquarate ligands are pendant whereas the other two bridge μ-1,3 to an adjacent symmetry-related lanthanum center (Figure 1). The La−O distances fall into two distinct ranges with those to the O$_{anisolesquarate}$ oxygen atoms being shorter than those to the aqua ligands (Table 2). There is no

(21) Robinson, R. A.; Stokes, R. H. *Electrolyte Solutions*, 2nd ed.; Butterworths, Academic Press, Inc.: London; New York, 1959. Bates, R.C. *J. Res. Natl. Bur. Stand. (U.S.)* **1962**, *66A*, 179.

Figure 1. Lanthanum environment in the polymeric complex {La(μ-CH$_3$-OC$_6$H$_5$C$_4$O$_3$)(CH$_3$OC$_6$H$_5$C$_4$O$_3$)$_2$(H$_2$O)$_4$·3H$_2$O}$_n$ (**1**).

Table 2. Selected Bond Lengths (Å) for Compound **1**

La−O(1A)	2.430(2)	La−O(1B)	2.443(3)
La−O(3C)	2.485(2)	La−O(3BA)	2.472(2)
La−O(21)	2.528(3)	La−O(22)	2.574(2)
La−O(23)	2.513(2)	La−O(24)	2.521(2)

Table 3. Comparative C$_4$-Ring C−C Bond Lengths (Å) in Compounds **1**−**4**^{a}
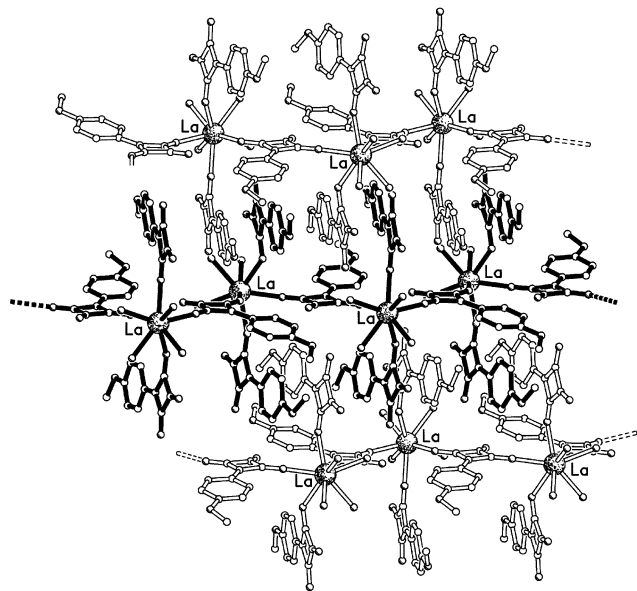
	C(1)−C(2)	C(2)−C(3)	C(3)−C(4)	C(4)−C(1)
1A	1.501(4)	1.514(4)	1.445(4)	1.412(4)
1B	1.509(4)	1.503(5)	1.437(4)	1.421(5)
1C	1.499(4)	1.485(5)	1.429(4)	1.441(4)
2A	1.478(7)	1.506(6)	1.456(6)	1.412(6)
2B	1.499(6)	1.496(6)	1.426(6)	1.426(7)
2C	1.504(6)	1.498(6)	1.438(6)	1.454(6)
2D	1.494(7)	1.511(6)	1.455(7)	1.426(6)
2E	1.504(7)	1.503(6)	1.423(6)	1.426(7)
2F	1.500(6)	1.488(6)	1.424(6)	1.452(6)
3A	1.488(11)	1.479(12)	1.436(12)	1.433(11)
3B	1.493(12)	1.504(12)	1.438(12)	1.435(12)
3C	1.489(11)	1.496(11)	1.438(11)	1.456(11)
3D	1.512(12)	1.521(11)	1.442(12)	1.400(11)
3E	1.503(13)	1.509(12)	1.424(11)	1.453(12)
3F	1.523(11)	1.484(11)	1.442(10)	1.439(11)
4A	1.485(11)	1.476(10)	1.418(10)	1.450(10)
4B	1.513(11)	1.485(11)	1.432(11)	1.437(11)
4C	1.498(11)	1.501(11)	1.442(11)	1.448(10)
4D	1.494(11)	1.498(11)	1.434(11)	1.436(12)
4E	1.533(11)	1.475(11)	1.437(10)	1.447(11)
4F	1.487(10)	1.482(10)	1.454(10)	1.440(11)
4G	1.491(10)	1.489(10)	1.440(10)	1.434(10)
4H	1.515(11)	1.486(10)	1.397(11)	1.433(11)
4I	1.492(10)	1.498(11)	1.455(10)	1.426(10)
4J	1.511(11)	1.514(12)	1.427(10)	1.459(11)
4K	1.483(11)	1.503(11)	1.414(10)	1.443(10)
4L	1.445(11)	1.487(10)	1.431(11)	1.420(10)

^{a} The labels in the first column refer to the ring (letter) in the structure (number) (e.g. **3E** refers to ring **E** in structure **3**).

significant difference in the equivalent bond lengths within both the bridging and pendant ligands. In each case the C$_4$-cycle has a pattern of one "short", one "intermediate", and two "long" bonds with a Δ(C−C)$_{max}$ of ca. 0.07 Å (Table 3). Within each ligand the squarate and phenyl rings are essentially coplanar, the maximum torsional twist about the bond linking the two ring systems being ca. 5°.

The polymer chain has a zigzag profile with the μ-1,3-bridging ligands essentially coplanar. Within this chain the nonbonded La···La separation is 8.80 Å. The pendant ligands

	2 (M = Eu)	**3** (M= Gd)		**2** (M = Eu)	**3** (M= Gd)
M(1)−O(1A)	2.349(3)	2.340(5)	M(1)−O(1B)	2.343(3)	2.327(6)
M(1)−O(3C)	2.391(3)	2.374(5)	M(1)−O(3EA)	2.352(3)	2.338(6)
M(1)−O(21)	2.458(3)	2.445(6)	M(1)−O(22)	2.439(3)	2.435(6)
M(1)−O(23)	2.445(3)	2.417(6)	M(1)−O(24)	2.450(3)	2.442(5)
M(2)−O(3B)	2.367(3)	2.350(6)	M(2)−O(1D)	2.375(3)	2.379(5)
M(2)−O(1E)	2.351(3)	2.344(6)	M(2)−O(3F)	2.370(3)	2.368(5)
M(2)−O(31)	2.419(3)	2.408(5)	M(2)−O(32)	2.453(3)	2.440(6)
M(2)−O(33)	2.479(3)	2.462(5)	M(2)−O(34)	2.449(3)	2.446(6)

Figure 2. $\pi-\pi$ stacking between adjacent polymer chains in the structure of **1**, showing the head-to-head and head-to-tail orientations of the anisolesquarate ligands.
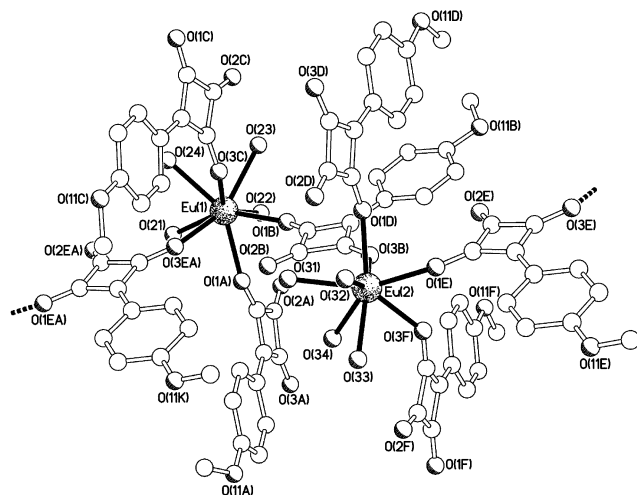
Figure 3. Environment of the two independent europium centers in the structure of **2**.

are oriented essentially orthogonal to the polymer chain, and adjacent chains are positioned such that these ligands interleave to form continuous $\pi-\pi$ stacks comprising a combination of both head-to-head and head-to-tail orientations of the anisolesquarate ligands (Figure 2). Within these stacks the mean interplanar separations are between ca. 3.3 and 3.5 Å.

$\{M(\mu\text{-}CH_3OC_6H_5C_4O_3)(CH_3OC_6H_5C_4O_3)_2(H_2O)_4\cdot$ $2.75H_2O\}_n$ [M = Eu (2), Gd (3)]. The X-ray structures of **2** (Figure 3) and **3** are isomorphous and are essentially the same as that observed for the lanthanum analogue **1**. The principal difference between these two isomorphs and **1** is the presence, in **2** and **3**, of two crystallographically independent lanthanide centers (and their associated pendant and bridging anisolesquarate ligands) within each polymer chain. The two independent lanthanide centers have a pseudoscrew relationship, and the perturbation of the polymer chain is small and is manifested in a small variation in the

intrachain Ln···Ln separations, which are 8.55 and 8.58 Å in both **2** and **3**. Both complexes exhibit the same pattern of Ln−O distances with those to the anisolesquarate ligands being consistently shorter than those to the aqua ligands (Table 4). Similarly the sequence of bond lengths within the C_4-cycles does not differ significantly from those seen in the lanthanum polymer **1** (Table 3). All of the anisolesquarate ligands have near-planar geometries, though here the torsional twist about the bond linking the phenyl and C_4-rings ranges between ca. 1 and 9°. The same pattern of interleaving of the pendant anisolesquarate ligands that was observed in **1** is also present in **2** and **3**.

$\{(CH_3OC_6H_5C_4O_3)_3Tb(H_2O)_4(\mu\text{-}CH_3OC_6H_5C_4O_3)\text{-}$ $(CH_3OC_6H_5C_4O_3)_2Tb(H_2O)_5\}\cdot H_2O$ (4). The single-crystal structure analysis of **4** shows that a further change in solid-state structure is observed when the ionic radius of the coordinating lanthanide center is reduced to that of Tb^{3+}. Here again we have two independent μ-1,3-bridged metal centers but the overall structure is binuclear monomeric. The complex crystallised with two independent monomers in the asymmetric unit so there are four different metal centers present (Figure 4). Though in each case the metal adopts a distorted 8-coordinate square antiprismatic coordination geometry comprised of eight oxygen atoms, the environments of the terbium centers within each binuclear unit are slightly different. The Tb(1) and Tb(3) atoms are linked to the oxygen atoms of four anisolesquarate and four aqua ligands, while Tb(2) and Tb(4) are bound to three anisolesquarate and five aqua ligands. Unlike the pattern seen for **1**−**3**, here there is an overlap between the ranges of the Tb−O$_{aqua}$ and Tb−O$_{anisolesquarate}$ bond distances (Table 5). The large standard deviations in the C−C bond lengths preclude any meaningful analysis of the pattern of bonding within the C_4-cycles (Table 3). The ligands, however, all have close to planar geometries, the torsional twists about the bond linking their C_4- and C_6-rings lying in the range ca. 2−9°. The arrangement of the pendant anisolesquarate ligands within the two independent binuclear monomers differs substantially. At one of the metal centers, the ligand orientations are essentially the same in both monomers [those on Tb(1) and Tb(3)]. At the other metal centers [Tb(2) and Tb(4)], in one case [Tb(2)] two of the ligands, **E** and **F**, enter into an essentially parallel head-to-head stacking arrangement (proximal) whereas the other pair, **L** and **K** [on Tb(4)], are essentially parallel but distal (see Figure 4). The really fascinating feature of this structure is what occurs at the supramolecular level. The two apparently disparate monomer conformations assemble via inter-monomer O−H···O hydrogen bonds to form a polymer chain
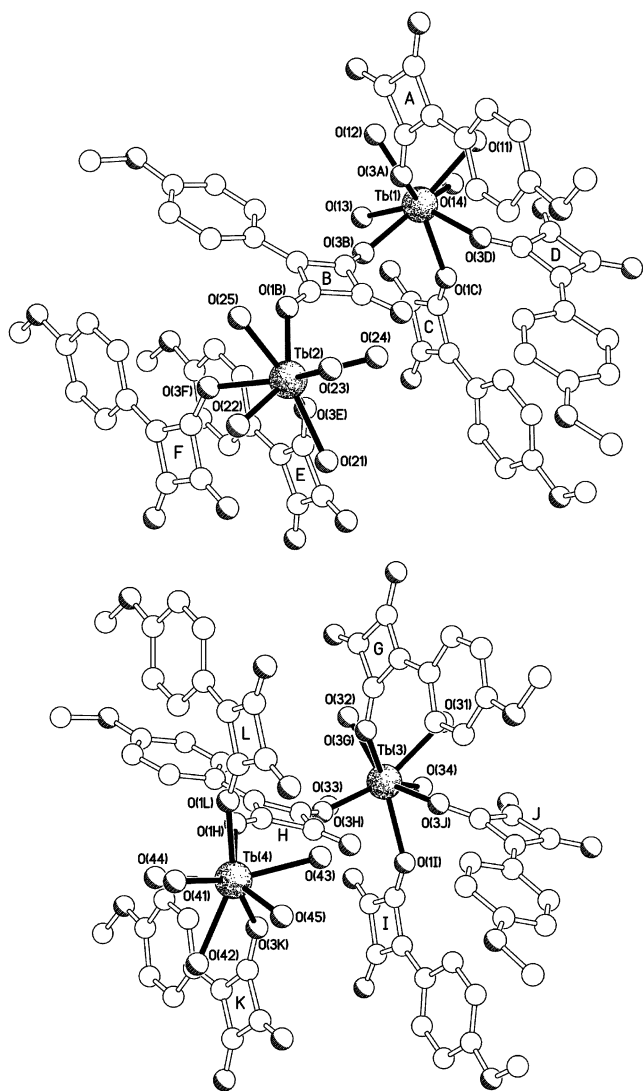
Figure 4. Environment of the two independent terbium centers in each of the two binuclear conformers in the structure of **4**.

Table 5. Selected Bond Lengths (Å) for Compound **4**

Tb(1)−O(3A)	2.374(5)	Tb(1)−O(3B)	2.287(6)
Tb(1)−O(1C)	2.402(5)	Tb(1)−O(3D)	2.329(5)
Tb(1)−O(11)	2.406(5)	Tb(1)−O(12)	2.374(5)
Tb(1)−O(13)	2.413(5)	Tb(1)−O(14)	2.433(5)
Tb(2)−O(1B)	2.361(5)	Tb(2)−O(3E)	2.352(5)
Tb(2)−O(3F)	2.365(5)	Tb(2)−O(21)	2.388(5)
Tb(2)−O(22)	2.462(5)	Tb(2)−O(23)	2.460(5)
Tb(2)−O(24)	2.421(5)	Tb(2)−O(25)	2.358(5)
Tb(3)−O(3H)	2.281(6)	Tb(3)−O(3J)	2.322(5)
Tb(3)−O(32)	2.380(5)	Tb(3)−O(3G)	2.383(5)
Tb(3)−O(31)	2.405(5)	Tb(3)−O(33)	2.411(5)
Tb(3)−O(1I)	2.420(5)	Tb(3)−O(34)	2.438(5)
Tb(4)−O(1L)	2.269(5)	Tb(4)−O(3K)	2.333(5)
Tb(4)−O(44)	2.340(5)	Tb(4)−O(45)	2.390(6)
Tb(4)−O(43)	2.413(5)	Tb(4)−O(1H)	2.440(5)
Tb(4)−O(41)	2.443(6)	Tb(4)−O(42)	2.463(5)

that mimics that seen in **1**−**3** (Figure 5). Furthermore, we see exactly the same pattern of head-to-head and head-to-tail stacking of the anisolesquarate rings of adjacent interleaving pseudo polymer chains.

This series of lanthanide anisolesquarate complexes potentially provides another example of the effect of the steric requirements of the monosubstituted squarate ligand on
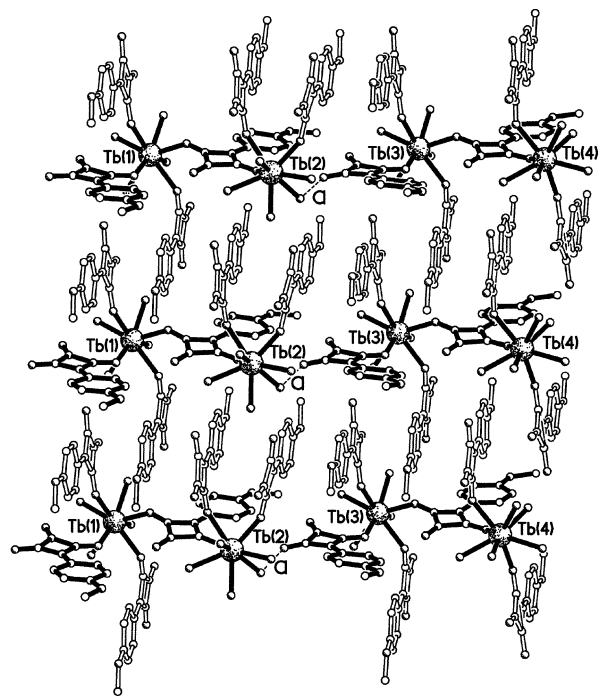

Figure 5. $\pi-\pi$ stacking between adjacent hydrogen bonded polymer chains in the structure of **4**, showing the head-to-head and head-to-tail orientations of the anisolesquarate ligands.

structure.[3−7] The decrease in ionic radius on going from La(III) (1.016 Å) to Eu(III) (0.950 Å) to Gd(III) (0.938 Å) is reflected in a shortening of the intrachain Ln···Ln separation from 8.80 Å (**1**) to 8.55 Å (**2**) to 8.58 Å (**3**). The polymer chain, however, is flexible enough to accommodate these changes without a marked change to the overall structure. For the case of Tb(III) (which has an ionic radius of 0.923 Å), however, the polymer chain "splits" into discrete binuclear units, though these are then hydrogen bonded to each other to give a pseudo polymer arrangement similar to the covalently linked polymers seen for **1**−**3**. Interestingly, the *intra*chain Tb(1)···Tb(2) and Tb(3)···Tb(4) separations of 8.53 and 8.51 Å, respectively, are slightly shorter than those seen in the Eu and Gd species, while the *inter*chain separations are significantly longer at 10.31 Å [Tb(2)···Tb(3)] and 10.59 Å [Tb(4)···Tb(1)].

Comparison with Ln Phenylsquarates. Globally, the structures of the lanthanide anisole- (this work) and phenylsquarates[4,6] are essentially the same, consisting of interleaved polymeric chains. A small difference between analogous anisole- and phenylsquarates of both Eu and Gd is a slight perturbation of the polymer chain resulting from the different steric demands of anisole vis-a-vis phenyl which is reflected by the presence of two independent metal centers in the anisole squarates; cf. one only unique metal in their phenylsquarate counterparts. A more substantial difference is provided by Tb anisolesquarate in which monomer units assemble, via hydrogen bonding, to form pseudo polymer chains that closely resemble the authentic ones observed in the La, Eu. and Gd anisolesquarates **1**−**3**.

The C_4-C_6 bond length in all the lanthanide compounds of the anisole- and phenylsquarate ligands is the same (range 1.442−1.447 Å), indicating no change in conjugation
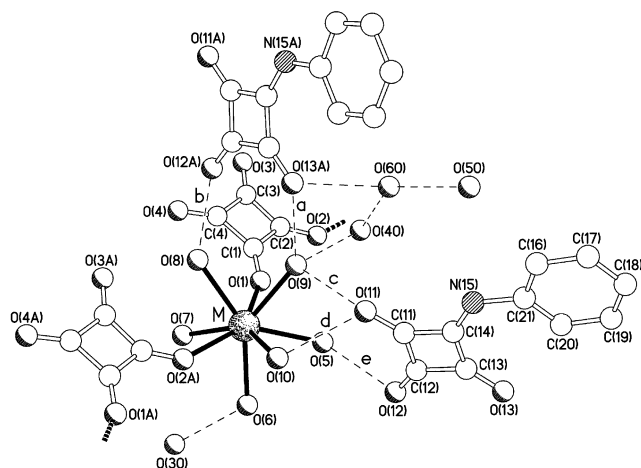
Figure 6. Lanthanide atom environment in **5**−**7**, showing the directly coordinated squarate and second-sphere coordinated anilinosquarate ions together with the hydrogen-bonded water molecules of crystallization. The hydrogen bonding distances O···O (Å) for the second-sphere coordinated ions are as follows for M = Eu, Gd, and Tb, respectively: (a) 2.72, 2.72, 2.71; (b) 2.69, 2.69, 2.70; (c) 2.85, 2.85, 2.85; (d) 2.82, 2.82, 2.81; (e) 2.75, 2.75, 2.75. (The positions of the hydrogen atoms were not reliably located.)

Table 6. Comparative Selected Bond Lengths (Å) for Compounds **5**−**7**

	5 (M = Eu)	**6** (M = Gd)	**7** (M = Tb)
M−O(1)	2.313(4)	2.311(3)	2.298(3)
M−O(2A)	2.369(4)	2.352(3)	2.343(3)
M−O(5)	2.420(4)	2.414(3)	2.399(3)
M−O(6)	2.407(4)	2.395(3)	2.385(3)
M−O(7)	2.421(4)	2.405(3)	2.392(3)
M−O(8)	2.391(4)	2.381(3)	2.363(3)
M−O(9)	2.473(4)	2.465(3)	2.452(3)
M−O(10)	2.420(4)	2.414(3)	2.392(3)

between these ring systems.[4,6] However, the bonding pattern within the C_4-cycle of the Ln anisolesquarate complexes is slightly different from that in the Ln phenylsquarate complexes. In the former, there is a pattern of one short, one intermediate, and two long while in the latter the pattern is two short and two long.[4,6]

$\{[Ln(\mu_2\text{-}C_4O_4)(H_2O)_6][C_6H_5NHC_4O_3]\cdot 4H_2O\}_n$ **[Ln = Eu (5), Gd (6), Tb (7)].** Single-crystal X-ray analyses of the products of the reactions between sodium anilinosquarate and $Ln(NO_3)_3 \cdot xH_2O$ (M = Eu, Gd, Tb), in a solvent system comprising water and THF, revealed the formation of an isomorphous series of complexes of constitution $\{[Ln(\mu_2\text{-}C_4O_4)(H_2O)_6][C_6H_5NHC_4O_3]\cdot 4H_2O\}_n$ [Ln = Eu (**5**), Gd (**6**), Tb (**7**)]. The geometry at the lanthanide center is square antiprismatic, the metal atom being bonded to the oxygen atoms of two squarate and six aqua ligands (Figure 6). The M−O_{aqua} and M−$O_{squarate}$ coordination distances fall into two distinct groups with those to the squarate oxygen atoms being shorter than those to the aqua ligands in all three complexes (Table 6). Adjacent lanthanide centers are linked μ-1,2 by the squarate ligands to form a cationic polymer chain, the Ln···Ln separation along the chain being the crystallographic *b* axis length (i.e. 7.62, 7.61, and 7.58 Å for **5**−**7**, respectively). Two anilinosquarate anions are hydrogen bonded directly to aqua ligands on the metal center (i.e. second sphere coordination), interactions a−e in Figure 6. Although there are no statistically significant differences
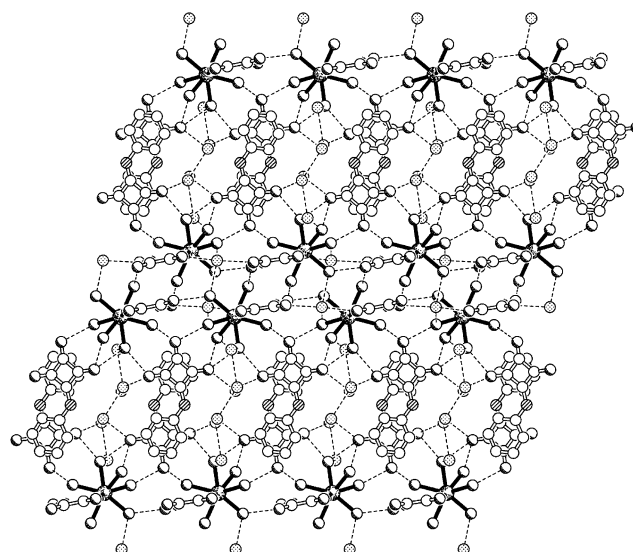
Figure 7. Part of the 3-dimensional hydrogen-bonded net present in the solid-state structures of **5**−**7**.

between the bond lengths of the squarate C_4-cycles within the polymer chain, there is a trend throughout the three isomorphous structures that suggests a pattern of short−long−short−long for the C(1)−C(2), C(1)−C(4), C(2)−C(3), and C(3)−C(4) linkages, respectively. A similar trend is also observed within the C_4-cycle of the anilinosquarate anion (Table 6). In contrast to the appreciably twisted conformation observed for the anilinosquarate ligand in a series of first-row transition metal complexes,[9] here the anion has a near-planar geometry, the two ring systems being inclined by only ca. 6°. The lengths of the C_4−N and C_6−N bonds are unchanged from those in the first-row transition metal complexes[9] and are very similar to those in the related compound 4-((4-(dimethylamino)phenyl)amino)-3-ethoxy-3-cyclobutene-1,2-dione.[22]

The cationic polymer chains and their second-sphere coordinated anilinosquarate anions are linked to their symmetry-related neighbors via a series of multiple of O−H···O hydrogen bonds involving the aqua ligands, the squarate oxygen atoms, and the four independent waters of crystallization to form a complex 3-dimensional network (Figure 7). Within this network the anilinosquarate anions are stacked head-to-tail across two independent centers of symmetry to from continuous "columns"; the mean interplanar separations between the C_4- and C_6-rings across the two inversion centers are in the ranges 3.46−3.49 and 3.57−3.58 Å, with associated centroid···centroid distances between 3.73−3.76 and 3.88−3.89 Å, respectively, over complexes **5**−**7**. In each case the ring systems are inclined by ca. 6°.

The origin of the squarate anions can be explained as being due to hydrolysis of the anilino substituent on some of the anilinosquarate anions. In the present series of syntheses, we have shown that this hydrolysis is metal-mediated since no hydrolysis of the pure ligand occurs in the absence of the metal salts over a range of pH values that include those

(22) Kolev, T.; Yancheva, D.; Schumann, M.; Kleb, D.-Chr.; Preut, H.; Bleckmann, P. *Z. Kristallogr.* **2001**, *216*, 241.
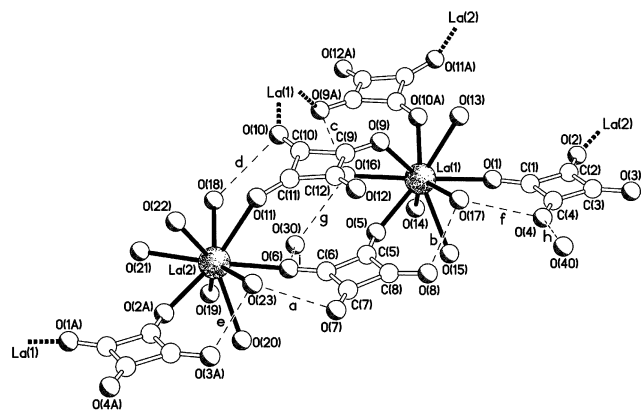
Figure 8. Environment of the two lanthanum centers in the structure of **8**. The hydrogen-bonding geometries O···O (Å), H···O (Å), and O–H···O (deg) are as follows: (a) 2.72, 1.82, 176; (b) 2.81, 1.92, 169; (c) 2.74, 1.85, 169; (d) 2.94, 2.08, 159; (e) 2.88, 1.98, 172; (f) 2.75, 1.87, 166; (g) 2.80, 1.90, 173; (h) 2.79, 1.93, 160; (i) 2.81, 1.91, 171.

observed under the conditions used for the preparation of the complexes. A similar hydrolysis problem was also encountered in initial attempts to synthesize first-row transition-metal and lanthanide complexes with three different (dialkylamino)squarate ligands.[2] The occurrence of hydrolysis of the anilinosquarate ligand in the above series of lanthanide complexes can, we believe, be attributed to the near coplanarity of the C_4- and C_6-rings and the nature of the metal. Presumably, in the series of transition-metal complexes the incompatibility of the metal and ligand orbital energies inhibits the hydrolysis, whereas for the lanthanides this incompatibility is absent. We have seen for example that in the case of lead(II) amino-, (dimethylamino)-, and (diethylamino)squarates no hydrolysis is observed[10,11] whereas all attempts to synthesize their first-row transition metal and lanthanide complexes failed, simple metal squarate complexes resulting due to hydrolysis of the dialkylamino substituents.[2] Furthermore, in the attempted syntheses of a series of first-row transition-metal methoxysquarates, hydrolysis only occurred in the case of the copper(II) complex whereas Mn(II), Co(II), Ni(II), and Zn(II) methoxysquarate complexes were successfully synthesized.[13]

Reaction of $La(NO_3)_3 \cdot 6H_2O$ with sodium anilinosquarate under experimental conditions identical with those used for **5**–**7** resulted in the formation of a crystalline product which was shown by single-crystal X-ray analysis to have the constitution $\{La_2(\mu_2\text{-}C_4O_4)_2(\mu_3\text{-}C_4O_4)(H_2O)_{11} \cdot 2H_2O\}_n$ (**8**). The complex has two independent lanthanum centers, both of which have distorted monocapped square antiprismatic geometries with aqua ligands occupying the capping positions. One metal center, La(1), is bonded to the oxygen atoms of five aqua and four squarate ligands, and the other, La(2), to the oxygen atoms of six aqua and three squarate ligands (Figure 8); there is no noticeable differentiation in the La–O_{aqua} and La–$O_{squarate}$ distances (Table 7). Of the three independent squarate ligands in the complex, two are μ-1,2-binucleating and the other μ-1,2,3-trinucleating. Within the three independent C_4-cycles there is no significant variation in the C–C bond lengths (all distances being essentially equal). The bridging interactions give rise to a tapelike
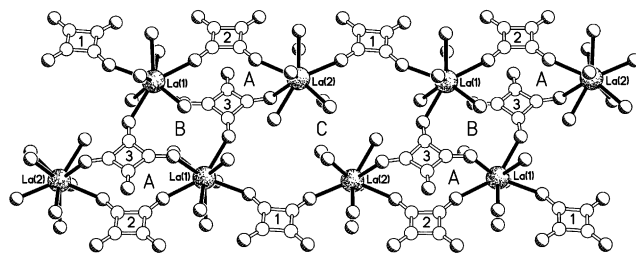
Figure 9. Part of the tape-like polymer chain showing the three types of macrocyclic rings present in the crystals of **8**.

Table 7. Selected Bond Lengths (Å) for Compound **8**

La(1)–O(5)	2.451(2)	La(1)–O(1)	2.489(2)
La(1)–O(16)	2.527(2)	La(1)–O(14)	2.540(2)
La(1)–O(13)	2.543(2)	La(1)–O(10A)	2.580(2)
La(1)–O(15)	2.592(2)	La(1)–O(9)	2.600(2)
La(1)–O(17)	2.658(2)	La(2)–O(2A)	2.436(2)
La(2)–O(6)	2.471(2)	La(2)–O(21)	2.516(2)
La(2)–O(19)	2.543(2)	La(2)–O(11)	2.547(2)
La(2)–O(20)	2.575(2)	La(2)–O(22)	2.591(2)
La(2)–O(23)	2.636(2)	La(2)–O(18)	2.647(2)

polymer chain containing three different macrocyclic rings **A**–**C** with ring sizes of 11, 10, and 20 atoms, respectively (Figure 9). Within these rings the transannular La···La distances range from 5.73 Å in ring **B** via 7.61 Å in ring **A** to 13.67 Å in ring **C**. The type 2 and type 3 squarate rings are partially overlapped with a centroid···centroid separation of 3.59 Å and a mean interplanar separation of only 3.07 Å, the rings being inclined by ca. 3°. Adjacent polymer chains are cross-linked by O–H···O hydrogen bonds, involving the hydrogen atoms of the aqua ligands and water molecules not utilized in intrachain hydrogen bonding, to form a three dimensional network. The closest structural analogy that we have identified is that of *catena*-tris(squarate)octaaquadieuropium(III)[23] which contains two independent europium centers, each of which is coordinated to three μ-1,2,3-trinucleating and one μ-1,2-binucleating squarate ligands. However, in this latter polymer there is no inversion center, the structure being polar with only two macrocyclic ring sizes, of 16 and 22 atoms.

Clearly, in complex **8**, all of the anilinosquarate ligands have been hydrolyzed to squarate since, in this case, the crystals were found to contain no residual cocrystallized anilinosquarate anions. We conjecture that a similar explanation to that we have proffered in the cases of complexes **5**–**7** (vide supra) is also applicable for complex **8**.

Conclusions

The pattern of bonding and extent of delocalization on the C_4-cycles in both the anisole- and phenylsquarate ligands are similar in spite of the presence of the electron-donating methoxy group in the former. The migration of the oxygen lone pairs on the methoxy group in the anisolesquarate ligand (C_6–$O_{methoxy}$ ca. 1.366 Å), which is significantly less than that observed in the methoxysquarate ligand (C_4–$O_{methoxy}$ = ca. 1.305 Å), does not continue into the C_4-ring. Thus, it seems that the anisole substituent is ineffective in influencing

(23) Petit, J.-F.; Gleizes, A.; Trombe, J.-C. *Inorg. Chim. Acta* **1990**, *167*, 51.

the extent of delocalization on the C_4-cycle in the mono-substituted anisolesquarate ligand because the atom with the mobile electron density is not attached directly to the C_4-cycle. Apparently, only substituents such as anilino, diphe-nylamino, and methoxy, in which the atom with the mobile electron density is directly attached to the C_4-cycle in monosubstituted squarate ligands, are capable of changing the electron density on this cycle.

The slight increase in steric bulk of the substituent on going from the phenyl- to the anisolesquarate ligand causes only small changes in the gross structure of their lanthanide complexes, but the changes in their primary structures are more substantial. Thus, any changes in the steric demand of the substituent, no matter how small, in monosubstituted squarate ligands must be considered when designing poly-meric complexes with specific characteristics. Attempts to form lanthanide complexes of anilinosquarate have in all instances failed due to hydrolysis of the anilino substituent. In the cases of Eu, Gd, and Tb it appears that only partial hydrolysis has occurred, the nonhydrolyzed molecules being retained and attached to the lanthanide inner coordination sphere via hydrogen bonding. This second sphere coordina-tion is not present in the case of La even though all of the experimental and crystallization conditions were the same. We believe that this disparity in the degree of hydrolysis may be related to the ionic radius of La(III) (1.016 Å), which differs appreciably from those of Eu(III), Gd(III), and Tb(III),

which range between 0.923 and 0.950 Å, and thus these metal ions have correspondingly different valence orbital energies. Thus, since the difference between the orbital energies of the monosubstituted squarate ligand and the metal center appear to be important in determining whether hydrolysis of the amine substituent on the squarate ring occurs or not; in the future we will need to investigate further how the orbital energies of these ligands could be tailored to prevent hydrolysis by the judicious selection of the substituent.

The anilinosquarate ligand is the first example of a monosubstituted squarate ligand in which the substituent shows such a wide range of orientations with respect to the C_4-cycle varying from coplanar to an orientation of ca. 27°. In all other such ligands that we have studied, the substituent is either consistently coplanar with the C_4-cycle or oriented at a specific angle to it. At present, the reason for this difference in behavior is unclear, but given the importance of this relative orientation to the hydrolysis of certain substituents on monosubstituted squarate ligands, it clearly warrants further study.

Supporting Information Available: Tables of X-ray data for the complexes in CIF format and thermal ellipsoid plots (Figures S1−S8). This material is available free of charge via the Internet at http://pubs.acs.org.

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