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Article

Complexes of Aminosquarate Ligands with First-Row Transition Metals and Lanthanides: New Insights into Their Hydrolysis

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Attempts at synthesizing first-row transition-metal complexes of the 3-hydroxy-4-[(1′*S*,2′*R*)-(2-hydroxy-1′,2′-diphenylethyl)amino]-3-cyclobutene-1,2-dione ligand in alcoholic solutions resulted in the formation of the monomers $[M(NH_2C_4O_3)_2(H_2O)_4]$ [M = Mn (**1**), Co (**2**), Ni (**3**), Cu (**4**), Zn (**5**)] instead, as a result of the hydrolysis of the ligand. **1**, **2**, and **3** are isomorphous (*C*2/*c*), with the metal atoms octahedrally coordinated to four aqua and two cis aminosquarate ligands. The copper and zinc complexes (**4** and **5**) have the same molecular formula as **1**–**3** but belong to the *C*2/*m* and *P*2(1)/*c* space groups respectively. **4** has square-pyramidal geometry with trans-oriented aminosquarate ligands in the basal plane; aqua ligands complete the coordination sphere. **5** has octahedral geometry, with four aqua and two trans-oriented aminosquarate ligands. Reaction of aqueous solutions of the anilinosquarate ligand with $Ln(NO_3)_3 \cdot xH_2O$ produced the eight-coordinate complexes $\{Sm(\mu\text{-}C_6H_5NHC_4O_3)_3(H_2O)_4 \cdot 3H_2O\}_n$ (**6**), $\{[M(\mu_2\text{-}C_4O_4)(H_2O)_6][C_6H_5NHC_4O_3] \cdot 4H_2O\}_n$ [M = Er (**7**), Yb (**8**)], $\{Sm(C_6H_5NHC_4O_3) (\mu_3\text{-}C_4O_4)(H_2O)_4 \cdot H_2O\}_n$ (**9**), and $\{[\{(C_6H_5NHC_4O_3)_2(H_2O)_5Yb\}_2(\mu\text{-}C_4O_4)] \cdot 4H_2O\}_n$ (**10**). **7** and **8** are isomorphous with the previously reported analogues Eu, Gd, and Tb ionic polymers. The presence of the squarate ligand in **7**–**10** is indicative of some form of hydrolysis of the anilinosquarate ligand during their syntheses. However, hydrolysis was not evident in the synthesis of **6**. The mechanism for the hydrolysis in the syntheses of **1**–**5** is apparently different from that for **7**–**10**.

Introduction

We have synthesized several transition-metal and lanthanide complexes with a variety of monosubstituted squarate ligands in order to fully understand their complexing properties.[1–4] However, some of these ligands containing substituents attached to the C$_4$ cycle on the squarate ring via atoms containing lone pairs were hydrolyzed during synthesis. For example, attempts at synthesizing metal complexes with methoxy-, amino-, dimethylamino-, diethyl-amino-, and anilinosquarate ligands resulted in the formation of compounds containing the unsubstituted squarate moiety.[2,3] Thus, this hydrolysis problem affected our ability to successfully synthesize complexes with these ligands. We therefore needed to understand what was responsible for the phenomenon in order to take the appropriate steps to prevent it. The fact that no hydrolysis occurred with the diphenylaminosquarate ligand suggested that the bulky out-of-plane phenyl groups sterically hindered nucleophilic attack by the water molecule, which is implicated in the hydrolysis.[4] Additionally, the size of the metal ion is also implicated because no hydrolysis occurred during the synthesis of the amino-, dimethylamino-, and diethylaminosquarate complexes of the large lead(II) ion.[5] Then, we had proposed an

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elimination-type mechanism for the hydrolysis. However, when the (2-hydroxy-1′,2′-diphenylethyl)amino group was used as the amino substituent, the hydrolysis appears to follow a different mechanism than that observed for the alkylamino and anilino substituents. In this Article, we report on the structures of five first-row transition-metal aminosquarate complexes, **1**−**5**, which were serendipitously obtained during the attempted syntheses of complexes of (2-hydroxy-1′,2′-diphenylethyl)aminosquarate. We have previously reported on our futile attempts at preparing these complexes directly using the aminosquarate ligand.[2] Additionally, to expand our investigation into the role that cationic size plays in the hydrolysis of the anilinosquarate ligand, we decided to attempt the synthesis of complexes using metal cations of both larger and smaller sizes relative to the Eu(III), Gd(III), and Tb(III) ions, whose reactions with this ligand we have reported on previously.[3] We also discuss the structures of five complexes, **6**−**10**, which were obtained by reacting Sm(III), Er(III), and Yb(III) ions with the anilinosquarate ligand, and mechanisms for the hydrolysis observed during the synthesis of some of these compounds, **1**−**10**.

Experimental Section

Preparation of the Ligands. 3-Hydroxy-4-[(1′S,2′R)-(2-hydroxy-1′,2′-diphenylethyl)amino]-3-cyclobutene-1,2-dione. 3-Hydroxy-4-[(1′S,2′R)-(2-hydroxy-1′,2′-diphenylethyl)amino]-3-cyclobutene-1,2-dione was prepared according to the method of H-B. Zhou et al.[6]

Sodium Anilinosquarate. 3-Anilino-4-hydroxycyclobut-3-ene-1,2-dione (anilinosquarate) was first prepared according to the method of Gauger and Manecke[7] as revised by Neuse and Green.[8] However, the best results were obtained using the following 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 an additional 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 37.80 g (100%) of crude anilinosquarate. The sodium salt of the anilinosquarate ligand was then prepared by dissolving the crude compound (37.80 g, 0.20 mol) in 100 mL of 2M 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: 26.60 g (63%). ^{1}H NMR (400 MHz, DMSO, δ): 6.82 (t, $J = 12.0$ Hz, 1H), 7.19 (m, 2H), 7.66 (d, $J = 12.0$ Hz, 2H), 9.28 (s, 1H).

Preparation of the Complexes.

(a) [M(NH$_2$C$_4$O$_3$)$_2$(H$_2$O)$_4$] [M = Mn (1), Co (2), Cu (4), Zn (5)]. A 10 mL aliquot of an ethanolic solution of M(NO$_3$)$_2$·6H$_2$O (3.24 × 10^{-4} mol) [M = Mn, Cu, Co, Zn] was added to 15 mL of an ethanolic solution of 3-hydroxy-4-[(1′S,2′-

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diphenylethyl)amino]-3-cyclobutene-1,2-dione (0.10 g, 3.24 × 10^{-4} mol). The resulting mixture was filtered and allowed to evaporate slowly at ∼28 °C until crystallization was complete.

[Mn(NH$_2$C$_4$O$_3$)$_2$(H$_2$O)$_4$] (1): colorless plates. Yield: 15%. Anal. Calcd for C$_8$H$_{12}$N$_2$O$_{10}$Mn: C, 27.4; H, 3.4; N, 8.0; Mn, 16.6. Found: C, 27.4; H, 3.5; N, 7.5; Mn, 16.7.

[Co(NH$_2$C$_4$O$_3$)$_2$(H$_2$O)$_4$] (2): pink needles. Yield: 15%. Anal. Calcd for C$_8$H$_{12}$N$_2$O$_{10}$Co: C, 27.1; H, 3.4; N, 7.9; Co, 16.6. Found: C, 27.0; H, 3.8; N, 7.6; Co, 16.7.

[Cu(NH$_2$C$_4$O$_3$)$_2$(H$_2$O)$_4$] (4): yellow prisms. Yield: 35%. Anal. Calcd for C$_8$H$_{12}$N$_2$O$_{10}$Cu: C, 26.7; H, 3.4; N, 7.8; Cu, 17.7. Found: C, 26.9.; H, 3.7; N, 7.5; Cu, 17.6.

[Zn(NH$_2$C$_4$O$_3$)$_2$(H$_2$O)$_4$] (5): colorless plates. Yield: 20%. Anal. Calcd for C$_8$H$_{12}$N$_2$O$_{10}$Zn: C, 25.3; H, 3.4; N, 7.8; Zn, 18.1. Found: C, 25.4.; H, 3.6; N, 7.1; Zn, 18.2.

(b) [Ni(NH$_2$C$_4$O$_3$)$_2$(H$_2$O)$_4$] (3): A 10 mL aliquot of a propan-1-ol solution of Ni(NO$_3$)$_2$·6H$_2$O (6.48 × 10^{-4} mol) was added to 15 mL of a propan-1-ol solution of 3-hydroxy-4-[(1′S,2′R)-(2-hydroxy-1′,2′-diphenylethyl)amino]-3-cyclobutene-1,2-dione (0.10 g, 3.24 × 10^{-4} mol). The resulting mixture was filtered and allowed to evaporate slowly at ∼28 °C until crystallization was complete.

[Ni(NH$_2$C$_4$O$_3$)$_2$(H$_2$O)$_4$] (3): pale-green platy needles. Yield: 10%. Anal. Calcd for C$_8$H$_{12}$N$_2$O$_{10}$Ni: C, 27.1; H, 3.4; N, 7.9; Ni, 16.5. Found: C, 27.7; H, 3.6; N, 7.9; Ni, 16.6.

(c) [Sm(μ-C$_6$H$_5$NHC$_4$O$_3$)$_3$(H$_2$O)$_4$·3H$_2$O]$_n$ (6), and {[Ln(C$_4$O$_4$)-(H$_2$O)$_6$][C$_6$H$_5$NHC$_4$O$_3$]·4H$_2$O}$_n$ [Ln = Er (7), Yb (8)]. A 15 mL aliquot of an aqueous solution of Ln(NO$_3$)$_3$·xH$_2$O (1.58 × 10^{-4} mol) [Ln = Sm, Er, Yb] 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 in a refrigerator at ∼5 °C until crystallization was complete.

[Sm(μ-C$_6$H$_5$NHC$_4$O$_3$)$_3$(H$_2$O)$_4$·3H$_2$O]$_n$ (6): colorless plates. Yield: 10%. Anal. Calcd for C$_{30}$H$_{32}$N$_3$O$_{16}$Sm: C, 42.8; H, 3.8; N, 5.0; Sm, 17.9. Found: C, 42.0; H, 3.0; N, 4.2; Sm, 16.9.

{[Er(μ_2-C$_4$O$_4$)(H$_2$O)$_6$][C$_6$H$_5$NHC$_4$O$_3$]·4H$_2$O}$_n$ (7): pale-pink blocks. Yield: 80%. Anal. Calcd for C$_{14}$H$_{26}$ErNO$_{17}$: C, 26.0; H, 4.0; Er, 25.8; N, 2.2. Found: C, 26.1; H, 3.3; Er, 25.9; N, 2.1.

{[Yb(μ_2-C$_4$O$_4$)(H$_2$O)$_6$][C$_6$H$_5$NHC$_4$O$_3$]·4H$_2$O}$_n$ (8): colorless blocks. Yield: 10%. Anal. Calcd for C$_{14}$H$_{26}$NO$_{17}$Yb: C, 25.7; H, 4.0; N, 2.1; Yb, 26.5. Found: C, 26.2; H, 4.2; N, 2.5; Yb, 27.5.

(d) {Sm(C$_6$H$_5$NHC$_4$O$_3$)(μ_3-C$_4$O$_4$)(H$_2$O)$_4$·H$_2$O}$_n$ (9) and {[{(C$_6$H$_5$NHC$_4$O$_3$)$_2$(H$_2$O)$_5$Yb}$_2$(μ-C$_4$O$_4$)]·4H$_2$O}$_n$ (10). A 15 mL aliquot of an aqueous solution of Ln(NO$_3$)$_3$·xH$_2$O [Ln = Sm, Yb] (1.58 × 10^{-4} mol) was added to 25 mL of an aqueous solution of sodium anilinosquarate (0.10 g, 4.74 × 10^{-4} mol). The resulting solution was filtered and allowed to evaporate slowly in a refrigerator at ca. 5 °C until crystallization was complete.

{Sm(C$_6$H$_5$NHC$_4$O$_3$)(μ_3-C$_4$O$_4$)(H$_2$O)$_4$·H$_2$O}$_n$ (9): colorless blocks. Yield: 20%. Anal. Calcd for C$_{14}$H$_{18}$NO$_{13}$Sm: C, 30.1; H, 3.2; N, 2.5; Sm, 26.9. Found: C, 30.5; H, 2.9; N, 2.4; Sm, 26.0.

{[{(C$_6$H$_5$NHC$_4$O$_3$)$_2$(H$_2$O)$_5$Yb}$_2$(μ-C$_4$O$_4$)]·4H$_2$O}$_n$ (10): colorless blocks. Yield: 18%. Anal. Calcd for C$_{44}$H$_{52}$N$_4$O$_{30}$Yb$_2$: C, 36.1; H, 3.6; N, 3.8; Yb, 23.7. Found: C, 35.0; H, 3.3; N, 3.6; Yb, 23.7.

X-ray Crystallography. Table 1 provides a summary of the crystallographic data for **1**−**10**. X-ray data are reported in CCDC codes 635017 to 635026 respectively. The absolute structure of {Sm(C$_6$H$_5$NHC$_4$O$_3$)(μ_3-C$_4$O$_4$)(H$_2$O)$_4$·H$_2$O}$_n$ (9) was determined by R-factor tests ($R_1^+ = 0.0575$, $R_1^- = 0.0596$) and by use of the Flack parameter ($x^+ = 0.0004$)

Elemental Analysis. C, H, N, Mn, Co, Ni, Cu, Zn, Sm, Er, and Yb analyses were performed by MEDAC Limited, Brunel Science Centre, Egham, Surrey, U.K.

Table 1. Crystallographic Data for **1**−**10**

data	1	2	3	4	5
chemical formula	$C_8H_{12}N_2O_{10}Mn$	$C_8H_{12}N_2O_{10}Co$	$C_8H_{12}N_2O_{10}Ni$	$C_8H_{12}N_2O_{10}Cu$	$C_8H_{12}N_2O_{10}Zn$
solvent				$3H_2O$	
fw	351.14	355.13	354.91	359.74	361.57
T (K)	150(2)	150(2)	150(2)	150(2)	150(2)
space group	$C2/c$	$C2/c$	$C2/c$	$P2(1)/c$	$C2/m$
a (Å)	11.9636(6)	11.7785(6)	11.7186(5)	10.7712(9)	15.0726(11)
b (Å)	11.7190(7)	11.6558(7)	11.6435(5)	9.0358(8)	6.4326(4)
c (Å)	8.9846(5)	8.9119(3)	8.8723(4)	13.1062(11)	6.2557(3)
β (deg)	95.172(3)	94.887(3)	94.796(3)	91.468(5)	97.299(4)
V (Å³)	1254.53(12)	1219.05(10)	1206.35(9)	1275.16(19)	601.66(6)
Z	4	4	4	4	2
ρ_{calcd} (mg/m³)	1.859	1.935	1.954	1.874	1.996
λ (Å)	0.71073	0.71073	0.71073	0.71073	0.71073
μ (mm⁻¹)	1.111	1.468	1.669	1.770	2.102
R1	0.0314	0.0273	0.0271	0.0792	0.0283
wR2	0.0907	0.0654	0.0602	0.2395	0.0731
data	6	7	8	9	10
chemical formula	$C_{30}H_{26}N_3O_3Sm$	$C_{14}H_{18}NO_{13}Er$	$C_{14}H_{18}O_{13}NYb$	$C_{14}H_{16}NO_{12}Sm$	$C_{44}H_{44}N_4OYb_2$
solvent	$3H_2O$	$4H_2O$	$3.125H_2O$	H_2O	$4H_2O$
fw	840.94	647.62	637.63	540.63	1462.98
T (K)	150(2)	150(2)	150(2)	150(2)	150(2)
space group	$P1$	$I2/a$	$P2/c$	$Pbc2(1)$	$P1$
a (Å)	6.58840(10)	16.4975(4)	32.7636(7)	8.2572(3)	7.8499(4)
b (Å)	7.9820(2)	7.5283(2)	7.4876(2)	10.2496(4)	8.1591(3)
c (Å)	32.0154(7)	35.4239(8)	35.4496(8)	41.7883(15)	21.9575(10)
α (deg)	84.0540(12)				82.432(2)
β (deg)	85.9342(14)	96.460(1)	95.9650(10)		89.256(2)
γ (deg)	73.0359(12)				65.1507(2)
V (Å³)	1600.26(6)	4371.65(19)	8649.4(4)	3536.7(2)	1267.28(10)
Z	2	8	16	8	1
ρ_{calcd} (mg/m³)	1.745	1.986	1.959	2.031	1.917
λ (Å)	0.71073	0.71073	0.71073	0.71073	0.71073
μ (mm⁻¹)	1.918	3.925	4.406	3.389	3.771
R1	0.0367	0.0290	0.0585	0.0575	0.0455
wR2	0.0880	0.0699	0.1290	0.1040	0.0894

Table 2. Selected Bond Lengths (Angstroms) and Angles (Degrees) for $[M(NH_2C_4O_3)_2(H_2O)]$M = Mn (**1**), Co (**2**), and Ni (**3**)

$M(NH_2C_4O_3)_2(H_2O)_4$	Mn	Co	Ni
M−O(1)	2.2067(12)	2.1293(12)	2.0957(12)
M−O(5)	2.1585(12)	2.0701(12)	2.0554(12)
M−O(6)	2.1769(12)	2.0926(13)	2.0392(12)
C(1)−C(2)	1.493(2)	1.497(2)	1.493(2)
C(2)−C(3)	1.473(2)	1.468(2)	1.469(2)
C(3)−C(4)	1.434(2)	1.433(2)	1.428(2)
C(1)−C(4)	1.452(2)	1.450(2)	1.449(2)
O(1)−C(1)	1.249(2)	1.256(2)	1.259(2)
O(2)−C(2)	1.238(2)	1.237(2)	1.236(2)
O(3)−C(3)	1.256(2)	1.258(2)	1.260(2)
N(4)−C(4)	1.315(2)	1.315(2)	1.319(2)
O(5)#1−M−O(5)	93.24(6)	93.65(7)	93.04(7)
O(5)#1−M−O(6)	80.88(5)	82.19(5)	82.25(5)
O(5)−M−O(6)	93.60(5)	92.50(5)	92.60(5)
O(5)−M−O(1)	89.84(5)	90.24(5)	90.68(5)
O(6)−M−O(1)	90.69(5)	90.69(5)	91.29(5)
O(6)#1−M−O(1)	95.04(5)	94.94(5)	94.14(5)

Results and Discussion

X-ray Crystal Structure of [M(NH₂C₄O₃)₂(H₂O)₄] [M = Mn (1), Co (2), Ni (3)]. Reaction of ethanolic solutions of M(NO₃)₂·6H₂O [M = Mn, Co, Ni] and 3-hydroxy-4-[(1′S,2′R)-(2-hydroxy-1′,2′-diphenylethyl)amino]-3-cyclobutene-1,2-dione resulted in the formation of isomorphous complexes of the formula {M(NH₂C₄O₃)₂(H₂O)₄}[M = Mn (**1**), Co (**2**), Ni (**3**)] instead of complexes of the [(2-hydroxy-1′,2′-diphenylethyl)amino]squarate ligand. The geometry about the metal atom in **1**, **2**, and **3** is distorted octahedral with cis angles between 80 and 95° (Figure 1, Table 2). Each metal atom is coordinated to two aminosquarate ligands,

which are oriented cis to each other and contain the substituent amino group positioned cis to the ligating O atoms [O(1) and O(1A)]. Four aqua ligands complete the coordination polyhedron about the metal atom.

The lengths of the bonds within the C₄ ring of the aminosquarate ligand are highly consistent for the three complexes. The angles between the NH₂ groups and their associated C₄ rings in **1**−**3** are sufficiently small to suggest coplanarity. It is noteworthy that these NH₂ groups were not further hydrolyzed in spite of this coplanarity, which we suggested as one of the reasons for the hydrolysis observed in our early attempts to synthesize metal complexes with the aminosquarate ligand directly.[2]

The structures of **1**−**3** are stabilized by six types of hydrogen bonds; both intra and intermolecular, the latter resulting in the formation of an extensive 3D network.

X-ray Crystal Structure of [Cu(NH₂C₄O₃)₂H₂O)₄]·3H₂O (4). Reaction of ethanolic solutions of Cu(NO₃)₂·6H₂O and 3-hydroxy-4-[(1′S,2′R)-(2′-hydroxy-1′,2′-diphenylethyl)amino]-3-cyclobutene-1,2-dione resulted in the formation of the aminosquarate, [Cu(NH₂C₄O₃)₂H₂O)₄]·3H₂O, instead of the copper complex of the (2′-hydroxy-1′,2′-diphenylethyl)-aminosquarate ligand. The complex is monomeric and exhibits a distorted square-pyramidal geometry with cis angles in the range of 83.52(19)−99.50(16)° (Figure 2, Table 3). The copper atom in this complex shows a significant Jahn−Teller distortion with four Cu−EnDashO distances [O(1), O(5), O(9), and O(10)] in the range of 1.928(5)−1.990(4) Å. The other two Cu−O distances [O(11) and
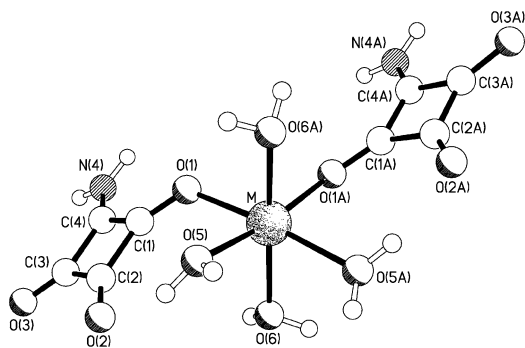
Figure 1. Molecular structure of [M(NH₂C₄O₃)₂(H₂O)₄]M = Mn (**1**), Co (**2**), and Ni (**3**).
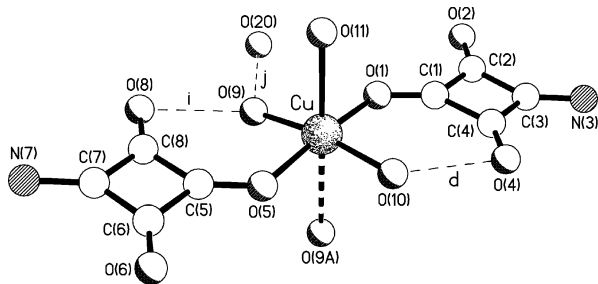
Figure 2. Molecular structure of [Cu(NH₂C₄O₃)₂H₂O)₄]·3H₂O (**4**).

Table 3. Selected Bond Lengths (Angstroms) and Angles (Degrees) for [Cu(NH₂C₄O₃)₂(H₂O)₄]·3H₂O (**4**)

Cu−O(1)	1.986(4)	O(1)−Cu−O(11)	86.70(18)
Cu−O(5)	1.990(4)	O(1)−Cu−O(9)#1	85.89(16)
Cu−O(9)	1.964(4)	O(5)−Cu−O(11)	99.50(16)
Cu−O(9)#1	2.707(5)	O(5)−Cu−O(9)#1	87.95(16)
Cu−O(10)	1.928(5)	O(9)−Cu−O(1)	85.72(19)
Cu−O(11)	2.297(4)	O(9)−Cu−O(11)	93.99(19)
C(1)−C(2)	1.461(8)	O(9)−Cu−O(5)	93.83(19)
C(2)−C(3)	1.435(8)	O(9)−Cu−O(9)#1	79.28(19)
C(3)−C(4)	1.432(9)	O(10)−Cu−O(1)	95.86(19)
C(1)−C(4)	1.459(9)	O(10)−Cu−O(5)	83.52(19)
O(1)−C(1)	1.259(8)	O(10)−Cu−O(11)	96.1(2)
O(2)−C(2)	1.256(7)	O(10)−Cu−O(9)#1	90.86(19)
O(4)−C(4)	1.256(9)		
N(3)−C(3)	1.317(8)		
C(5)−C(6)	1.462(8)		
C(6)−C(7)	1.436(8)		
C(7)−C(8)	1.435(8)		
C(5)−C(8)	1.457(8)		
C(5)−O(5)	1.272(7)		
C(6)−O(6)	1.251(8)		
C(8)−O(8)	1.257(8)		
C(7)−N(7)	1.335(7)		

O(9A)] are much longer at 2.297(4) and 2.707(5) Å, respectively. Thus, instead of being octahedral, the coordination may be better described as being square pyramidal with a weak interaction in the "vacant" sixth site. This weak interaction serves to link the complex into dimer pairs about a center of symmetry.

Each metal center in the complex is coordinated to two aminosquarate ligands and three aqua ligands. The two aminosquarate ligands are oriented trans to each other and are attached via the oxygens O(1) and O(5) in the basal plane. There are also two trans disposed aqua ligands [O(9) and O(10)] in the basal plane. The third aqua ligand occupies the apical position [O(11)] in the square pyramid. This compound is the first-known example of a monosubstituted squarate complex with a five-coordinate metal center. The
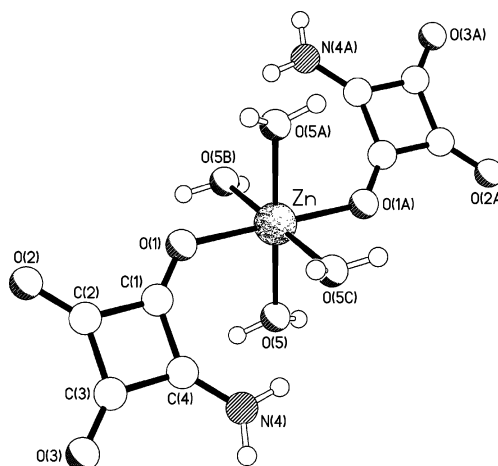
Figure 3. Molecular structure of [Zn(NH₂C₄O₃)₂(H₂O)₄] (**5**).

Table 4. Selected Bond Lengths (Angstroms) and Angles (Degrees) for [Zn(NH₂C₄O₃)₂(H₂O)₄] (**5**)

Zn−O(1)	2.0658(19)
Zn−O(5)	2.1017(14)
C(1)−C(2)	1.464(4)
C(2)−C(3)	1.471(4)
C(3)−C(4)	1.465(4)
C(1)−C(4)	1.452(4)
O(1)−C(1)	1.254(3)
O(2)−C(2)	1.252(3)
O(3)−C(3)	1.243(3)
N(4)−C(4)	1.309(4)
O(5)−Zn−O(1)	91.07(5)
O(5)−Zn−O(1)#1	83.93(5)
O(5)−Zn−O(5)#2	92.84(8)
O(5)−Zn−O(5)#3	87.16(8)

orientation of the amino substituents in **4** is different from that observed for the isomorphous aminosquarates [M(NH₂-C₄O₃)₂(H₂O)₄] [M = Mn (**1**), Co (**2**), Ni (**3**)] (vide supra), in which the amino substituent is oriented cis to the ligating oxygen. We note that **4** is the only example of a complex of a monosubstituted squarate ligand, containing a substituent attached to the C₄ ring via an atom with a mobile electron pair, in which the substituent is oriented trans to the ligating oxygen.[1b,9]

The complex contains 12 different types of hydrogen-bonding interactions, which result in an extensive hydrogen-bonding network comprising both intramolecular and intermolecular N−H···O and O−H···O bonds.

X-ray Crystal Structure of [Zn(NH₂C₄O₃)₂(H₂O)₄] (5). Reaction of ethanolic solutions of Zn(NO₃)₂·6H₂O and 3-hydroxy-4-[(1′S,2′R)-(2′-hydroxy-1′,2′-diphenylethyl)amino]-3-cyclobutene-1,2-dione produced the aminosquarate, [Zn-(NH₂C₄O₃)₂(H₂O)₄], instead of a complex of the starting ligand. Structural studies showed the complex to be monomeric. The geometry at the metal center is slightly distorted octahedral with cis angles in the range of 83.93(5)−92.84-(8)° (Figure 3, Table 4).

The central Zn atom lies on a crystallographic inversion center, which results in the trans orientation of the two-coordinated aminosquarate ligands. Additionally, the substituents [N(4) and N(4A)] on the aminosquarate ligands are

(9) Piggot, P. M. T.; Hall, L. A.; White, A. J. P.; Williams, D. J.; Thompson, L. K. *Inorg. Chem.* **2004**, *43*, 1167.
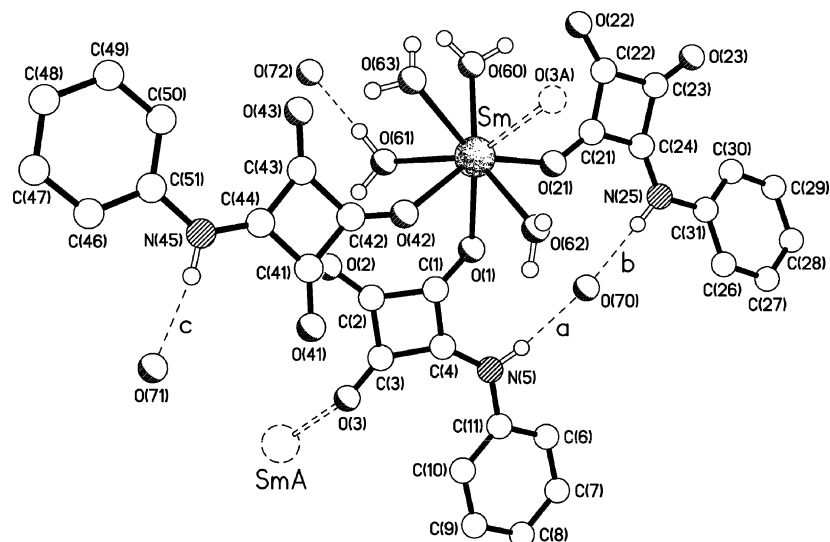
Figure 4. Metal environment in the polymeric complex {Sm(μ-C$_6$H$_5$NHC$_4$O$_3$)$_3$(H$_2$O)$_4$·3H$_2$O}$_n$ (**6**).

Table 5. Selected Bond Lengths (Angstroms) and Angles (Degrees) for {Sm(μ-C$_6$H$_5$NHC$_4$O$_3$)$_3$(H$_2$O)$_4$·3H$_2$O}$_n$ (**6**)[a]

Sm−O(21)	2.342(2)	C(21)−C(24)	1.438(5)	O(21)−Sm−O(3)#1	78.31(9)
Sm−O(3)#1	2.368(2)	C(21)−C(22)	1.452(5)	O(21)−Sm−O(1)	70.50(8)
Sm−O(1)	2.392(2)	O(22)−C(22)	1.252(4)	O(1)−Sm−O(42)	78.45(8)
Sm−O(42)	2.394(2)	C(22)−C(23)	1.480(5)	O(21)−Sm−O(60)	75.84(9)
Sm−O(60)	2.442(2)	O(23)−C(23)	1.235(4)	O(3)#1−Sm−O(60)	79.30(9)
Sm−O(62)	2.468(3)	C(23)−C(24)	1.473(5)	O(21)−Sm−O(62)	85.20(9)
Sm−O(61)	2.478(3)	C(24)−N(25)	1.326(4)	O(3)#1−Sm−O(62)	71.29(8)
Sm−O(63)	2.494(2)	O(41)−C(41)	1.247(4)	O(1)−Sm−O(62)	74.55(8)
O(1)-C(1)	1.260(4)	C(41)−C(44)	1.443(5)	O(42)−Sm−O(62)	71.65(9)
C(1)−C(4)	1.433(5)	C(41)−C(42)	1.461(5)	O(1)−Sm−O(61)	71.26(8)
C(1)−C(2)	1.478(4)	O(42)−C(42)	1.250(4)	O(42)−Sm−O(61)	75.97(9)
O(2)−C(2)	1.232(4)	C(42)−C(43)	1.472(5)	O(3)#1−Sm−O(63)	77.68(9)
C(2)−C(3)	1.484(4)	O(43)−C(43)	1.251(4)	O(42)−Sm−O(63)	72.23(8)
O(3)−C(3)	1.253(4)	C(43)−C(44)	1.460(5)	O(60)−Sm−O(63)	71.34(8)
O(3)−Sm#2	2.368(2)	C(44)−N(45)	1.329(4)	O(61)−Sm−O(63)	81.92(9)
C(3)−C(4)	1.460(5)				
C(4)−N(5)	1.326(5)				
O(21)−C(21)	1.265(4)				

[a] Symmetry transformations used to generate equivalent atoms: #1: $x + 1$, $y − 1$, z; #2: $x − 1$, $y + 1$, z.

oriented cis to the ligating oxygens [O(1) and O(1A)], respectively (Figure 3). The expected cis-directing effect of the aminosquarate ligand is not observed in **5**, although it is exhibited by the analogous methoxysquarate ligand in Zn methoxysquarate [Zn(CH$_3$OC$_4$O$_3$)$_2$(H$_2$O)$_4$].[1b]

This complex is stabilized by a 3D network of both intramolecular and intermolecular N−H···O and O−H···O bonds.

X-ray Crystal Structure of {Sm(μ-C$_6$H$_5$NHC$_4$O$_3$)$_3$(H$_2$O)$_4$· 3H$_2$O}$_n$ (6). The polymeric complex {Sm(μ-C$_6$H$_5$NHC$_4$O$_3$)$_3$-(H$_2$O)$_4$·3H$_2$O}$_n$ (**6**) was synthesized by adding 10% v/v THF to a mixture of aqueous solutions of sodium anilinosquarate and Sm(NO$_3$)$_3$·6H$_2$O. The samarium atom in this complex shows square-antiprismatic geometry and is O-bonded to four aqua and four anilinosquarate ligands; three of the anilinosquarate ligands are crystallographically unique. The anilinosquarate ligand in this complex adopts both pendant and μ-1,3-bridging coordination modes. Each Sm atom along the polymer chain is simultaneously coordinated to two μ-1,3-bridging anilinosquarate ligands [ligating atoms O(1) and O(3A)] and two pendant anilinosquarate groups [ligating atoms O(21) and O(42)] (Figure 4).

The Sm−O$_{anilinosquarate}$ and Sm−O$_{aqua}$ coordination distances fall into two distinct groups, with those to the anilinosquarate oxygen atoms being shorter [2.342(2)−2.394(2) Å] than those to the aqua ligands [2.442(2)−2.494(2) Å] (Table 5). Although the anilinosquarate ligand in **6** adopts two different coordination modes, there are no significant differences in the corresponding C−C bond lengths on the respective C$_4$ rings (Table 5). In one type of pendant ligand, the ligating oxygen atom [O(21)] is cis to the anilino substituent, whereas in the other type, the ligating oxygen atom [O(42)] is trans to the substituent. This is similar to lanthanum diphenylami-nosquarate, La[(C$_6$H$_5$)$_2$NC$_4$O$_3$]$_3$(H$_2$O)$_6$,[4a] but different from all of the other monosubstituted squarate complexes contain-ing pendant groups.[1e,4b] For the three unique anilinosquarate ligands, the inclinations between the C$_4$− and C$_6$− rings are ca. 26, 17, and 5°, respectively [ligating atoms O(1), O(21), and O(42)].

6 exists as continuous 1D polymer chains (the O(3) oxygen atom in one asymmetric unit being bonded to the Sm atom of an adjacent asymmetric unit). These chains are then linked by O−H···O hydrogen bonds to form sheets. Three of the four anilinosquarate ligands hydrogen bond to the waters of
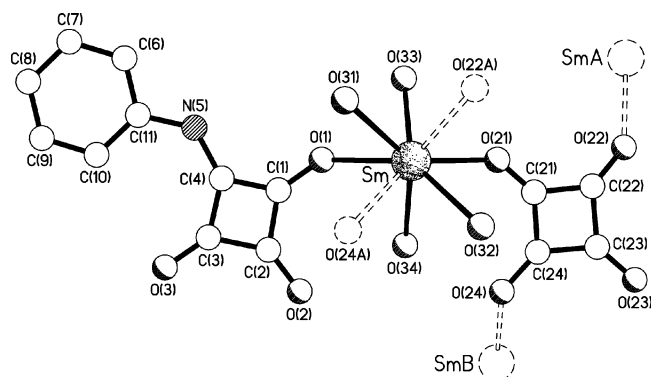
Figure 5. Molecular structure of $\{Sm(C_6H_5NHC_4O_3)(\mu_3-C_4O_3)_3(H_2O)_4 \cdot H_2O\}_n$ (**9**) showing one of the two independent molecules in the crystal. (The positions of the hydrogen atoms were not reliably located).

crystallization; interactions **a**, **b**, and **c** in Figure 4. There are no $\pi-\pi$ interactions in this complex, which, however, adopts a bilayer motif.

X-ray Crystal Structure of $\{[Er(\mu_2-C_4O_4)(H_2O)_6][C_6H_5-NHC_4O_3] \cdot 4H_2O\}_n$ **(7).** $\{[Er(\mu_2-C_4O_4)(H_2O)_6][C_6H_5NHC_4O_3] \cdot 4H_2O\}_n$ is isomorphous with the Eu, Gd, and Tb analogues, which were previously reported.[3] X-ray structural analysis of an ytterbium complex synthesized under the same conditions as **7** revealed a compound of the formula $\{[Yb(\mu_2-C_4O_4)(H_2O)_6][C_6H_5NHC_4O_3] \cdot xH_2O\}_n$ (**8**), which was isostructural with **7** but crystallized in the $P2/c$ space group [cf. $I2/a$ (No. 15) for **7**] (Supporting Information).

X-ray Structure of $\{Sm(C_6H_5NHC_4O_3)(\mu_3-C_4O_4)(H_2O)_4 \cdot H_2O\}_n$ **(9).** X-ray structural analysis of $\{Sm(C_6H_5NHC_4O_3)-(\mu_3-C_4O_4)(H_2O)_4 \cdot H_2O\}_n$ (**9**), obtained on reacting aqueous solutions of sodium anilinosquarate and $Sm(NO_3)_3 \cdot 6H_2O$, revealed two independent molecules in the asymmetric unit. The coordination polyhedron about the samarium atom in each asymmetric unit is square antiprismatic. All of the Sm atoms are bonded to the oxygen atom of one pendant anilinosquarate, three trismonodentate squarate, and four aqua ligands (Figure 5). The presence of the squarate group in **9** suggests that some form of hydrolysis of the anilinosquarate ligand has occurred. The Sm−O distances in the independent molecules are in the range of 2.391(13)−2.474(14) Å and 2.379(12)−2.485(11) Å, respectively (Table 6). In this complex, the ligating oxygen atom [O(1)] on the anilinosquarate ligand is cis to the substituent; the two ring systems have near-planar geometry with an orientation of ca. 4°. The inclination of the two rings is similar to that observed for the pendant ligand with the ligating oxygen trans to the anilino substituent in **6**. Comparison of the bond lengths of the squarate C_4 cycles within the polymer chain is futile, because of the large esd's (Table 6).

In the crystal structure of **9**, the asymmetric units link to one another to produce independent 2D sheets. The compound has a bilayer motif with alternating anilinosquarate and squarate ligands, which results in a zigzag conformation.

The positions of the H atoms were not located, and hence there is no information as to the hydrogen-bonding interactions in this structure.

X-ray Structure of $\{[\{(C_6H_5NHC_4O_3)_2(H_2O)_5Yb\}_2(\mu-C_4O_4)] \cdot 4H_2O\}_n$ **(10).** The reaction between $Yb(NO_3)_3 \cdot 5H_2O$

and sodium anilinosquarate in aqueous solution produced crystals whose structural analysis revealed the formation of the centrosymmetric dimer $\{[\{(C_6H_5NHC_4O_3)_2(H_2O)_5Yb\}_2-(\mu-C_4O_4)] \cdot 4H_2O\}_n$ (**10**), Figure 6. This complex has a crystallographic inversion symmetry, and each ytterbium center shows square-antiprismatic geometry being bonded to five aqua and two pendant anilinosquarate ligands; the coordination polyhedron is completed by an oxygen atom of a μ-1,3-bridging squarate group. Again, the presence of the squarate group in **10** suggests that some form of hydrolysis of the anilinosquarate ligand occurred as was observed for **9** (vide supra). The Yb−O distances fall within the range of 2.263(4)−2.374(4) Å, with those of the aqua [2.295(4)−2.374(4) Å] and squarate [2.309(4) Å] ligands being longer than those of the anilinosquarate [2.263(4)−2.327(4) Å] groups. (Table 7). The anilinosquarate groups have the ligating oxygen oriented cis to the anilino substituent. Comparison of the C−C bond lengths of the squarate and anilinosquarate C_4 cycles in this complex is not feasible because of the large esd's (Table 7). There is a marginal difference in the inclinations of the C_4- and phenyl ring systems in the two independent anilinosquarate ligands [ca. 10 and 15° for the N(5) and N(25) ligands, respectively].

In the tertiary structure, the dimeric Yb_2 units pack to form separate parallel chains. These chains adopt a bilayer motif such that all of the anilinosquarate ligands are located on the outer surface of the chains with the bridging squarate groups and aqua ligands occupying the interior portions. Thus, the complex possesses hydrophobic and hydrophilic layers. There are no intermolecular interactions of note between contiguous chains.

In each Yb_2 dimer, there are two types of intramolecular hydrogen bonds, which occur between the H atoms of two neighboring NH groups and the O atom of a nearby water of crystallization [**a**, H(5)···O(60); **b**, H(25)···O(60)], Figure 6. There is an additional pair of symmetry-related hydrogen bonds in the dimer.

Hydrolysis of Aminosquarate Ligands. We have previously reported on several incidents of metal-mediated hydrolysis of aminosquarate ligands.[1b,2,3] In these examples, the hydrolysis always resulted in the complete removal of the amino substituent to produce squaric acid and the consequent formation of metal complexes containing the squarate group. However, the attempted synthesis of first-row transition-metal complexes of 3-hydroxy-4-[(1′S,2′R)-(2-hydroxy-1′,2′-diphenylethyl)amino]-3-cyclobutene-1,2-dione resulted in the fragmentation of the substituent instead of its complete removal. This is the first example of this type of hydrolysis of an aminosquarate ligand. We propose that a possible mechanism for this hydrolysis involves a metal-mediated S_N1-type reaction as illustrated in Scheme 1. The participation of the metal in the hydrolysis is confirmed by the fact that the ligand remains intact (as evidenced by NMR analysis) in the absence of the metal.

In the cases of the hydrolysis reactions we reported on previously, in which the entire amino substituent was removed, we propose a mechanism involving an elimination-type reaction as follows:

Table 6. Selected Bond Lengths (Angstroms) and Angles (Degrees) for {Sm(C$_6$H$_5$NHC$_4$O$_3$)(μ_3- C$_4$O$_4$)(H$_2$O)$_4$·H$_2$O}$_n$ (**9**)

Sm−O(22)#1	2.391(13)	Sm′−O(22′)#4	2.382(14)	O(22)#1−Sm−O(32)	78.9(5)
Sm−O(32)	2.395(13)	Sm′−O(32′)	2.401(15)	O(32)−Sm−O(34)	78.9(5)
Sm−O(1)	2.399(12)	Sm′−O(24′)#5	2.440(11)	O(1)−Sm−O(34)	72.3(5)
Sm−O(34)	2.434(11)	Sm′−O(34′)	2.447(11)	O(22)#1−Sm−O(21)	76.2(4)
Sm−O(21)	2.447(9)	Sm′−O(21′)	2.447(10)	O(32)−Sm−O(21)	74.5(4)
Sm−O(24)#2	2.453(12)	Sm′−O(33′)	2.467(12)	O(34)−Sm−O(21)	75.4(4)
Sm−O(31)	2.459(12)	Sm′−O(31′)	2.485(11)	O(32)−Sm−O(24)#2	74.5(5)
Sm−O(33)	2.474(11)	O(1′)−C(1′)	1.24(2)	O(1)−Sm−O(24)#2	75.9(5)
O(1)−C(1)	1.28(2)	C(1′)−C(2′)	1.48(2)	O(34)−Sm−O(24)#2	75.9(5)
C(1)−C(4)	1.39(3)	C(1′)−C(4′)	1.50(3)	O(22)#1−Sm−O(31)	73.0(5)
C(1)−C(2)	1.46(2)	O(2′)−C(2′)	1.24(2)	O(1)−Sm−O(31)	75.6(5)
O(2)−C(2)	1.265(19)	C(2′)−C(3′)	1.55(3)	O(24)#2−Sm−O(31)	71.1(4)
C(2)−C(3)	1.47(2)	O(3′)−C(3′)	1.248(18)	O(22)#1−Sm−O(33)	77.9(5)
O(3)−C(3)	1.269(17)	C(3′)−C(4′)	1.42(2)	O(1)−Sm−O(33)	69.3(4)
C(3)−C(4)	1.452(19)	C(4′)−N(5′)	1.32(2)	O(21)−Sm−O(33)	73.6(4)
C(4)−N(5)	1.37(2)	N(5′)−C(11′)	1.435(15)	O(31)−Sm−O(33)	83.9(5)
N(5)−C(11)	1.404(15)	O(21′)−C(21′)	1.314(17)	O(22′)#4−Sm′−O(32′)	77.3(6)
O(21)−C(21)	1.227(15)	C(21′)−C(24′)	1.40(2)	O(1′)−Sm′−O(24′)#5	76.3(5)
C(21)−C(24)	1.46(2)	C(21′)−C(22′)	1.47(2)	O(32′)−Sm′−O(24′)#5	74.5(5)
C(21)−C(22)	1.464(19)	O(22′)−C(22′)	1.282(17)	O(1′)−Sm′−O(34′)	72.7(5)
O(22)−C(22)	1.228(16)	O(22′)−Sm′#2	2.382(14)	O(32′)−Sm′−O(34′)	79.0(5)
C(22)−C(23)	1.48(2)	C(22′)−C(23′)	1.43(2)	O(24′)#5−Sm′−O(34′)	74.4(5)
O(23)−C(23)	1.25(2)	C(22′)−C(24′)	2.03(2)	O(22′)#4−Sm′−O(21′)	77.3(4)
C(23)−C(24)	1.46(2)	O(23′)−C(23′)	1.26(2)	O(32′)−Sm′−O(21′)	75.8(4)
O(24)−C(24)	1.292(16)	C(23′)−C(24′)	1.48(2)	O(34′)−Sm′−O(21′)	74.9(4)
O(22)−Sm#3	2.391(13)	O(24′)−C(24′)	1.274(16)	O(1′)−Sm′−O(33′)	68.4(4)
O(24)−Sm#4	2.453(12)	O(24′)−Sm′#6	2.440(11)	O(22′)#4−Sm′−O(33′)	79.8(6)
				O(21′)−Sm′−O(33′)	72.0(4)
				O(1′)−Sm′−O(31′)	73.0(5)
				O(22′)#4−Sm′−O(31′)	74.6(5)
				O(24′)#5−Sm′−O(31′)	73.5(4)
				O(33′)−Sm′−O(31′)	82.1(5)

Table 7. Selected Bond Lengths (Angstroms) and Angles (Degrees) for {[{(C$_6$H$_5$NHC$_4$O$_3$)$_2$(H$_2$O)$_5$Yb}$_2$ (μ-C$_4$O$_4$)]·4H$_2$O}$_n$ (**10**)

Yb−O(1)	2.263(4)	O(1)−Yb−O(51)	76.43(14)
Yb−O(51)	2.295(4)	O(1)−Yb−O(21)	71.80(14)
Yb−O(41)	2.309(4)	O(41)−Yb−O(21)	76.70(14)
Yb−O(21)	2.327(4)	O(1)−Yb−O(52)	73.69(14)
Yb−O(52)	2.352(4)	O(41)−Yb−O(52)	76.13(13)
Yb−O(53)	2.357(4)	O(21)−Yb−O(52)	75.83(14)
Yb−O(54)	2.370(4)	O(51)−Yb−O(53)	77.67(14)
Yb−O(50)	2.374(4)	O(41)−Yb−O(53)	73.11(14)
O(1)−C(1)	1.256(7)	O(1)−Yb−O(54)	81.54(15)
C(1)−C(4)	1.444(8)	O(51)−Yb−O(54)	80.27(15)
C(1)−C(2)	1.451(8)	O(52)−Yb−O(54)	70.56(15)
O(2)−C(2)	1.247(7)	O(53)−Yb−O(54)	68.41(14)
C(2)−C(3)	1.481(8)	O(51)−Yb−O(50)	70.62(15)
O(3)−C(3)	1.233(8)	O(41)−Yb−O(50)	79.44(14)
C(3)−C(4)	1.464(9)	O(21)−Yb−O(50)	75.99(14)
C(4)−N(5)	1.325(8)	O(53)−Yb−O(50)	80.81(14)
N(5)−C(11)	1.414(6)		
O(21)−C(21)	1.261(7)		
C(21)−C(24)	1.425(8)		
C(21)−C(22)	1.461(8)		
O(22)−C(22)	1.257(7)		
C(22)−C(23)	1.483(8)		
O(23)−C(23)	1.238(7)		
C(23)−C(24)	1.473(8)		
C(24)−N(25)	1.332(8)		
N(25)−C(31)	1.412(6)		
O(41)−C(41)	1.273(7)		
C(41)−C(42)	1.457(8)		
C(41)−C(42)#1	1.464(8)		
O(42)−C(42)	1.251(7)		
C(42)−C(41)#1	1.464(8)		

It is assumed that the carbocation in Scheme 1 would be stabilized by the phenyl ring attached to the carbon bearing the positive charge. The involvement of the carbocation should also facilitate the formation of the kinetically favored metal−amino complex instead of the thermodynamically favored metal−squarate complex. We assume that, under the reaction conditions, complexation of the metal to the aminosquarate ligand occurs before the ligand has an opportunity to hydrolyze to squaric acid. However, in Scheme 2, the mechanism favors the formation of the metal squarate. Here, the hydrolysis of the aminosquarate ligand to squaric acid occurs prior to complexation. This explains why all of the previous attempts to synthesize aminosquarate complexes of first-row transition and lanthanide metals produced complexes of squaric acid instead. In the series of lanthanide anilinosquarate complexes described in this paper (vide supra), there was no evidence of hydrolysis during the synthesis of {Sm(μ-C$_6$H$_5$NHC$_4$O$_3$)$_3$(H$_2$O)$_4$·3H$_2$O}$_n$ (**6**). However, for **7**−**10**, the presence of the squarate ligand suggests that hydrolysis of some of the anilinosquarate starting material occurred during synthesis. It should be noted that pure anilinosquarate, (as evidenced by NMR spectroscopy), was utilized in the syntheses of the lanthanide complexes (**7**−**10**), and we have already shown categorically that the hydrolysis is metal mediated.[3] In **6**, **9**, and **10** the anilinosquarate groups are coordinated, whereas **7** and **8** contain free anilinosquarate anions similar to the previously synthesized isomorphous {[Ln(μ-C$_4$O$_4$)(H$_2$O)$_6$][C$_6$H$_5$NHC$_4$O$_3$]·4H$_2$O}$_n$ (Ln = Eu, Gd, Tb).[3] Thus, it appears that for the anilinosquarate ligand, the hydrolysis to squaric acid occurs sufficiently slowly such that the resulting complexes contain both squarate and anilinosquarate moieties.

The polarity of the solvent system used in the syntheses appears to play some role in determining the extent of the hydrolysis of the anilinosquarate ligand and, consequently, the nature of the complex formed. For instance, Sm complexes **6** and **9** were prepared under identical conditions except that in the synthesis of the former, the solvent used
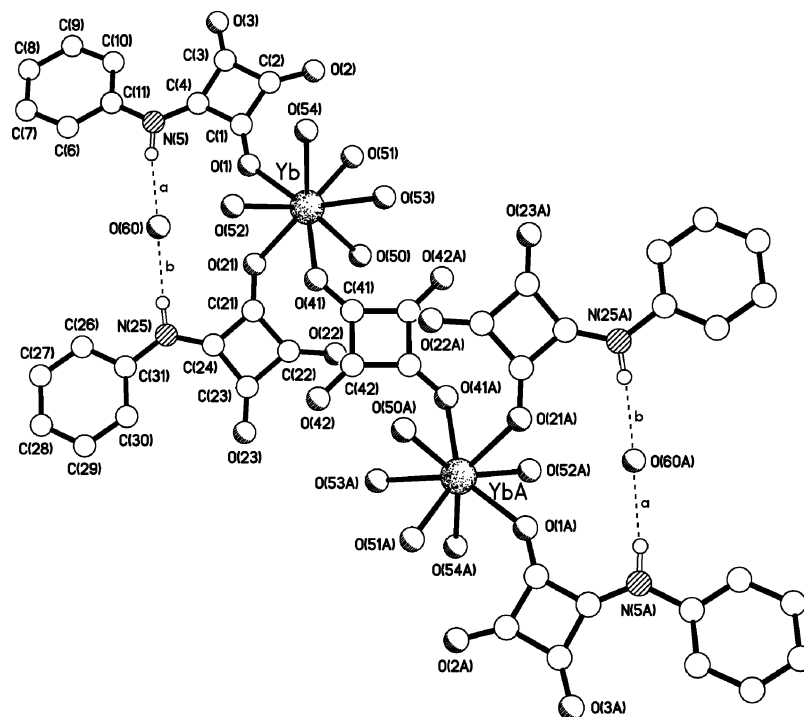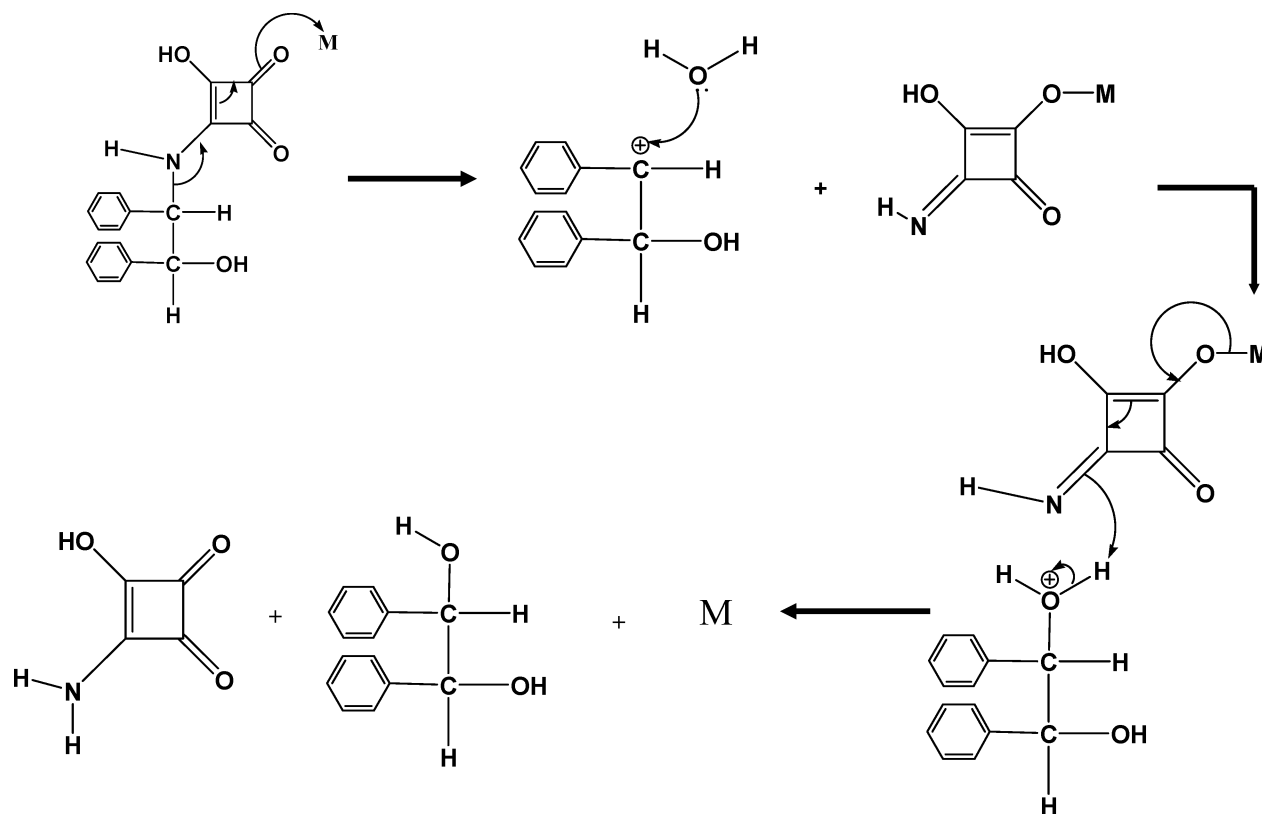
Figure 6. Molecular structure of $\{[\{(C_6H_5NHC_4O_3)_2(H_2O)_5Yb\}_2(\mu\text{-}C_4O_4)]\cdot 4H_2O\}_n$ (**10**). The hydrogen-bonding geometries are [N···O], [H···O] (Å), [N−H···O] (°); (**a**) 2.93, 2.04, 169; (**b**) 3.04, 2.17, 164.

Scheme 1

was a mixture of water and THF, whereas for the latter, water was the solvent. In the less-polar solvent system used in the synthesis of **6**, no hydrolysis of the anilinosquarate ligand was apparent (the complex contained no squarate groups), whereas in the more-polar aqueous medium, the presence of the squarate groups indicates

that hydrolysis occurred to some extent. This is not surprising because any possible proposed mechanistic pathway for the hydrolysis of the anilinosquarate ligand would involve charged intermediates, the stabilities of which would be dependent on the polarity of the solvent system.

Scheme 2
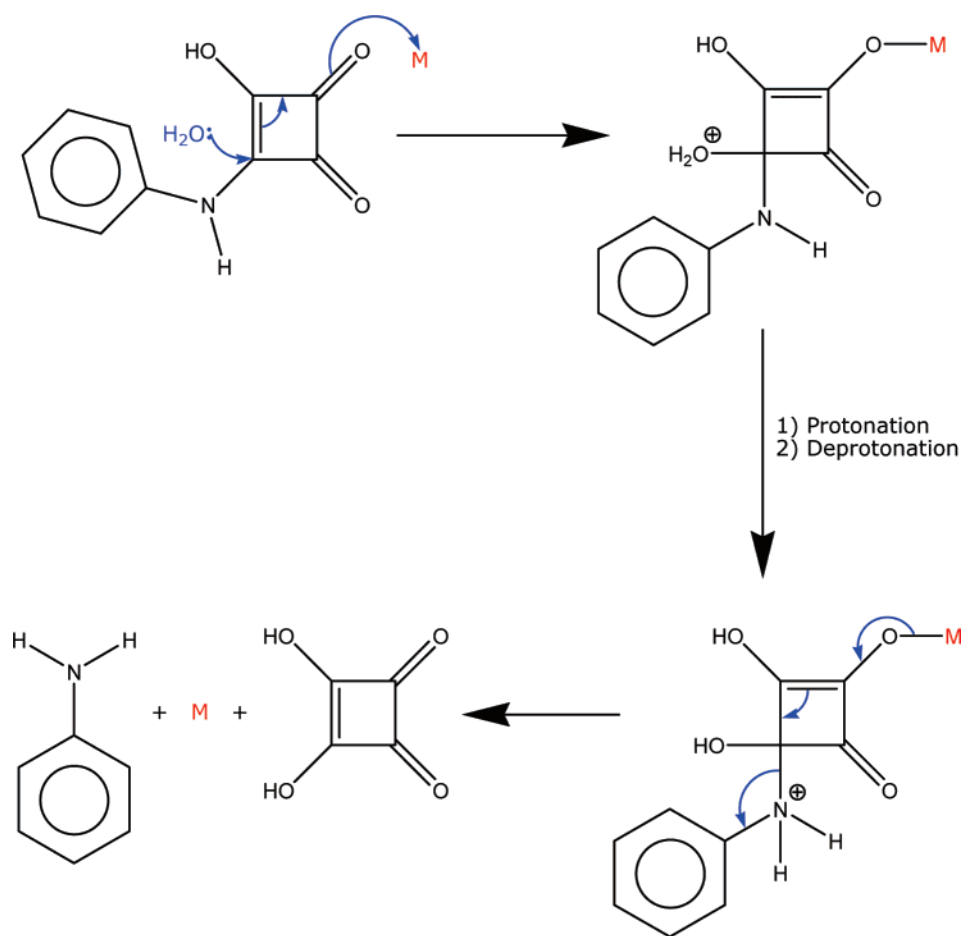
The size and oxidation state of the metal cation also appears to determine whether hydrolysis occurs.[9] Additionally, when hydrolysis occurs, these parameters influence the nature of the product. This is not surprising because the hydrolysis step, regardless of the mechanism, requires electron transfer from the ligand to the metal. We have previously postulated that the efficiency of this electron transfer is dependent on the compatibility of the metal and ligand orbital energies. In the examples being considered, it appears that the susceptibility of the ligand to hydrolysis is invariant for metals within a narrow range of ionic radii, but a noticeable variation occurs outside this range. For example, in the syntheses of Eu, Gd, Tb, and Er complexes with the anilinosquarate ligand, hydrolysis of the anilinosquarate ligand occurs consistently. However, for Sm and Yb, both coordination and hydrolysis of the anilinosquarate ligand can occur simultaneously.

Conclusions

Metal-mediated hydrolysis of the amino substituents of monosubstituted aminosquarates can result in either the complete replacement or the fragmentation of the substituent depending on the mechanistic pathway followed. Whether hydrolysis occurs is dependent on the size and oxidation state of the metal, whereas the nature of the hydrolysis appears to be dependent on the polarity of the solvent system and the identity of the metal. It also appears that the hydrolysis that results in the fragmentation of the amino substituent can possibly be used as a route for the synthesis of complexes of monosubstituted squarate ligands that cannot be achieved directly.

Supporting Information Available: Tables of X-ray data for the complexes in CIF format. This material is available free of charge via the Internet at http://pubs.acs.org.

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