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Lanthanide Complexes of 3-Diphenylamino-4-hydroxycyclobut-3-ene-1,2-dione (Diphenylaminosquarate)

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Complexation of the ligand 3-diphenylamino-4-hydroxycyclobut-3-ene-1,2-dione (diphenylaminosquarate) with metal salts of La, Eu, Gd and Tb produced the first set of lanthanide complexes with a monosubstituted aminosquarate ligand. The lanthanum complex $La[(C_6H_5)_2NC_4O_3]_3(H_2O)_6{\cdot}5H_2O$ (**1**) is monomeric and crystallizes in the triclinic space group $P\bar{1}$, with a nine-coordinate La center bonded to three pendant diphenylaminosquarate groups and six aqua ligands. The Eu, Gd, and Tb complexes $[M(\mu\text{-}(C_6H_5)_2NC_4O_3)((C_6H_5)_2NC_4O_3)(NO_3)(OH_2)_4]_2{\cdot}4H_2O$ (**2**−**4**) are isomorphous (also $P\bar{1}$), each metal atom being nine-coordinate and bridged to its neighbor by two diphenylaminosquarate ligands in a μ-1,2- fashion; the coordination polyhedron around each metal is completed by a pendant diphenylaminosquarate ligand, four aqua ligands, and a chelating nitrate ion. The resistance of the diphenylamino substituent to hydrolysis, *vis-à-vis* the hydrolysis of dialkylamino substituents, is discussed.

Introduction

After successfully synthesising a number of lead complexes with a range of dialkylaminosquarate ligands we attempted the synthesis of an analogous series of complexes with transition metals and lanthanides.[1,2] All of the lead complexes had polymeric structures with the lead atoms arranged linearly and it was anticipated that transition metal and lanthanide compounds with similar structures would exhibit a number of desirable properties, such as antiferromagnetism and semiconductivity, that depend on such linear arrangements of metal atoms.[2,3] However, all of the syntheses that we attempted using dialkylaminosquarate ligands resulted in the hydrolysis of the substituent amino group and in the majority of cases produced the same complexes that were obtained when squaric acid was used.[4] It was eventually demonstrated that this hydrolysis was in fact mediated by the transition and lanthanide metals. We thus decided to investigate whether this problem could be circumvented by using an aromatic amino substituent instead. Although with first row transition metal complexes the accuracy to which C−C bond lengths (and hence the subtle changes in ligand geometry) can be determined by X-ray crystallography is appreciably higher than with lanthanides, we used the latter because of their coordination number complementarity with lead, which is known to form polymeric complexes of the type desired.[1,2] Here we report the results of the reactions between La(III), Eu(III), Gd(III), and Tb(III) ions with the ligand 3-diphenylamino-4-hydroxycyclobut-3-ene-1,2-dione (diphenylaminosquarate) and describe and compare the structures of the complexes formed.

Experimental Section

Preparation of 3-Diphenylamino-4-hydroxycyclobut-3-ene-1,2-dione (Diphenylaminosquarate). Dimethoxycyclobutenedione was prepared according to the method of Cohen and Cohen.[5]

A 100 mL amount of a solution of diphenylamine (5.91 g, 3.50×10^{-2} mol) in reagent grade diethyl ether was added to 100 mL of an equimolar ethereal solution of dimethoxycyclobutenedione (5.00 g, 3.50×10^{-2} mol), and the mixture was filtered. The filtrate was then stirred for 24 h after which it was evaporated on a rotary evaporator to produce a yellow oil. A 100 mL amount of 3 M HCl was then added to a solution of the yellow oil in 200 mL of acetone, and the mixture was stirred for 24 h. This solution was then pumped down on a rotary evaporator to give a green oil which was subsequently dissolved in 200 mL of acetone. The solution of the green oil was then filtered and the filtrate evaporated to dryness to give a green solid which was recrystallized from boiling water (yield, 5 g, 54%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 3.4 (s, 1H), 7.2 (m, 5H), 7.4 (m, 5H).

Preparation of the Metal Complexes. $La[(C_6H_5)_2NC_4O_3]_3(H_2O)_6{\cdot}5H_2O$ (1). A 20 mL amount of a methanolic solution of $LaCl_3{\cdot}7H_2O$ (0.20 g, 5.4×10^{-4} mol) was added to 20 mL of a methanolic solution

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

	1	**2**	**3**	**4**	**5**
chemical formula	$C_{48}H_{42}N_3O_{15}La{\cdot}5H_2O$	$C_{64}H_{56}N_6O_{26}Eu_2{\cdot}4H_2O$	$C_{64}H_{56}N_6O_{26}Gd_2{\cdot}4H_2O$	$C_{64}H_{56}N_6O_{26}Tb_2{\cdot}4H_2O$	$C_{16}H_{11}NO_3{\cdot}H_2O$
fw	1129.8	1701.1	1711.7	1715.1	283.3
space group	$P\bar{1}$ (No. 2)	$P\bar{1}$ (No. 2)	$P\bar{1}$ (No. 2)	$P\bar{1}$ (No. 2)	$P2_1/c$ (No. 14)
T (°C)	−70	−70	−70	−70	20
a (Å)	9.279(1)	9.201(1)	9.196(1)	9.184(1)	7.746(1)
b (Å)	13.371(3)	9.746(1)	9.756(1)	9.741(1)	26.450(2)
c (Å)	20.137(3)	19.056(1)	19.062(1)	19.038(1)	6.910(1)
α (deg)	95.15(1)	78.05(1)	78.14(1)	78.17(1)	−
β (deg)	97.28(1)	82.33(1)	82.33(1)	82.40(1)	92.06(1)
γ (deg)	92.32(2)	88.01(1)	88.05(1)	88.13(1)	−
V (Å^3)	2464.8(8)	1656.8(2)	1658.6(3)	1652.2(2)	1414.8(2)
Z	2	1[a]	1[a]	1[a]	4
ρ_{calcd} (g cm^{-3})	1.522	1.705	1.714	1.724	1.330
λ (Å)	1.54178	1.54178	0.71073	0.71073	1.54178
μ (cm^{-1})	74.0	142.4	20.8	22.2	8.0
R_1[b]	0.082	0.055	0.029	0.033	0.061
wR_2[c]	0.198	0.141	0.065	0.076	0.175

[a] The molecule has crystallographic C_i symmetry. [b] $R_1 = \sum||F_o| - |F_c||/\sum|F_o|$. [c] $wR_2 = \{\sum[w(F_o^2 - F_c^2)^2]/\sum[w(F_o^2)^2]\}^{1/2}$.

of diphenylaminosquarate (0.05 g, 1.9×10^{-4} mol). The resulting light green solution was filtered and left to evaporate slowly at approximately 28(2) °C until crystal formation was complete (yield, 19%). Anal. Calcd for $C_{48}H_{52}N_3O_{20}La$: C, 51.05; H, 4.60; N, 3.71; La, 12.26. Found: C, 51.37; H, 4.26; N, 3.71; La, 12.95.

$[M(\mu\text{-}(C_6H_5)_2NC_4O_3)((C_6H_5)_2NC_4O_3)(NO_3)(OH_2)_4]_2{\cdot}4H_2O$ [M = Eu (2), Gd (3), Tb (4). Since complexes **2**, **3**, and **4** were prepared using similar procedures, only the preparation of **2** is described. A 20 mL amount of a methanolic solution of $Eu(NO_3)_3{\cdot}5H_2O$ (0.24 g, 5.7×10^{-4} mol) was added to 20 mL of a methanolic solution of diphenylaminosquarate (0.05 g, 1.9×10^{-4} mol). The resulting mixture was then filtered and left to evaporate slowly at approximately 28(2) °C until crystallization was complete (yield, ca. 20% in each case). (*Note*: Yields were calculated on the first set of good quality crystals obtained in each case and do not represent the total quantities obtained).

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

Anal. Calcd for $C_{64}H_{64}N_6O_{30}Eu_2$: C, 45.14; H, 3.76; N, 4.93; Eu, 17.87. Found: C, 45.44; H, 3.83; N, 5.32; Eu, 17.73.

Anal. Calcd for $C_{64}H_{64}N_6O_{30}Gd_2$: C, 44.87; H, 3.74; N, 4.90; Gd, 18.37. Found: C, 44.93; H, 3.65; N, 4.84; Gd, 18.66.

Anal. Calcd for $C_{64}H_{64}N_6O_{30}Tb_2$: C, 44.78; H, 3.73; N, 4.90; Tb, 18.53. Found: C, 44.35; H, 3.62; N, 4.89; Tb, 18.30.

NMR Spectrum. The NMR spectrum was measured on a Bruker DRS 400 spectrometer.

Crystallographic Analyses. Table 1 provides a summary of the crystallographic data for compounds **1**−**5**. Structures **1**−**4** were solved by the heavy atom method, that of **5** by direct methods; all refined by full-matrix least-squares based on F^2. In **1**, three of the five included water molecules were found to be disordered over two partial occupancy sites; in each case only the major occupancy atoms were refined anisotropically. The full-occupancy non-hydrogen atoms in all five structures were refined anisotropically with the phenyl rings being treated as optimized rigid bodies. In each structure the C−H hydrogen atoms were placed in calculated positions, assigned isotropic thermal parameters, $U(H) = 1.2U_{eq}(C)$, and allowed to ride on their parent atoms. In **2**−**4**, the hydrogen atoms of both the ligated and the included solvent water molecules were located from ΔF maps, assigned isotropic thermal parameters, $U(H) = 1.2U_{eq}(O)$, and refined subject to an O−H distance constraint. In **5** the O−H hydrogen atoms were located from a ΔF map and refined isotropically subject to an O−H distance constraint; in **1** the O−H hydrogen atoms could not be located. Computations were carried out using the SHELXTL PC program system.[6]

The crystallographic data (excluding structure factors) for the structures reported in Table 1 have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication number CCDC 132370−132374. Copies of the data can be obtained free of charge on application to The Director, CCDC, 12 Union Road, Cambridge, CB12 1EZ, UK (Fax: +44 (1223)336−033; e-mail: teched@ccdc.cam.ac.uk).

Results and Discussion

The X-ray analysis of the complex (**1**) formed between lanthanum chloride and 3-diphenylamino-4-hydroxycyclobut-3-ene-1,2-dione (diphenylaminosquarate) reveals a structure in which the La is coordinated to six aqua ligands and three monodentate diphenylaminosquarate ligands (Figure 1). The geometry at La is monocapped square antiprismatic [O(40) as the capping atom] with two of the diphenylaminosquarate ligands cis and the third [containing O(1)] pseudo-trans. The La−O distances are in the range 2.475(7)−2.616(8) Å, the shortest distance being that to the pseudo-trans positioned diphenylaminosquarate ligand (Table 1). A notable feature of the cis-coordinated diphenylaminosquarate ligands is that coordination is via the oxygen diametrically opposite to the *N*-diphenyl substituent whereas for the trans ligand it is via an oxygen cis to the *N*-diphenyl group. To a degree, the overall geometry of the complex is probably controlled by the intramolecular O−H···O hydrogen bonds present between the aqua ligands and diphenylaminosquarate oxygen atoms. In all three diphenylaminosquarate ligands the plane defined by the amino N and its three substituents is rotated significantly out of the C_4-ring plane (by between 15 and 21°). Similarly the phenyl rings are also all rotated substantially out of the $N-C_3$ plane (by angles ranging between 36 and 50°). The only noticeable pyramidalisation at N (0.06 Å out of plane) occurs in the O(1) ligand where the coordinated oxygen is cis to the diphenylamino group. In the other two ligands the geometry is essentially planar. In all three diphenylaminosquarate ligands the $N-C_4$ distance is significantly shorter than the N−Ph distances. In the pair of cis-oriented diphenylaminosquarate ligands the C_4-rings are inclined by 21° and although having a centroid−centroid separation of 3.66 Å do not overlap sufficiently for any significant $\pi-\pi$ interactions to occur.

An analysis of short intermolecular contacts indicates the formation of hydrogen bonded chains of complexes that extend in the crystallographic *a* direction. However, the failure to locate the aqua hydrogen atoms precludes detailed discussion of O−H···O interactions.

The X-ray analysis of the related Eu, Gd, and Tb complexes formed between $Ln(NO_3)_3{\cdot}5H_2O$ (Ln = Eu, Gd, Tb) and the

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

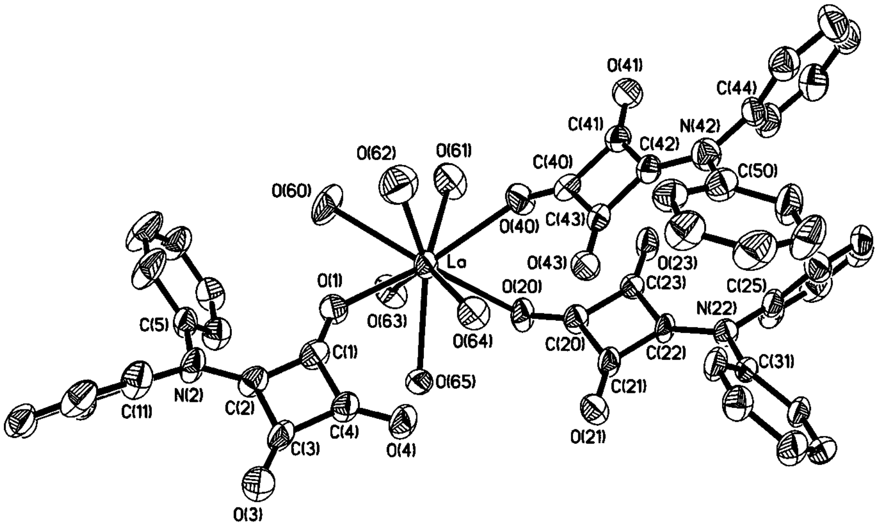

Figure 1. Molecular structure of La[$(C_6H_5)_2NC_4O_3]_3(H_2O)_6$ (**1**) (50% probability ellipsoids).

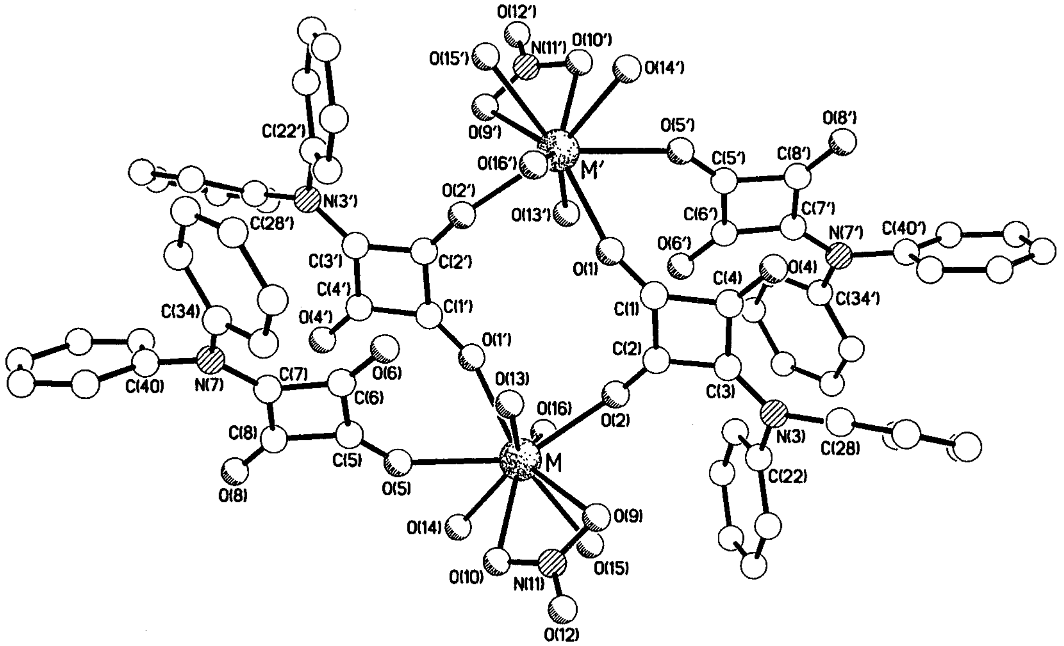

Figure 2. Molecular structure of $[M(\mu\text{-}(C_6H_5)_2NC_4O_3)((C_6H_5)_2NC_4O_3)(NO_3)(OH_2)_4]_2 \cdot 4H_2O$ (M = Eu, Gd, Tb) (**2**−**4**).

diphenylaminosquarate ligand revealed the formation of an isomorphous series of structures that differ significantly from that obtained with La (Figure 2). Here, the diphenylaminosquarate ligand adopts two very different coordination modes. Each lanthanide center is coordinated to three diphenylaminosquarate ligands, four aqua ligands and an asymmetrically bound bidentate nitrate ion in a distorted monocapped square antiprismatic geometry, with one of the nitrate oxygen atoms [O(9)] acting as the capping atom. Only one of the diphenylaminosquarate ligands coordinates via the oxygen atom trans to the diphenylamino substituent (cf two in the La complex) whereas the other two are bismonodentate bridging μ-1,2- to an adjacent Ln center (Figure 2) producing a centrosymmetric dimeric structure.

The Ln−O distances range from 2.314(5) to 2.615(5) Å (Ln = Eu), 2.301(3) to 2.615(3) Å (Ln = Gd), and 2.281(3) to 2.617(3) Å (Ln = Tb), respectively, the shortest distance being to one of the oxygen atoms of the bridging ligands while the longest is to the capping nitrate oxygen (Table 2). There is a small but noticeable decrease in the shortest Ln−O distance as one progresses from Eu to Tb, the shortest Ln−O distance in the monomeric La structure being significantly longer [2.475(7) Å] than any of those in the bridged isomorphous series reflecting the effect of the progressive reduction in ionic radius.

An analysis of the pattern of bonding within the diphenylaminosquarate ligands throughout the isomorphous series of complexes reveals a consistent trend wherein the longer pair of bonds within each C_4-cycle are those not bonded to the diphenylamino group. This effect has also been observed in a series of complexes with the monosubstituted squarate ligands 3-methyl-4-hydroxycyclobut-3-ene-1,2-dione (methylsquarate) and 3-methoxy-4-hydroxycyclobut-3-ene-1,2-dione (methoxysquarate).[7,8] A pattern of delocalization, which is explicable in terms of the resonance hybrid that can be derived from the various resonance forms of the ligand, is apparent and extends between the two trans ring oxygen atoms via the carbon attached to the diphenylamino group. In the case where the coordination to the metal is via the oxygen atom cis to the diphenylamino

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

La−O(1)	2.475(7)	La−O(63)	2.510(8)
La−O(64)	2.524(7)	La−O(40)	2.527(7)
La−O(61)	2.556(8)	La−O(62)	2.559(10)
La−O(20)	2.577(8)	La−O(65)	2.592(7)
La−O(60)	2.616(8)	O(1)−C(1)	1.237(13)
C(1)−C(2)	1.43(2)	C(1)−C(4)	1.476(14)
N(2)−C(2)	1.358(14)	C(2)−C(3)	1.470(14)
O(3)−C(3)	1.215(13)	C(3)−C(4)	1.47(2)
O(4)−C(4)	1.255(13)	O(20)−C(20)	1.268(12)
C(20)−C(23)	1.458(14)	C(20)−C(21)	1.489(13)
O(21)−C(21)	1.250(12)	C(21)−C(22)	1.436(14)
N(22)−C(22)	1.347(12)	C(22)−C(23)	1.456(13)
O(23)−C(23)	1.231(12)	O(40)−C(40)	1.243(13)
C(40)−C(43)	1.48(2)	C(40)−C(41)	1.49(2)
O(41)−C(41)	1.224(13)	C(41)−C(42)	1.464(14)
N(42)−C(42)	1.356(13)	C(42)−C(43)	1.436(14)
O(43)−C(43)	1.249(13)		
O(1)−La−O(63)	94.6(3)	O(1)−La−O(64)	76.6(2)
O(63)−La−O(64)	141.9(3)	O(1)−La−O(40)	138.5(3)
O(63)−La−O(40)	126.3(3)	O(64)−La−O(40)	74.3(2)
O(1)−La−O(61)	138.9(3)	O(63)−La−O(61)	70.1(3)
O(64)−La−O(61)	138.1(3)	O(40)−La−O(61)	63.8(3)
O(1)−La−O(62)	74.4(3)	O(63)−La−O(62)	138.4(3)
O(64)−La−O(62)	75.5(3)	O(40)−La−O(62)	70.1(3)
O(61)−La−O(62)	91.8(4)	O(1)−La−O(20)	131.4(2)
O(63)−La−O(20)	80.7(3)	O(64)−La−O(20)	78.3(3)
O(40)−La−O(20)	69.6(3)	O(61)−La−O(20)	85.0(3)
O(62)−La−O(20)	136.4(3)	O(1)−La−O(65)	68.6(3)
O(63)−La−O(65)	67.8(3)	O(64)−La−O(65)	74.5(3)
O(40)−La−O(65)	128.7(2)	O(61)−La−O(65)	131.2(3)
O(62)−La−O(65)	136.6(3)	O(20)−La−O(65)	64.9(2)
O(1)−La−O(60)	68.2(3)	O(63)−La−O(60)	69.9(3)
O(64)−La−O(60)	135.0(3)	O(40)−La−O(60)	115.9(3)
O(61)−La−O(60)	70.7(3)	O(62)−La−O(60)	68.8(3)
O(20)−La−O(60)	146.6(3)	O(65)−La−O(60)	115.0(3)

group the Ln−O bond is significantly shorter than the corresponding bond length when the metal coordinates via an oxygen atom trans to the group. This can be attributed to the presence of a partial negative charge, through resonance, on the cis-ligating oxygen that shortens the $Ln-O_{cis}$ contact relative to the $Ln-O_{trans}$ distance. A similar pattern is also observed for the ligand in the monomeric La complex where the coordination is via the oxygen atom cis to the diphenylamino group.

The pyramidalization at each of the ligand nitrogen centers is small, ranging between 0.02 and 0.04 Å throughout the series. The inclinations of the plane of the diphenylamino group to the plane of the C_4-cycle in the pendant and bridging diphenylaminosquarate ligands are 19 and 15°, respectively. The inclinations of the associated phenyl rings to the plane of the diphenylamino group are 42 and 49° in the pendant diphenylamino ligand and 39 and 53° in the bridging ligand.

The dimers are linked principally by pairs of O−H···O hydrogen bonds (O···O, H···O 2.92, 2.06 Å; O−H···O, 161°) between the aqua ligand O(14) in one molecule and the nitrate oxygen atom O(12) in another. These interactions are supplemented by additional hydrogen bonds between one of the included water molecules and (i) one of the other aqua ligands O(15) in one dimer (2.68, 1.78 Å; 173°) and (ii) the coordinated diphenylaminosquarate oxygen O(5) in another (3.11, 2.34 Å; 144°) and *vice versa*. All these interactions combine to form hydrogen-bonded tapes, the edges of which are bounded by the diphenylamino groups. Adjacent tapes are cross-linked by O−H···O hydrogen bonds between the other unique included water molecule and (i) the carbonyl oxygen atom O(6) in one tape (2.75, 1.92 Å; 152°) and (ii) the carbonyl oxygen O(8) of the next (2.76, 1.87 Å; 169°), to form sheets, the surfaces of which are populated by the phenyl rings.

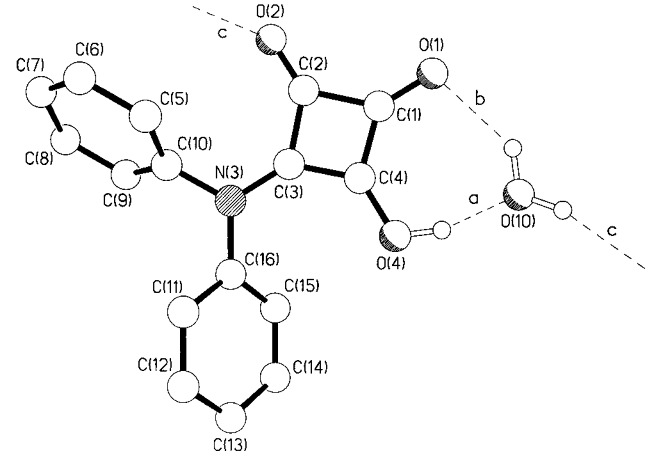

Figure 3. Molecular structure of 3-diphenylamino-4-hydroxycyclobut-3-ene-1,2-dione (**5**). The geometries of the hydrogen bonds involving the included water molecule are: [O···O], [H···O] distances (Å) [O−H···O] angles (deg); (a) 2.54, 1.67, 163; (b) 2.88, 2.13, 140; (c) 2.74, 1.87, 164.

As was observed for the transition metal complexes of both methylsquarate[7] and methoxysquarate,[8] the pattern of bonding in the C_4-ring in complexes **1**−**4** is the same regardless of the coordination mode. However, the individual ring dimensions vary as a function of the nature of the ring substituent, that is, the Δ(C−C) values change. The degree of multiple bond localization observed in the ligand C_4-ring in the first row transition metal complexes with methylsquarate [$\Delta(C-C) = 0.09$ Å] and methoxysquarate [$\Delta(C-C) = 0.05$ Å] is not observed in the lanthanide complexes **1**−**4** where Δ(C−C) is only ca. 0.03 Å. In free ligand **5** (Figure 3) the Δ(C−C) parameter analysis is not meaningful since the ring now effectively contains one short and three long bonds (Table 4). Thus on complexation the loss of the hydroxyl proton and subsequent migration of the electron density into the metal orbitals results in a dramatic change in the pattern of bonding in the C_4-ring. We conclude that in the metal complexes the change in Δ(C−C) is due to the diphenylamino substituent pushing more electron density into the C_4-ring than the methyl and methoxy substituents, resulting in an increased delocalization in the ring and thus a smaller Δ(C−C).

Complexes **1**−**4** represent the first examples of complexes between lanthanides and monosubstituted squarate ligands where the ligands coordinate in a μ-1,2- fashion. So far as we are aware, this type of coordination has only previously been seen in complexes with squaric acid and in the lead (II) complexes of dialkylaminosquarate ligands.[9−11]

A monomeric complex was obtained with La while dimeric complexes were obtained with the other three metals presumably because in the preparation of the La complex lanthanum chloride was used (instead of the metal nitrate as was the case for the Eu, Gd, and Tb species) since it gave better quality crystals. Preparation of the Eu complex using europium chloride instead of the nitrate gave a crystalline product [$a = 9.159(1)$ Å, $b = 13.481(1)$ Å, $c = 20.280(2)$ Å, $\alpha = 96.290(9)°$, $\beta = 96.20(1)°$, $\gamma = 93.510(8)°$, $V = 2467.3(4)$ Å^3] isomorphous with La-$[(C_6H_5)_2NC_4O_3]_3(H_2O)_6{\cdot}5H_2O$ (**1**). The chloride ion obviously

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Table 3. Selected Bond Lengths (Å) and Angles (deg) for Complexes **2**−**4**

	2 [M = Eu]	**3** [M = Gd]	**4** [M = Tb]		**2** [M = Eu]	**3** [M = Gd]	**4** [M = Tb]
M−O(1′)	2.372(5)	2.365(3)	2.350(3)	M−O(2)	2.314(5)	2.301(3)	2.281(3)
M−O(5)	2.509(5)	2.503(3)	2.488(3)	M−O(9)	2.615(5)	2.615(3)	2.617(3)
M−O(10)	2.506(5)	2.502(3)	2.488(3)	M−O(13)	2.416(5)	2.403(3)	2.390(3)
M−O(14)	2.449(4)	2.438(3)	2.421(3)	M−O(15)	2.416(5)	2.397(3)	2.380(3)
M−O(16)	2.510(5)	2.498(3)	2.487(3)	C(1)−O(1)	1.233(8)	1.234(5)	1.240(5)
C(1)−C(2)	1.471(9)	1.472(5)	1.465(6)	C(1)−C(4)	1.496(9)	1.487(5)	1.486(6)
C(2)−O(2)	1.248(8)	1.251(5)	1.251(5)	C(2)−C(3)	1.439(9)	1.442(5)	1.442(6)
C(3)−N(3)	1.353(9)	1.344(5)	1.345(5)	C(3)−C(4)	1.449(10)	1.454(5)	1.456(6)
C(4)−O(4)	1.237(8)	1.231(5)	1.230(5)	C(5)−O(5)	1.238(9)	1.231(5)	1.232(5)
C(5)−C(6)	1.465(10)	1.476(5)	1.479(6)	C(5)−C(8)	1.488(10)	1.493(5)	1.499(6)
C(6)−O(6)	1.256(9)	1.245(5)	1.242(5)	C(6)−C(7)	1.429(10)	1.448(5)	1.446(6)
C(7)−N(7)	1.371(9)	1.346(5)	1.355(6)	C(7)−C(8)	1.443(10)	1.458(5)	1.462(6)
C(8)−O(8)	1.230(9)	1.224(5)	1.219(5)				
O(2)−M−O(1′)	82.3(2)	82.30(10)	82.02(11)	O(2)−M−O(15)	85.3(2)	85.10(10)	84.80(11)
O(1′)−M−O(15)	141.4(2)	141.27(10)	141.28(11)	O(2)−M−O(13)	79.1(2)	79.00(10)	78.80(12)
O(1′)−M−O(13)	79.0(2)	78.95(10)	78.91(11)	O(15)−M−O(13)	134.0(2)	133.91(10)	133.53(11)
O(2)−M−O(14)	140.4(2)	140.70(10)	140.73(11)	O(1′)−M−O(14)	96.6(2)	96.49(9)	97.10(11)
O(15)−M−O(14)	71.0(2)	71.42(10)	71.47(11)	O(16)−M−O(9)	131.2(2)	131.21(9)	131.54(10)
O(13)−M−O(14)	139.8(2)	139.63(10)	139.89(12)	O(2)−M−O(10)	125.9(2)	126.10(9)	126.19(11)
O(1′)−M−O(10)	139.3(2)	139.33(10)	139.49(11)	O(15)−M−O(10)	75.8(2)	75.94(10)	75.99(11)
O(13)−M−O(10)	79.0(2)	79.28(11)	79.44(12)	O(14)−M−O(10)	79.3(2)	78.94(9)	78.56(11)
O(2)−M−O(5)	145.0(2)	145.08(9)	145.03(11)	O(5)−M−O(9)	112.7(2)	112.68(9)	112.70(11)
O(1′)−M−O(5)	70.4(2)	70.49(10)	70.61(11)	O(15)−M−O(5)	129.7(2)	129.81(10)	130.16(11)
O(13)−M−O(5)	74.5(2)	74.72(10)	74.99(11)	O(14)−M−O(5)	66.6(2)	66.15(9)	66.27(10)
O(10)−M−O(5)	70.9(2)	70.83(10)	70.91(11)	O(10)−M−O(9)	49.8(2)	49.99(9)	50.04(10)
O(2)−M−O(16)	74.2(2)	74.31(9)	74.50(11)	O(1′)−M−O(16)	69.4(2)	69.58(9)	69.46(10)
O(15)−M−O(16)	72.1(2)	71.77(9)	71.96(10)	O(14)−M−O(9)	120.0(2)	120.02(9)	119.70(10)
O(13)−M−O(16)	140.7(2)	140.83(10)	140.79(11)	O(14)−M−O(16)	68.6(2)	68.67(9)	68.66(11)
O(10)−M−O(16)	140.3(2)	139.85(9)	139.74(10)	O(15)−M−O(9)	67.7(2)	67.81(9)	67.71(10)
O(5)−M−O(16)	113.9(2)	113.88(9)	113.53(10)	O(2)−M−O(9)	76.1(2)	76.11(9)	76.16(10)
O(1′)−M−O(9)	141.9(2)	141.91(9)	141.63(11)	O(13)−M−O(9)	66.5(2)	66.45(10)	66.23(11)

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

O(1)−C(1)	1.223(3)	C(1)−C(4)	1.460(4)
C(1)−C(2)	1.503(3)	O(2)−C(2)	1.210(3)
C(2)−C(3)	1.479(3)	N(3)−C(3)	1.348(3)
N(3)−C(16)	1.425(2)	N(3)−C(10)	1.425(2)
C(3)−C(4)	1.398(3)	O(4)−C(4)	1.309(3)
O(1)−C(1)−C(4)	136.7(2)	O(1)−C(1)−C(2)	135.5(2)
C(4)−C(1)−C(2)	87.7(2)	O(2)−C(2)−C(3)	136.9(2)
O(2)−C(2)−C(1)	134.9(2)	C(3)−C(2)−C(1)	88.1(2)
C(3)−N(3)−C(16)	121.5(2)	C(3)−N(3)−C(10)	119.3(2)
C(16)−N(3)−C(10)	119.1(2)	N(3)−C(3)−C(4)	136.6(2)
N(3)−C(3)−C(2)	132.4(2)	C(4)−C(3)−C(2)	91.1(2)
O(4)−C(4)−C(3)	132.9(2)	O(4)−C(4)−C(1)	134.0(2)
C(3)−C(4)−C(1)	93.0(2)	C(9)−C(10)−N(3)	120.2(2)
C(5)−C(10)−N(3)	119.8(2)	C(15)−C(16)−N(3)	121.1(2)
C(11)−C(16)−N(3)	118.8(2)		

does not have the ability to coordinate bidentately whereas the nitrate ion can. It is not readily apparent why polymerization has not occurred in any of these complexes.

Resistance of the Substituent to Hydrolysis. The hydrolysis of the substituent dialkylamino groups that occurred during the attempted syntheses of transition metal and lanthanide complexes with dialkylaminosquarate ligands[4] does not occur when diphenylaminosquarate is used. A comparison of the N−C_4 bond lengths in dimethylaminosquarate [1.300(2) Å][4] and diphenylaminosquarate [1.348(3) Å, Table 4, Figure 3] shows that in both cases migration of the nitrogen lone pairs into the C_4-ring occurs though the degree is clearly greater in the former. The analogous distance in the diphenylaminosquarate ligands in complexes **1**−**4** [ca. 1.345(5) Å, Tables 2 and 3] is again short, and indicates that a similar migration also occurs here. The reduced susceptibility to hydrolysis of **5** cf. dimethylaminosquarate is a consequence of two major factors, one electronic and the other steric. First, the near coplanarity of the amino group with the C_4-ring in dimethylaminosquarate (ca. 2°) compared with **5** (11°) and complexes of the latter (15−21°) facilitates electron migration from the amino group. Second, the steric hindrance resulting from the out-of-plane tilting of the phenyl groups (in the range 35−50° in **1**−**4**) shields the substituted ring carbon atom from nucleophilic attack.

Conclusions

In this paper we have reported the first set of complexes of a monosubstituted squarate ligand with metals of large coordination numbers. These lanthanide complexes of diphenylaminosquarate have provided important additional information on the complexing properties of monosubstituted squarate ligands. For example it is now apparent, after comparison with complexes of methoxysquarate and methylsquarate, that substituents possessing lone pairs that can migrate into the C_4-ring have a profound effect on the extent of delocalization within the ring. We also now have a substantially improved understanding of the hydrolysis problems caused by such substituents and are thus now in a much better position to predict those most likely to facilitate the formation of complexes with the desired semiconducting and molecular magnetic properties.

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Supporting Information Available: X-ray crystallographic files, in CIF format, containing data for the structures of **1**−**5** and Figures S1−S4 showing packing diagrams and coordination polyhedra of structures **1**−**4** are available free of charge via the Internet at http://pubs.acs.org.

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