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Lanthanide(III)–copper(II) squarates: synthesis, crystal structure, magnetism and thermal behaviour of $[La_2Cu(C_4O_4)_4(H_2O)_{16}]\cdot 2H_2O$ and $[Gd_2Cu(C_4O_4)_4(H_2O)_{12}]\cdot 2H_2O$*

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Abstract

$[La_2Cu(C_4O_4)_4(H_2O)_{16}]\cdot 2H_2O$ and $[Gd_2Cu(C_4O_4)_4(H_2O)_{12}]\cdot 2H_2O$ were obtained as single crystals from a mixture of squaric acid and metal chlorides in water. The structures, determined from X-ray diffraction data, are made of heterobimetallic layers in which hydrated Ln(III) and Cu(II) cations are related by squarate anions, according to a scheme which depends on the lanthanoid. Both compounds were submitted to thermal gravimetric and differential analyses in an oxygenated atmosphere, yielding Ln_2CuO_4 oxides as final decomposition products. The magnetic study of $[Gd_2Cu(C_4O_4)_4(H_2O)_{12}]\cdot 2H_2O$ showed no significant spin coupling between Gd(III) and Cu(II).

Introduction

Ligands able to associate two different cations of block-d and/or block-f elements into ordered one- or two-dimensional systems are worth studying. We used the ligands dithiooxalate $(S_2C_2O_2)^{2-}$, and dithiosquarate $(S_2C_4O_2)^{2-}$, to develop systems in which either two block-d [1] or one block-d and one block-f [2] elements were orderly associated into polymeric or oligomeric chains. More complicated, occasionally two-dimensional, chaining was obtained by using an extra ligand such as glycine, alanine, oxalate or squarate [3]. Due to their planar tetradentate morphology, the ligands squarato, $(C_4O_4)^{2-}$, and dithiosquarato, $(S_2C_4O_2)^{2-}$, are of special interest when looking for two-dimensional heterometallic systems. The systematic study of lanthanide squarates [4], especially those prepared under pseudo hydrothermal conditions [5], confirmed the ability of the squarate ligand to give rise to two-dimensional arrays with various coordination modes including chelation and μ-bridging.

Our interest in molecular ferromagnet [6] led us to use the squarate ligand to prepare two-dimensional heterobimetallic complexes. We chose to work on the pairs Cu(II)–Mn(II) and Cu(II)–Gd(III). This latter choice was also dictated by the recent interest aroused from copper oxide superconducting ceramics and we extended our study to the Cu(II)–La(III) and Cu(II)–Y(III) complexes. Thus the thermal decomposition of the Cu(II)–Ln(III) complexes were analyzed in view of their potential use as precursors of the oxides via soft chemistry. The results concerning Cu(II)–Mn(II) will be published elsewhere. We present here results concerning the Cu(II)–La(III) and Cu(II)–Gd(III) complexes. The yttrium derivative will not be further evoked since it was found to be isostructural with the gadolinium one.

Experimental

Synthesis and characterization

$[La_2Cu(C_4O_4)_4(H_2O)_{16}]\cdot 2H_2O$

0.2 mmol of squaric acid in 30 ml of water was added to a mixed solution of copper chloride (0.4 mmol) and lanthanum chloride (0.6 mmol) in 20 ml of water at 30–40 °C under stirring. After a few minutes, a yellow precipitate appeared and was filtered. Upon evaporation, the solutions yielded yellow crystals. Elemental

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analyses, carried out by the Laboratoire Central de Micro-analyse du CNRS (Lyon), were consistent with the formula $La_2Cu(C_4O_4)_4(H_2O)_{18}$. *Anal.* Found: La, 24.71: Cu, 5.64; C, 17.49; H, 3.44. Calc. for $La_2CuC_{16}H_{36}O_{34}$: La, 24.97; Cu, 5.70; C, 17.24; H, 3.23%.

$[Gd_2Cu(C_4O_4)_4(H_2O)_{12}]\cdot 2H_2O$

0.5 mmol of squaric acid in 40 ml of water was added to a mixed solution of copper chloride (0.7 mmol) and gadolinium chloride (0.3 mmol) in 260 ml of water. Upon evaporation, the yellow-greenish solution yielded green crystals. Elemental analyses were consistent with the formula $Gd_2Cu(C_4O_4)_4(H_2O)_{14}$. *Anal.* Found: Gd, 29.33; Cu, 6.53; C, 18.05; H, 2.59. Calc. for $Gd_2CuC_{16}H_{28}O_{30}$: Gd 29.16; Cu, 5.89; C, 17.82; H, 2.62%.

In the following, the compounds are abbreviated $[La_2Cu]$ and $[Gd_2Cu]$, respectively.

Crystal structure determinations

The crystal systems, accurate cell constants, space groups and intensity data were obtained from single crystals mounted on an Enraf-Nonius CAD4 diffractometer. The crystal data and conditions of intensity measurement and structure determination are gathered in Table 1. Both compounds crystallize in the monoclinic system with systematic absences relevant of space groups $P2_1/c$ for $[La_2Cu]$ and $C2/c$ or Cc for $[Gd_2Cu]$. The data were corrected for absorption (empirical corrections). The structure determinations were carried out by using the Patterson and Fourier map techniques, and refined by applying the full-matrix, least-squares techniques using computer DEC VAX 11-730 and programs given in ref. 7. Throughout the refinement, the minimized function was $\Sigma(|F_o|-|F_c|)^2$ where $|F_o|$ and $|F_c|$ are the observed and calculated structure factor amplitudes. The atomic scattering factors and anomalous terms are those of Cromer and Waber [8]. The non-H atoms were refined anisotropically. All water H atoms were localized and introduced in the refinements as fixed contributors. No significant feature appeared in the final difference-Fourier maps. The final reliability factors and largest (variable shift)/(e.s.d.) ratios appear in Table 1. The atomic positional parameters and equivalent isotropic thermal coefficients are listed in Tables 2 and 3, respectively.

Magnetic susceptibility measurement

Magnetic susceptibility measurements in the 4–300 K temperature range were carried out with a Faraday-type magnetometer equipped with a helium continuous flow cryostat at the Laboratoire de Chimie de Coordination du C.N.R.S. de Toulouse. $HgCo(NCS)_4$ was used as a susceptibility standard.

Thermal analyses

Thermogravimetry analyses (TGA) were carried out on a SETARAM B85 microbalance controlled by a SETARAM TGC85 programmer. Thermal decomposition were recorded for 30–35 mg samples in a mixed (He, O_2) flow with a heating rate of 5 °/min. A SETARAM M5 microanalyser was used for differential

TABLE 1. Crystal data for $[La_2Cu(C_4O_4)_4(H_2O)_{16}]\cdot 2H_2O$ and $[Gd_2Cu(C_4O_4)_4(H_2O)_{12}]\cdot 2H_2O$

	$[La_2Cu]$	$[Gd_2Cu]$
Crystal system	monoclinic	monoclinic
Space group	$P2_1/c$	$C2/c$
a (Å)	6.780(2)	13.784(1)
b (Å)	32.311(4)	8.219(1)
c (Å)	8.162(2)	26.268(2)
β (°)	111.55(2)	94.20(7)
V (Å^3)	1663(1)	2968(2)
Z	2	4
Molecular weight	1113.4	1078.1
ρ_{calc} (g/cm^3)	2.22	2.41
$\mu(\lambda$ Mo K$\alpha)$ (cm^{-1})	32.59	52.70
Scan mode	θ–0.67θ	θ–2θ
Take-off angle (°)	2.4	3.3
Max. Bragg angle (°)	28	32
Reflections collected	3246	5123
Reflections used	2603 ($I>2\sigma(I)$)	4241 ($I>3\sigma(I)$)
Variables	241	224
Weighting scheme: w^{-1}	$\sigma^2(F_o)+(0.015F_o)^2+0.1$	$\sigma^2(F_o)+(0.005F_o)^2+1$
Max. (variable shift)/(e.s.d.)	0.01	0.01
$R=\Sigma(\|F_o\|-\|F_c\|)/\Sigma F_o$	0.018	0.024
$R_w=[\Sigma w(\|F_o\|-\|F_c\|)^2/\Sigma wF_o^2]^{1/2}$	0.028	0.028
Goodness of fit	1.03	0.95

TABLE 2. Final atomic fractional coordinates and equivalent isotropic displacement parameters for $[Gd_2Cu(C_4O_4)_4(H_2O)_{12}]\cdot 2H_2O$

Atom	*x*/*a*	*y*/*b*	*z*/*c*	*B* (Å^2)
Gd	0.67302(1)	0.50993(2)	0.31515(1)	1.076(2)
Cu	1/2	1/2	1/2	1.536(9)
Ow(1)	0.7835(2)	0.7293(3)	0.3208(1)	1.84(4)
Ow(2)	0.6456(2)	0.5843(3)	0.2257(1)	2.00(5)
Ow(3)	0.5142(2)	0.4299(3)	0.3388(1)	1.67(4)
Ow(4)	0.7354(2)	0.2985(3)	0.3704(1)	2.17(5)
Ow(5)	0.6113(2)	0.3900(4)	0.4724(1)	2.79(5)
Ow(6)	0.4373(2)	0.5750(3)	0.4166(1)	1.95(5)
Ow(7)	0.5922(2)	1.0994(4)	0.5872(1)	2.24(5)
O(11)	0.8190(2)	0.4142(3)	0.27711(9)	1.52(4)
O(21)	0.9314(2)	0.2460(3)	0.1859(1)	1.83(4)
O(31)	0.9884(2)	0.6050(3)	0.1459(1)	2.21(5)
O(41)	0.8714(2)	0.7700(3)	0.23354(9)	1.57(4)
O(12)	0.5714(2)	0.7066(3)	0.5052(1)	1.98(5)
O(22)	0.6746(2)	0.5967(3)	0.40176(9)	1.77(4)
O(32)	0.7477(2)	0.9661(3)	0.38846(9)	1.81(4)
O(42)	0.6404(3)	1.0694(3)	0.4902(1)	2.83(6)
C(11)	0.8656(2)	0.4662(4)	0.2406(1)	1.23(5)
C(21)	0.9170(2)	0.3882(4)	0.2001(1)	1.27(5)
C(31)	0.9423(2)	0.5502(4)	0.1810(1)	1.33(5)
C(41)	0.9897(2)	0.6251(4)	0.2211(1)	1.14(5)
C(12)	0.6204(3)	0.7733(4)	0.4726(1)	1.46(5)
C(22)	0.6668(3)	0.7281(4)	0.4265(1)	1.35(5)
C(32)	0.6996(3)	0.8943(4)	0.4206(1)	1.39(5)
C(42)	0.6518(3)	0.9421(4)	0.4665(1)	1.62(5)

TABLE 3. Final atomic fractional coordinates and equivalent isotropic displacement parameters for $[La_2Cu(C_4O_4)_4(H_2O)_{16}]\cdot 2H_2O$

Atom	*x*/*a*	*y*/*b*	*z*/*c*	*B* (Å^2)
La	0.03606(3)	0.15709(1)	0.33443(2)	1.044(3)
Cu	0	0	0	1.41(1)
Ow(1)	−0.0232(4)	0.20581(8)	0.0612(3)	2.31(5)
Ow(2)	0.3833(4)	0.13637(8)	0.5803(3)	2.27(5)
Ow(3)	0.2695(4)	0.13236(8)	0.1715(3)	2.13(5)
Ow(4)	−0.2518(4)	0.12994(8)	0.0472(3)	2.04(5)
Ow(5)	−0.2596(4)	0.11998(8)	0.4160(3)	2.05(5)
Ow(6)	0.0549(4)	0.1871(1)	0.6328(3)	3.11(6)
Ow(7)	−0.2118(4)	0.03762(7)	0.0340(3)	2.06(5)
Ow(8)	0.2767(4)	0.05168(8)	0.0558(3)	1.90(5)
Ow(9)	−0.1050(5)	0.10672(9)	−0.2039(4)	3.40(7)
O(11)	0.2674(4)	0.21844(8)	0.3784(3)	2.20(5)
O(21)	0.6790(4)	0.19657(7)	0.7251(3)	2.00(5)
O(31)	0.7510(4)	0.29417(8)	0.8146(3)	2.08(5)
O(41)	0.3817(4)	0.31676(7)	0.4463(3)	1.86(5)
O(12)	0.1017(4)	−0.01815(7)	0.2467(3)	1.83(5)
O(22)	0.0721(4)	0.07893(7)	0.3444(3)	1.71(5)
O(32)	0.3968(4)	0.05985(8)	0.7458(3)	2.15(5)
O(42)	0.3747(4)	−0.03795(7)	0.6489(3)	2.06(5)
C(11)	0.4061(5)	0.2391(1)	0.4950(4)	1.45(6)
C(21)	0.5867(5)	0.2295(1)	0.6533(4)	1.42(6)
C(31)	0.6235(5)	0.2735(1)	0.6904(4)	1.48(6)
C(41)	0.4520(5)	0.2834(1)	0.5261(4)	1.34(6)
C(12)	0.1721(5)	0.0046(1)	0.3845(4)	1.26(6)
C(22)	0.1651(5)	0.0477(1)	0.4286(4)	1.26(6)
C(32)	0.3064(5)	0.0390(1)	0.6108(4)	1.52(6)
C(42)	0.3007(5)	−0.0055(1)	0.5669(4)	1.47(6)

thermal analyses (TDA). In a typical procedure, a 10 mg sample was placed in a platinum crucible and heated in static air at a heating rate of 5 °/min with α-Al_2O_3 as a standard for temperature and DTA measurements.

Description and discussion of the structures

$[Gd_2Cu(C_4O_4)_4(H_2O)_{12}]\cdot 2H_2O$

The C-type unit cell contains four unit formulae. The copper atoms are at the inversion centers (0, 0, 0), ($\frac{1}{2}$, $\frac{1}{2}$, $\frac{1}{2}$), (0, 0, $\frac{1}{2}$) and ($\frac{1}{2}$, $\frac{1}{2}$, 0). The other atoms occupy sites of general positions. Main bond lengths and angles are gathered in Table 4. There are two independent squarate anions which will be referred to as sq1 and sq2. The structure is made of layers of formula $[(\mu_3\text{-sq1})Gd(H_2O)_4]_2(\mu_2\text{-sq2})_2[Cu(H_2O)_4]$, the mean planes of which are parallel to the *b* axis and correspond to the indices (2 0 2).

Within a layer (Fig. 1), the gadolinium atoms and sq1 ligands form double chains $\{[(\mu_3\text{-sq1})Gd]_2\}_\infty$, parallel to the *b* axis. The ligand sq1 is tris-monodentate at O11, O21 and O31. The chains are bridged by [sq2–Cu–sq2] entities, the *cis* oxygen atoms O12 and O22 being bound to Cu and Gd, respectively (Fig. 1). Four water molecules (w1, w2, w3, w4) achieve the eight-fold coordination of the gadolinium atom into an asymmetrical square antiprism (Fig. 2(a)). The range of Gd–O bond lengths is rather narrow (2.36–2.44 Å) with no significant difference between water and squarate oxygen atoms. The copper atom is in an elongated centrosymmetric octahedral environment made of two sq2 oxygen atoms and two couples of water molecules, with two sets of short distances, 2×Cu–O12 = 1.962(3), 2×Cu–Ow5 = 1.964(3) Å, and one set of larger distances, 2×Cu–Ow6 = 2.377(3) Å.

Both squarate ligands are planar, with atom-to-mean-plane distances no larger than 0.03 Å for sq1 and 0.02 Å for sq2. From a layer to the next one, the ligands sq1 are related by two-fold rotations around axes quite parallel to their mean planes (angles between normal and axis equals 89.8°), so they face to each other and widely overlap. The overlap scheme (Fig. 3(a)) involves a staggered configuration, and the distance between the mean planes is equal to 3.24 Å at the center of the overlap area. The ligands sq2 from neighboring layers are related by inversion, so their mean planes are strictly parallel. They overlap only partially (Fig. 3(b)) with a distance of 3.68 Å between mean planes. The layers are interconnected through several sets of H bonds (Table 4), either directly from the intralayer molecules w2 and w6, or through the intervening non-

TABLE 4. Interatomic distances (Å) and bond angles (°) in $[Gd_2Cu(C_4O_4)_4(H_2O)_{12}]\cdot 2H_2O$

Around Gd

Gd–O(11)	2.441(3)	Gd–Ow(1)	2.358(3)
Gd–O(21)$^{\mathrm{i}}$	2.415(2)	Gd–Ow(2)	2.431(3)
Gd–O(41)$^{\mathrm{ii}}$	2.405(2)	Gd–Ow(3)	2.410(3)
Gd–O(22)	2.383(2)	Gd–Ow(4)	2.384(3)

Around Cu (point symmetry: 1)

Cu–O(12)	1.962(2)	O(12)–Cu–Ow(5)	91.3(1)
Cu–Ow(5)	1.964(3)	O(12)–Cu–Ow(6)	90.8(1)
Cu–Ow(6)	2.377(3)	Ow(5)–Cu–Ow(6)	91.2(1)

Squarate ligands

	j=1	j=2		j=1	j=2
C(1j)–C(2j)	1.469(5)	1.458(5)	O(1j)–C(1j)–C(2j)	134.4(3)	138.2(3)
C(2j)–C(3j)	1.473(4)	1.450(5)	O(1j)–C(1j)–C(4j)	135.5(3)	131.8(3)
C(3j)–C(4j)	1.458(5)	1.470(5)	C(2j)–C(1j)–C(4j)	90.1(2)	90.0(3)
C(4j)–C(1j)	1.451(4)	1.466(5)	O(2j)–C(2j)–C(3j)	134.3(3)	135.0(3)
C(1j)–O(1j)	1.266(4)	1.255(4)	O(2j)–C(2j)–C(1j)	136.1(3)	134.5(3)
C(2j)–O(2j)	1.247(4)	1.269(4)	C(3j)–C(2j)–C(1j)	89.5(2)	90.5(3)
C(3j)–O(3j)	1.242(4)	1.258(4)	O(3j)–C(3j)–C(4j)	133.8(3)	134.3(3)
C(4j)–O(4j)	1.265(4)	1.233(4)	O(3j)–C(3j)–C(2j)	136.6(3)	135.6(3)
			C(4j)–C(3j)–C(2j)	89.6(2)	90.1(3)
			O(4j)–C(4j)–C(1j)	134.6(3)	134.3(3)
			O(4j)–C(4j)–C(3j)	134.6(3)	136.3(3)
			C(1j)–C(4j)–C(3j)	90.8(2)	89.4(3)
			Gd–O(1j)–C(1j)	132.8(2)	
			Gd–O(2j)–C(2j)	130.4(2)	138.5(2)
			Gd–O(4j)–C(4j)	133.1(2)	

H-bonding

Intralayer

Ow(1)–O(32)	2.706(4)	Ow(1)–Hw(11)...O(32)	153.3(2)
Ow(1)–O(41)	2.691(4)	Ow(1)–Hw(21)...O(41)	170.4(2)
Ow(2)–O(11)$^{\mathrm{i}}$	2.757(4)	Ow(2)–Hw(22)...O(11)$^{\mathrm{i}}$	144.3(2)
Ow(3)–O(31)$^{\mathrm{ii}}$	2.701(4)	Ow(3)–Hw(13)...O(31)$^{\mathrm{ii}}$	160.5(2)
Ow(3)–Ow(6)	2.653(4)	Ow(3)–Hw(23)...Ow(6)	155.4(2)
Ow(4)–O(32)$^{\mathrm{iii}}$	2.776(4)	Ow(4)–Hw(24)...O(32)$^{\mathrm{iii}}$	156.9(2)
Ow(5)–O(42)$^{\mathrm{iii}}$	2.700(4)	Ow(5)–Hw(15)...O(42)$^{\mathrm{iii}}$	172.4(2)
Ow(5)–O(22)	2.708(4)	Ow(5)–Hw(25)...O(22)	141.7(2)

Interlayer

Ow(2)–Ow(3)$^{\mathrm{iv}}$	2.694(4)	Ow(2)–Hw(12)...Ow(3)$^{\mathrm{iv}}$	167.1(2)
Ow(4)–Ow(7)$^{\mathrm{v}}$	2.683(4)	Ow(4)–Hw(14)...Ow(7)$^{\mathrm{v}}$	157.7(2)
Ow(6)–O(32)$^{\mathrm{vi}}$	2.810(4)	Ow(6)–Hw(16)...O(32)$^{\mathrm{vi}}$	172.6(2)
Ow(7)–O(31)$^{\mathrm{vii}}$	2.751(4)	Ow(7)–Hw(17)...O(31)$^{\mathrm{vii}}$	158.1(2)
Ow(7)–O(42)	2.695(4)	Ow(7)–Hw(27)...O(42)	117.6(2)

Shortest intermetallic distances

Gd–Cu	5.5652(4)	Gd–Cu$^{\mathrm{iv}}$	5.6631(5)
Gd–Gd$^{\mathrm{ii}}$	5.8457(5)		

Code of equivalent positions: $^{\mathrm{i}}=\frac{3}{2}-x,\ \frac{1}{2}+y,\ \frac{1}{2}-z$; $^{\mathrm{ii}}=\frac{3}{2}-x,\ y-\frac{1}{2},\ \frac{1}{2}-z$; $^{\mathrm{iii}}=x,\ y-1,\ z$; $^{\mathrm{iv}}=1-x,\ y,\ \frac{1}{2}-z$; $^{\mathrm{v}}=\frac{3}{2}-x,\ \frac{3}{2}-y,\ 1-z$; $^{\mathrm{vi}}=x-\frac{1}{2},\ y-\frac{1}{2},\ z$; $^{\mathrm{vii}}=x-\frac{1}{2},\ \frac{3}{2}-y,\ \frac{1}{2}+z$.

coordinated water molecules w7. Intralayer H-bonding also takes place (Table 4).

$[La_2Cu(C_4O_4)_4(H_2O)_{16}]\cdot 2H_2O$

The unit cell contains two unit formulae. The copper atoms are at the inversion centers (0, 0, 0) and (0, ½, ½). The other atoms occupy sites of general positions. Main bond lengths and angles are gathered in Table 5. There are two independent squarate anions which will be referred to as sq1 and sq2. The structure is made of layers of formula $[(\mu_2\text{-sq1})La(H_2O)_6]_2(\mu_2\text{-sq2})_2[Cu(H_2O)_4]$, the mean planes of which are parallel to the *b* axis and correspond to the indices (1 0 −2).

Within a layer (Fig. 4), the lanthanum atoms and sq1 ligands form chains $[(\mu_2\text{-sq1})La]_\infty$, parallel to [1 0 2]. The ligand sq1 is *trans*-bis-monodentate at O11

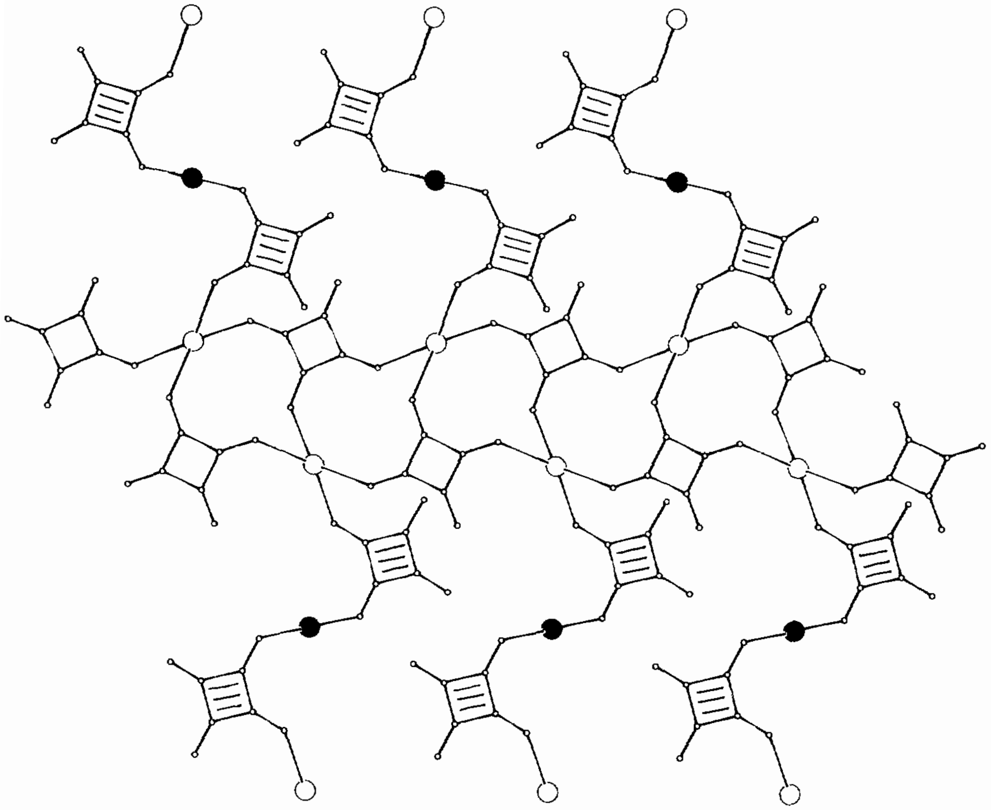

Fig. 1. A view of the two-dimensional chaining of Gd(III) (large open circles) and Cu(II) (large filled circles) cations through sq1 and sq2 (hatched) squarate ligands in [Gd_2Cu]. Water molecules bound to cations have not been drawn for the sake of clarity.

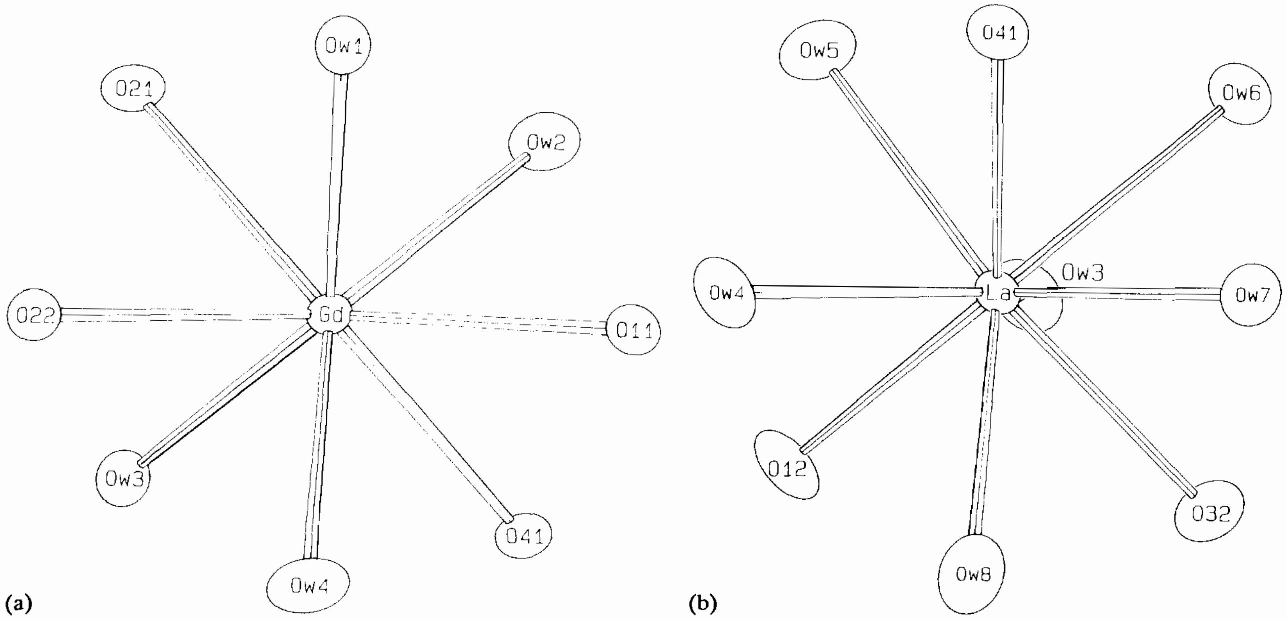

Fig. 2. The coordination polyhedron of: (a) Gd(III) in [Gd_2Cu]; (b) La(III) in [La_2Cu].

and O31. The chains are bridged by [sq2–Cu–sq2] entities, the *cis* oxygen atoms O12 and O22 being bound to Cu and La, respectively (Fig. 4). Six water molecules (w1, w2, w3, w4, w5, w6) achieve the nine-fold coordination of the lanthanum atom into an asymmetrical monocapped square antiprism (Fig. 2(b)). The range of La–O bond lengths range from 2.45 to 2.64 Å, the water oxygen atoms being farther (2.54–2.64 Å) than

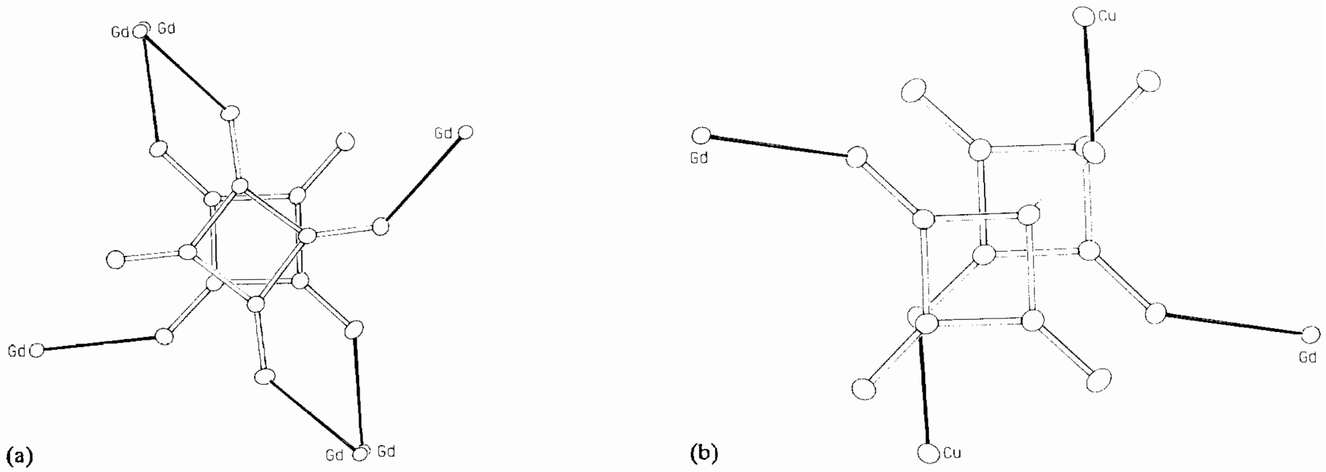

Fig. 3. The overlap scheme of squarate ligands in [Gd$_2$Cu]: (a) ligands sq1; (b) ligands sq2.

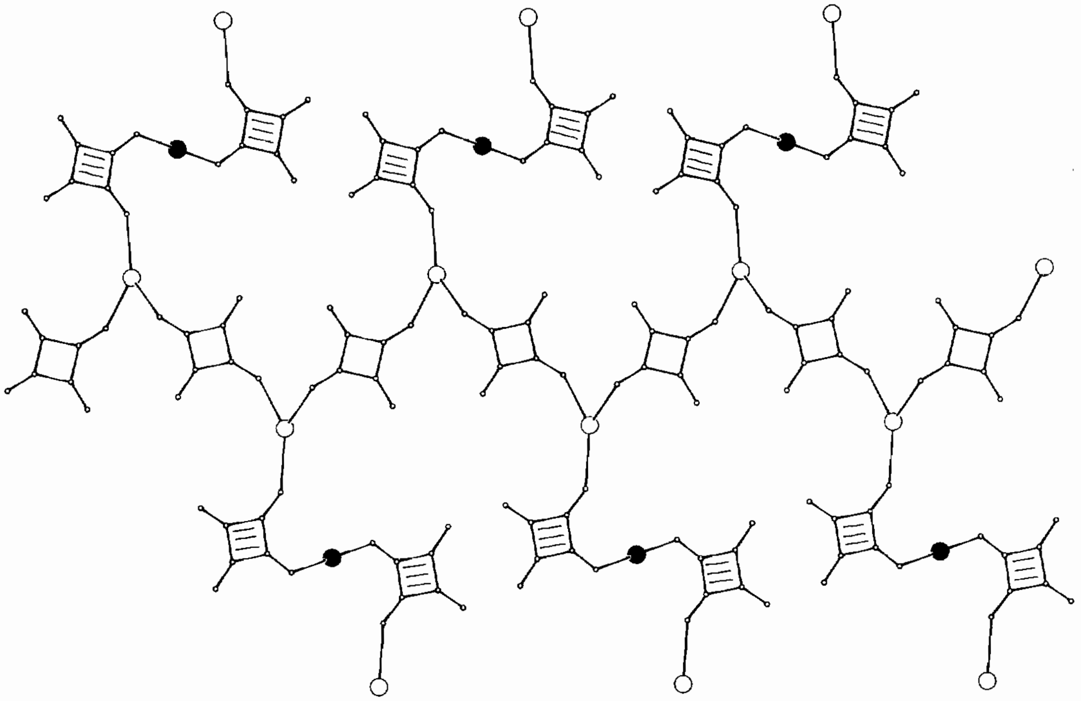

Fig. 4. A view of the two-dimensional chaining of La(III) (large open circles) and Cu(II) (large filled circles) cations through sq1 and sq2 (hatched) squarate ligands in [La$_2$Cu]. Water molecules bound to cations have not been drawn for the sake of clarity.

the squarate oxygen atoms (2.45–2.54 Å). The copper atom is in an elongated centrosymmetric octahedral environment made of two sq2 oxygen atoms and two couples of water molecules, with two sets of short distances, 2×Cu–O12 = 1.963(2), 2×Cu–Ow7 = 1.978(3) Å, and one set of larger distances, 2×Cu–Ow8 = 2.426(2) Å.

The ligands sq1 are quite perpendicular to the glide-mirrors *c* (angle between normals = 90.8°) which cut them, and are inclined by 38.2° onto the *c* axis. Therefore they form stacks parallel to the *c* axis: the repeat distance is equal to *c*/2 and the plane-to-plane distance to 3.21 Å. The resulting weak overlap between adjacent units is shown on Fig. 5(a). The ligands sq2 are related by inversion and form stacks parallel to the *a* axis with plane-to-plane distances alternately equal to 3.31 Å (inversion through (0, 0, ½)) and 3.20 Å (inversion through (½, 0, ½)). The overlap scheme is shown on Fig. 5(b). The ligands related by inversion through (0, 0, ½) belong to neighbouring layers separated by the translation **c**, and those related by inversion through (½, 0, ½) belong to layers separated by the translation

TABLE 5. Interatomic distances (Å) and bond angles (°) in $[La_2Cu(C_4O_4)_4(H_2O)_{16}]\cdot 2H_2O$

Around La					
La–O(11)	2.471(2)	La–Ow(1)	2.637(3)	La–Ow(4)	2.591(2)
La–O(31)^{i}	2.452(3)	La–Ow(2)	2.559(2)	La–Ow(5)	2.623(3)
La–O(22)	2.536(2)	La–Ow(3)	2.541(3)	La–Ow(6)	2.580(3)
Around Cu (point symmetry: 1)					
Cu–O(12)	1.963(2)		O(12)–Cu–Ow(7)	92.2(1)	
Cu–Ow(8)	2.426(2)		O(12)–Cu–Ow(8)	93.28(9)	
Cu–Ow(7)	1.977(3)		Ow(7)–Cu–Ow(8)	95.85(9)	
Squarate ligands					
	j=1	j=2		j=1	j=2
C(1j)–C(2j)	1.450(4)	1.445(4)	O(1j)–C(1j)–C(2j)	135.5(3)	137.5(3)
C(2j)–C(3j)	1.455(5)	1.470(4)	O(1j)–C(1j)–C(4j)	134.6(3)	131.3(3)
C(3j)–C(4j)	1.452(4)	1.477(5)	C(2j)–C(1j)–C(4j)	89.9(2)	91.3(2)
C(4j)–C(1j)	1.465(5)	1.459(4)	O(2j)–C(2j)–C(3j)	135.0(2)	136.0(3)
C(1j)–O(1j)	1.256(4)	1.279(4)	O(2j)–C(2j)–C(1j)	134.9(3)	134.1(3)
C(2j)–O(2j)	1.264(4)	1.253(4)	C(3j)–C(2j)–C(1j)	90.0(2)	89.9(2)
C(3j)–O(3j)	1.256(4)	1.245(4)	O(3j)–C(3j)–C(4j)	135.1(3)	134.6(3)
C(4j)–O(4j)	1.260(4)	1.247(4)	O(3j)–C(3j)–C(2j)	134.6(3)	135.8(3)
			C(4j)–C(3j)–C(2j)	90.3(2)	89.5(2)
			O(4j)–C(4j)–C(1j)	136.9(2)	135.0(3)
			O(4j)–C(4j)–C(3j)	133.5(3)	135.9(3)
			C(1j)–C(4j)–C(3j)	89.6(2)	89.1(2)
			La–O(1j)–C(1j)	142.7(2)	
			La–O(3j)–C(3j)	133.4(2)	
			La–O(2j)–C(2j)		147.4(2)
H-bonding					
Intralayer					
Ow(2)–O(21)		2.731(3)	Ow(2)–H(12)...O(21)		166.4(2)
Ow(2)–O(32)		2.803(4)	Ow(2)–H(22)...O(32)		162.4(2)
Ow(3)–Ow(8)		2.779(4)	Ow(3)–H(23)...Ow(8)		169.9(2)
Ow(4)–Ow(9)		2.693(5)	Ow(4)–H(14)...Ow(9)		166.9(2)
Ow(4)–O(41)^{i}		2.884(4)	Ow(4)–H(24)...O(41)^{ii}		168.7(2)
Ow(9)–O(12)^{ii}		2.884(4)	Ow(9)–H(19)...O(12)^{i}		168.0(2)
Interlayer					
Ow(3)–O(41)^{vi}		2.772(4)	Ow(3)–H(13)...O(41)^{vi}		166.2(2)
Ow(5)–O(42)^{vii}		2.759(3)	Ow(5)–H(15)...O(42)^{vii}		173.7(2)
Ow(6)–O(41)^{viii}		2.704(3)	Ow(6)–H(16)...O(41)^{viii}		171.7(2)
Ow(6)–O(21)^{ix}		2.927(4)	Ow(6)–H(26)...O(21)^{ix}		157.4(2)
Ow(7)–O(32)^{iii}		2.917(3)	Ow(7)–H(27)...O(32)^{iii}		150.8(2)
Ow(8)–O(42)^{iv}		2.722(3)	Ow(8)–H(28)...O(42)^{iv}		157.3(2)
Ow(8)–O(32)^{v}		2.941(4)	Ow(8)–H(18)...O(32)^{v}		165.8(2)
Ow(9)–Ow(5)^{v}		2.919(4)	Ow(9)–H(29)...Ow(5)^{v}		167.3(2)
Shortest intermetallic distances					
Cu–La	5.7258(3)	Cu–Cu^{x}	6.780(2)	La–La^{x}	6.780(2)

Code of equivalent positions: $^{i}=x-1, \frac{1}{2}-y, z-\frac{1}{2}$; $^{ii}=-x, -y, -z$; $^{iii}=x-1, y, z-1$; $^{iv}=1-x, -y, 1-z$; $^{v}=x, y, z-1$; $^{vi}=x, \frac{1}{2}-y, z-\frac{1}{2}$; $^{vii}=-x, -y, 1-z$; $^{viii}=x, \frac{1}{2}-y, \frac{1}{2}+z$; $^{ix}=x-1, y, z$; $^{x}=1+x, y, z$.

a + **c**. The layers are also interconnected through several sets of H bonds (Table 5), either directly from the intralayer water molecules w2, w3, w5, w6, w7 and w8, or through the non-coordinated water molecules w9. Intralayer H-bonding also takes place (Table 5).

Magnetism of $[Gd_2Cu(C_4O_4)_4(H_2O)_{12}]\cdot 2H_2O$

In order to put into evidence an occasional spin coupling between Cu(II) and Gd(III) centers, the magnetic susceptibility of $[Gd_2Cu]$ was measured from 300 to 4.2 K. Both Cu(II) and Gd(III) cations have spin only magnetic contributions (d^9, $S=1/2$; f^7, $S=7/2$, $L=0$). The effective moment calculated for two Gd(III) and one Cu(II) centers is $\mu_{eff}=11.36$ μ_B. The moment measured at room temperature was equal to the calculated one and remained constant down to 30 K. From 30 to 4.2 K it sligthly decreased to 10.5 μ_B. The susceptibility obeyed the Curie–Weiss law: $\chi^{-1}=0.0621T+0.0404$ ($R=0.99998$) from which the

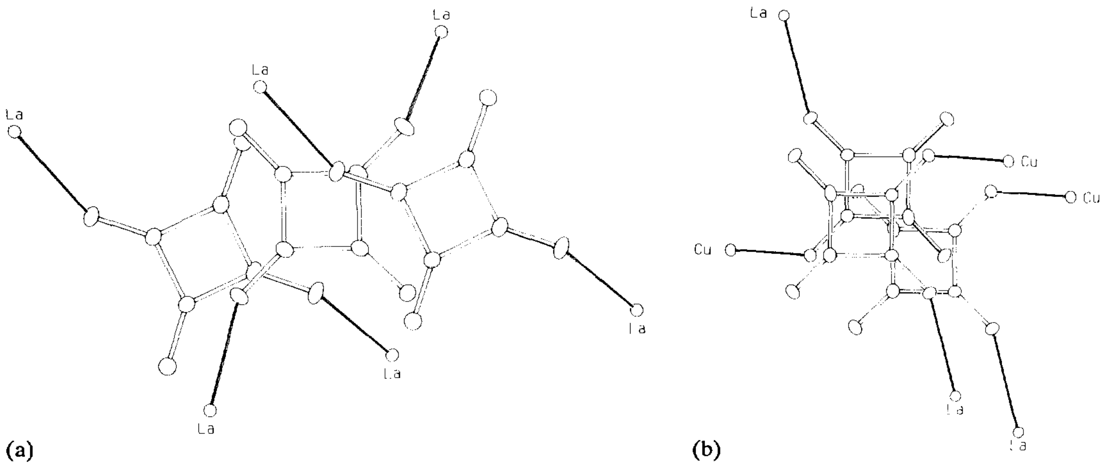

Fig. 5. The overlap scheme of squarate ligands in [La_2Cu]: (a) ligands sq1; (b) ligands sq2.

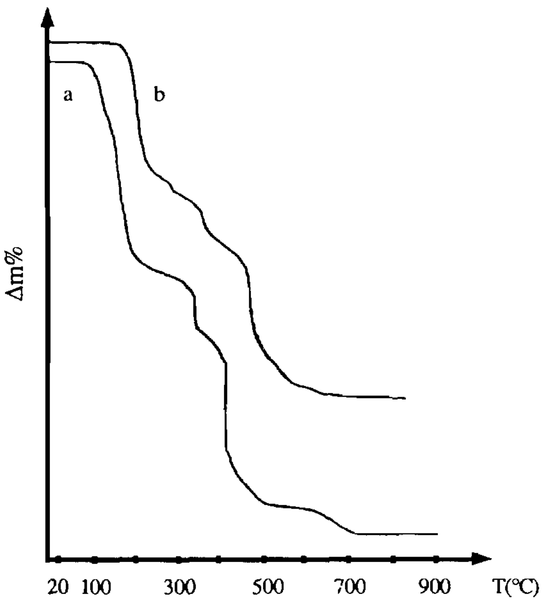

Fig. 6. Thermal gravimetric analysis of: (a) [La_2Cu]; (b) [Gd_2Cu].

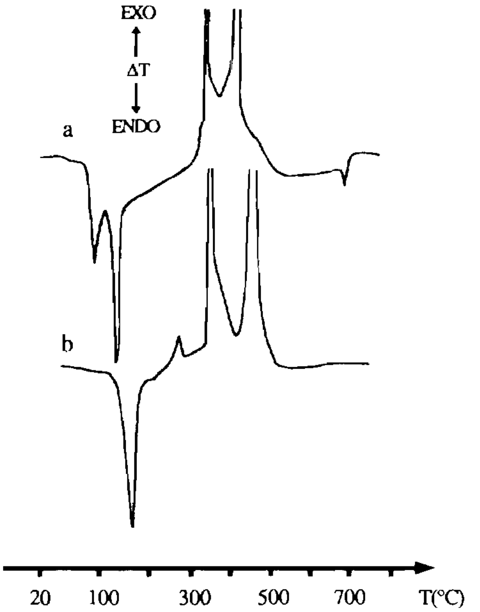

Fig. 7. Thermal differential analysis of: (a) [La_2Cu]; (b) [Gd_2Cu].

Curie temperature $\Theta = -0.6$ K can be deduced. There is no significant spin coupling between magnetic centers. The reason for it lies in the nature of f-block elements and that of the squarate anion as well. The lanthanide cations are not the best candidates to magnetic interactions through orbital overlap because of the innerness of the f orbitals. However several cases of ferromagnetic coupling between Cu(II) and Gd(III) centers were recently reported by Gatteschi and co-workers [9] and Blake *et al.* [10]. Moreover, the Cu–squarate–Gd geometry observed here is not adapted to a strong overlap between Cu and Gd orbitals. Several copper(II) squarato complexes with bis-monodentate bonding of squarato to Cu were recently shown to exhibit only weak short range antiferromagnetic coupling: the coupling constants $J = 0$, -0.35 and -3.6 cm^{-1} were measured on (μ-1,3 squarate) and (μ-1,2 squarate) complexes [11].

Thermal analyses

The thermal analysis curves are presented in Figs. 6 (TGA) and 7 (TDA). The absence of clear plateaus below 600 °C makes the TGA curves difficult to interpret. For both compounds, dehydration occurs first and is a two stage process. For [La_2Cu], the loss of weight begins at 90 °C, inflects at 115 °C and terminates at 290 °C where decomposition of the squarate ligand starts. At the inflexion point, four of the eighteen water molecules have been lost: they might be the two free water molecules and the two ones weakly bound to copper. The dehydration of [Gd_2Cu] starts higher, at 165 °C. Thirteen of the fourteen water molecules correspond to the first loss of weight. The second loss, between 265 and 275 °C, corresponds to the departure of the last water molecule, but also to the starting decomposition of the squarate ligand. For both compounds, the DTA curves show two endothermic peaks corresponding to the dehydration process: 95 and 135 °C for [La_2Cu], 170 and 210 °C for [Gd_2Cu]. The anhydrous derivatives cannot be isolated.

The decomposition of the squarate ligand comprises two main steps which are not clearly definite. For [La_2Cu], the first step is marked by a loss of weight that starts smoothly at 290 °C, goes on steeper between 340 and 350 °C, and terminates smoothly at 400 °C. At this point, the observed loss agrees with the formation of $La_2(C_4O_4)_3$, CuO. The second step begins smoothly with the formation of $La_2(CO_3)_3$ which may be considered as completed after the sharp loss of weight around 415 °C. Then the carbonate gradually loses weight up to 520 °C where a plateau is reached corresponding to the stable oxycarbonate $La_2O_2(CO_3)$ [12]. Complete decarbonatation takes places between 685 and 715 °C. For [Gd_2Cu], the first step ends around 390 °C and the weight loss is compatible with the formation of a product having the formula $Gd_2(C_4O_4)_3$, CuO; no carbonate nor oxycarbonate forms during the second step. The DTA curves show two exothermic peaks due to the decomposition of the squarate ligand: at 340 and 415 °C for [La_2Cu]; at 350 and 460 °C for [Gd_2Cu]. The decarbonatation of $La_2O_2(CO_3)$ is marked by an endotherm around 695 °C.

The samples achieve constant weight around 700 °C where 63.5% and 65.4% of the initial weights have been lost for [La_2Cu] and [Gd_2Cu], respectively. These values agree fairly well with the calculated ones (63.6 and 64.4, respectively) for the formation of the oxides La_2CuO_4 and Gd_2CuO_4 which was furthermore confirmed by X-ray powder diffraction.

That the ligands bound to copper would decompose distinctly prior to the ones bound to lanthanoid agrees with what was observed for the homometallic compounds: decomposition of pure copper squarate occurs sharply at 270 °C [13] while pure lanthanum squarate and pure gadolinium squarate do not decompose before 450 and 455 °C, respectively [4]. As to the formation of carbonato and oxycarbonato species for [La_2Cu] and not for [Gd_2Cu], it may be simply related to the decrease in basicity when going from La^{3+} to Gd^{3+}.

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