Rare earth metal squarates incorporating ethylene glycol ligand with a three-dimensional framework structure: $RE(C_4O_4)_{1.5}(C_2H_6O_2)$ (RE = Y, La–Nd, Sm–Lu)†

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Fifteen isostructural rare earth metal squarates incorporating ethylene glycol ligand with the formula $RE(C_4O_4)_{1.5}(C_2H_6O_2)$ (RE = Y, La–Nd, Sm–Lu) have been synthesized under hydrothermal conditions and structurally characterized by single-crystal and powder X-ray diffraction, ^{13}C CPMAS NMR, absorption spectroscopy, and magnetic susceptibility. A variable-temperature *in situ* powder X-ray diffraction study on the Ce compound was also performed to determine its thermal stability. Each RE^{3+} cation in the structure is bonded to six squarate anions and one neutral ethylene glycol chelate, and each $C_4O_4^{2-}$ anion coordinates to four RE^{3+} cations such that a new 3-D framework is formed. They are the first examples of organic–inorganic hybrids which contain both squarate and ethylene glycol ligands.

Introduction

Coordination polymers are metal coordination compounds where each metal center binds to more than one polyatomic ligand to create an infinite array of metal centers.[1] They are of great interest not only for their potential as functional solid materials, but also for their intriguing, often complicated, architectures and topologies. Carboxylates such as benzene-1,3,5-tricarboxylate and polypyridines such as 4,4′-bipyridine are common bridging ligands used in the synthesis of these polymers.

We have been interested in the synthesis of mixed hybrid materials, namely coordination polymers containing more than one kind of polyatomic ligand. A large number of mixed hybrids combining organic ligands such as oxalate or 4,4′-bipyridine with tetrahedral phosphate or phosphite groups have been reported.[2] Recently, we have been trying to extend our studies to incorporate larger carbon oxo anions such as squarate into the framework structure. Salts of 3,4-dihydroxy-3-cyclobutene-1,2-dione ($H_2C_4O_4$) are known as squarates. The squarate dianion is a monocyclic carbon oxo anion with aromaticity. It can act as a chelate, or a bridge between two metal ions, or a fourfold unidentate ligand between metals.[3] The literature has been enriched by many squarate-based coordination polymers possessing structural features for interesting zeolitic, luminescent, and magnetic properties.[4] However, there are only a few reports on mixed hybrid materials which contain a squarate dianion and a second kind of bridging ligand. Konar *et al.* reported a ferromagnetic Fe(II) coordination polymer, $[Fe(C_4O_4)(4,4'\text{-bpy})(2H_2O)]\cdot 3H_2O$, with a 3-D interpenetrating network.[5] A lanthanide sulfate-squarate, $La_2(H_2O)_4(SO_4)_2(C_4O_4)$, with a 3-D framework structure was reported by Akkari *et al.*[6] Yang and Mao synthesized a Mn(II) squarate diphosphonate, $\{Mn[NH(CH_2PO_3H)_2](H_2O)_2\}_2\{Mn(C_4O_4)(H_2O)_4\}\cdot(C_4H_2O_4)$ and a Cu(I) squaratophosphonate, $Cu_3(H_3L)(bipy)_2\cdot 2H_2O$ ($H_5L = C_4HO_3N(CH_2PO_3H_2)_2$), in which the new ligand squarato-iminodiphosphonate ligand was formed by the condensation reaction between one C=O group of squaric acid and the amino group of $NH(CH_2PO_3H_2)_2$.[7] Recently, we have also synthesized several lanthanide squarate-phosphites, $[Ln(H_2O)(C_4O_4)_{0.5}(HPO_3)]$ (Ln = Sm, Eu, and Gd), whose 3-D frameworks contain inorganic sheets of lanthanide phosphites pillared by squarate ligands.[8] Herein, we report a series of rare earth metal squarates incorporating ethylene glycol ligand with the formula $RE(C_4O_4)_{1.5}(C_2H_6O_2)$ (RE = Y, La–Nd, Sm–Lu). To our knowledge, there are no reports about the mixed hybrids containing the squarate anion and the ethylene glycol molecule as ligands whatever the metals. This paper deals with their synthesis and structural characterization by single-crystal and powder X-ray diffraction, ^{13}C CPMAS NMR, absorption spectroscopy, and magnetic susceptibility. To determine the thermal stability of the structure, a variable-temperature *in situ* powder X-ray diffraction study on the Ce compound was also performed.

Experimental

Synthesis

The reagents, $RE(NO_3)_3\cdot xH_2O$, $H_2C_4O_4$ and ethylene glycol, were obtained from commercial sources and used without purification. Hydrothermal reactions were performed in a Teflon™-lined, 23-mL autoclave at 180 °C for the Y compound and 165 °C for all the other compounds for 3d followed by slow cooling to room temperature at 12 °C h^{-1}. Crystals of $RE(C_4O_4)_{1.5}(C_2H_6O_2)$ (RE = Y (**1**), La (**2**), Ce (**3**), Pr (**4**), Nd (**5**), Sm (**6**), Eu (**7**), Gd (**8**), Tb (**9**), Dy (**10**), Ho (**11**), Er (**12**), Tm (**13**), Yb (**14**), Lu (**15**)) were obtained by heating a reaction mixture of 0.5 mmol of rare earth metal nitrates, 2 mmol of squaric acid, 5 mL of ethylene glycol and 5 mL of H_2O under the hydrothermal conditions. The products

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were filtered, washed with deionized water, rinsed with ethanol, and dried in a desiccator at room temperature. The initial and final pH values of the solution for the La compound, for example, were 2 and 3, respectively. The Pr compound is olive, the Nd compound is light purple, the Eu, Tb and Lu compounds are light yellow, the Dy compound is brown, the Ho and Er compounds are pink, and the other compounds are colorless. These fifteen compounds are isostructural, as indicated by single-crystal and powder X-ray diffraction (Fig. S1, ESI†). The structures of all fifteen compounds have been determined by single-crystal X-ray diffraction. Powder X-ray data were collected on a Shimadzu XRD-6000 automatic powder diffractometer with Cu Kα radiation equipped with a scintillation detector. Data were collected in the range $5^\circ \leq 2\theta \leq 50^\circ$ using the θ–2θ mode in a Bragg–Brentano geometry. Single-phase products of all fifteen compounds were obtained and characterized by powder X-ray diffraction and elemental analysis. The yields for all compounds were nearly quantitative based on the rare earth metals. Anal. Found (calcd): C 30.03 (30.12), H 1.84 (1.90) for **1**; C 25.94 (26.04), H 1.59 (1.64) for **2**; C 25.92 (25.95), H 1.59 (1.63) for **3**; C 25.90 (25.90), H 1.49 (1.63) for **4**; C 25.60 (25.67), H 1.53 (1.62) for **5**; C 25.08 (25.25), H 1.71 (1.59) for **6**; C 25.05 (25.15), H 1.65 (1.58) for **7**; C 24.68 (24.80), H 1.69 (1.56) for **8**; C 24.62 (24.70), H 1.64 (1.55) for **9**; C 24.13 (24.47), H 1.78 (1.54) for **10**; C 24.18 (24.32), H 1.65 (1.53) for **11**; C 24.04 (24.18), H 1.58 (1.52) for **12**; C 23.88 (24.08), H 1.59 (1.52) for **13**; C 23.49 (23.83), H 1.61 (1.50) for **14**; C 23.53 (23.72), H 1.58 (1.49) for **15**.

Thermogravimetric analysis (TGA) was carried out on powder samples of all fifteen compounds using a Perkin Elmer thermal analyzer. The samples were heated under flowing oxygen from 50 to 900 °C with a heating rate of 10 °C min^{-1}. The TGA curves showed a one-step weight loss for **3**, and a weight loss in two or more steps for the other four compounds (Fig. 1). The total weight losses of 64.5, 56.3, 71.3, 55.1 and 54.5% between 300 and 650 °C for **1**, **2**, **3**, **4** and **5**, respectively, were in good agreement with the values of 64.6, 55.9, 69.7, 54.1 and 55.1% calculated according to the following equations: $2\ \mathrm{RE(C_4O_4)_{1.5}(C_2H_6O_2)} + 7.5\ \mathrm{O_2} \rightarrow \mathrm{RE_2O_3} + 12\ \mathrm{CO_2} + 2\ \mathrm{C_2H_6O_2}$ for **1**, **2** and **5**, $\mathrm{Ce(C_4O_4)_{1.5}(C_2H_6O_2)} + 4\ \mathrm{O_2} \rightarrow \mathrm{CeO_2} + 6\ \mathrm{CO_2} + \mathrm{C_2H_6O_2}$ for **3**, and $6\ \mathrm{Pr(C_4O_4)_{1.5}(C_2H_6O_2)} + 23.5\ \mathrm{O_2} \rightarrow \mathrm{Pr_6O_{11}} + 36\ \mathrm{CO_2} + 6\ \mathrm{C_2H_6O_2}$ for **4**. The final decomposition products were $\mathrm{Y_2O_3}$ (JCPDS 43-1036), $\mathrm{La_2O_3}$ (JCPDS 5-0602), $\mathrm{CeO_2}$ (ICSD 53995), $\mathrm{Pr_6O_{11}}$ (JCPDS 42-1121) and $\mathrm{Nd_2O_3}$ (JCPDS 43-1023), as indicated by powder X-ray diffraction. The TGA curves for compounds **6–15** are given in Fig. S2.†

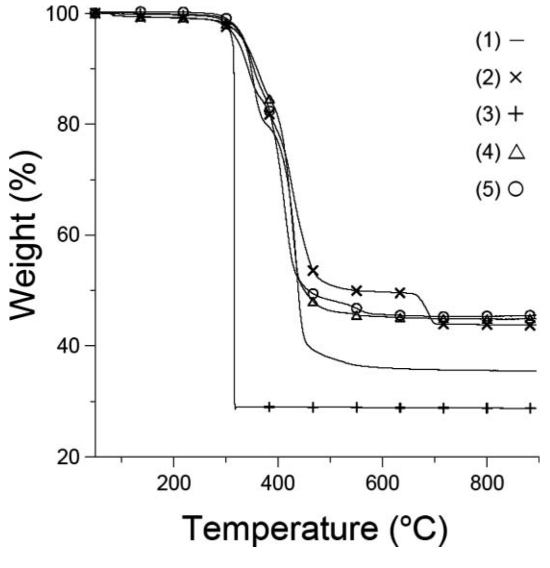

Fig. 1 Thermogravimetric analysis of the Y (**1**), La (**2**), Ce (**3**), Pr (**4**) and Nd (**5**) compounds under flowing oxygen from 50 to 900 °C with a heating rate of 10 °C min^{-1}.

To determine the thermal stability of the structure, a variable-temperature (30–600 °C) *in situ* powder X-ray diffraction study on the Ce compound was performed. The results show that the framework structure is retained up to 300 °C and the compound decomposes to $\mathrm{CeO_2}$ at higher temperatures (Fig. S3†).

Single-crystal X-ray diffraction

The fifteen compounds are isostructural; therefore, only compound **5** is discussed. A pillar-like light purple crystal of **5** with dimensions $0.48 \times 0.06 \times 0.06$ mm^3 was selected for indexing and intensity data collection on a Bruker Kappa APEX II CCD diffractometer equipped with a normal-focus 3 kW sealed-tube X-ray source. Intensity data were collected at room temperature in 1814 frames with ω scans (width 0.25° per frame), and the program SADABS was used for absorption correction ($T_{\mathrm{min/max}} = 0.6532/0.7457$). On the basis of reflection conditions, statistics of intensity distribution, successful solution and refinement of the structure, the space group was determined to be $C2/c$ (No. 15). The structure of **5** was determined by direct methods and subsequent difference Fourier syntheses. The H atoms in the ethylene glycol ligand were located in difference Fourier maps and refined with isotropic thermal parameters. The final cycles of least-square refinement including atomic coordinates and anisotropic thermal parameters for all non-hydrogen atoms converged at $R_1 = 0.0156$, $wR_2 = 0.0387$. The final difference electron density maps were featureless, and the highest peak and deepest hole were 0.488 and −0.756 e Å^{-3}, respectively. All calculations were performed using the SHELXTL version 5.1 software package.[9]

Magnetic susceptibility

Variable-temperature magnetic susceptibility $\chi(T)$ data were obtained on a powder sample of 51.4 mg of **5** from 2 to 300 K in a magnetic field of 2000 gauss after zero-field cooling using a Quantum Design SQUID magnetometer. Correction for diamagnetism was made according to Selwood.[10]

Absorption spectroscopy

Diffuse reflectance UV-Vis spectrum of the Nd compound was measured using a Cary 300 Bio UV-Visible Spectrophotometer. A powder sample was loaded in a quartz cell with Suprasil windows and the spectrum was measured at room temperature in the spectral range from 200 to 850 nm.

Solid-state NMR spectroscopy

The ^{13}C NMR experiment was performed on the La compound using a Varian Infinityplus-500 NMR spectrometer equipped with a 4-mm Chemagnetics probe with a resonance frequency of 125.363 MHz. The Hartmann–Hahn conditions for $^1\mathrm{H} \rightarrow {}^{13}\mathrm{C}$

CPMAS (cross-polarization magic angle spinning) experiments were determined using adamantane. The chemical shift was externally referenced to tetramethylsilane at 0 ppm.

Results and discussion

Structure

Crystallographic data for all fifteen compounds are summarized in Table 1. Selected bond lengths for compound **5** are listed in Table 2. The fifteen rare earth metals form a series of isostoichiometric compounds with the same crystal structure; therefore, only the structure of **5** is discussed. The unit cell volumes of compounds **2** to **15** show a steady contraction in size across the series because of the lanthanide contraction (Fig. S4†). The structure of **5** is constructed of the following crystallographically distinct building units: one NdO_8 polyhedron, three squarate ligands, and one ethylene glycol ligand. All atoms are in general positions. $C(1)_2C(2)_2O_4$ and $C(3)_2C(4)_2O_4$ are at 4d and 4a special positions, respectively, with a center of symmetry, $C(5)_2C(6)_2O_4$ is at the 4e special position with a 2-fold axis of symmetry, but ethylene glycol has no symmetry. Therefore, each unit cell contains 8 NdO_8 polyhedra, 12 squarate anions, and 8 ethylene glycol molecules. The coordination environment of the Nd atom and atom labeling scheme are shown in Fig. 2. The Nd^{3+} cation is eight-fold coordinated by oxygen atoms in a geometry of distorted trigonal dodecahedron which is a common structure for eight-coordination. Each Nd^{3+} cation is bonded to six squarate anions and chelated by one neutral ethylene glycol molecule, and each $C_4O_4^{2-}$ anion coordinates to four Nd^{3+} cations such that a new 3-D framework structure is formed (Fig. 3). The arrangement of the NdO_8 dodecahedra in the structure approximates to a cubic-primitive lattice and every NdO_8 has six neighbors in octahedral symmetry.

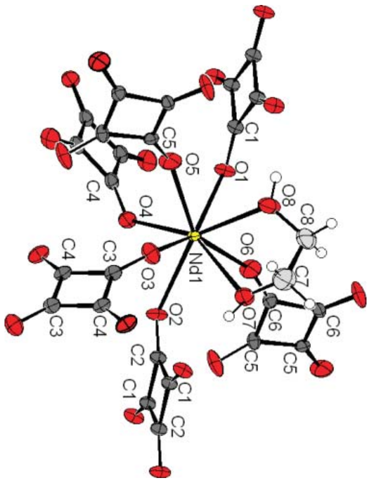

Fig. 2 The coordination environments of the Nd^{3+} ion in the structure of **5** showing the atom labeling scheme. Thermal ellipsoids are shown at 50% probability.

Squarates may act as chelates, or bridges between two metal ions, or fourfold unidentate ligands between metals. In the structure of **5**, each squarate anion coordinates to four Nd^{3+} cations. As mentioned earlier only a few hybrid framework materials which combine squarate ligand and another moiety have been reported. The neutral ethylene glycol ligand presents a bidentate coordination to a Nd^{3+} ion. To our knowledge, this unusual coordination mode of ethylene glycol is observed for the first time in coordination polymers, although a good number of

Table 1 Crystallographic data for $RE(C_4O_4)_{1.5}(C_2H_6O_2)$ (RE = Y (**1**), La (**2**), Ce (**3**), Pr (**4**), Nd (**5**), Sm (**6**), Eu (**7**), Gd (**8**), Tb (**9**), Dy (**10**), Ho (**11**), Er (**12**), Tm (**13**), Yb (**14**), Lu (**15**))

	1	**2**	**3**	**4**	**5**	**6**	**7**	**8**	**9**	**10**	**11**	**12**	**13**	**14**	**15**
Chemical formula	$C_8H_6O_8Y$	$C_8H_6LaO_8$	$C_8H_6CeO_8$	$C_8H_6O_8Pr$	$C_8H_6NdO_8$	$C_8H_6O_8Sm$	$C_8H_6EuO_8$	$C_8H_6GdO_8$	$C_8H_6O_8Tb$	$C_8H_6DyO_8$	$C_8H_6HoO_8$	$C_8H_6ErO_8$	$C_8H_6O_8Tm$	$C_8H_6O_8Yb$	$C_8H_6LuO_8$
Formula weight	319.04	369.04	370.25	371.04	374.37	380.48	382.09	387.38	389.05	392.63	395.06	397.39	399.06	403.17	405.10
a/Å	12.7516(6)	13.1606(6)	13.0958(5)	13.0212(7)	12.9884(5)	12.9151(8)	12.8772(5)	12.8545(6)	12.8156(5)	12.7668(5)	12.7571(5)	12.7172(5)	12.6881(5)	12.6497(15)	12.6351(5)
b/Å	12.0784(6)	12.3974(6)	12.3373(5)	12.2987(7)	12.2543(5)	12.2146(7)	12.1834(5)	12.1603(6)	12.1362(5)	12.1015(5)	12.0918(5)	12.0666(5)	12.0386(5)	12.0106(14)	12.0129(5)
c/Å	12.5437(6)	12.8717(6)	12.8153(5)	12.7671(8)	12.7418(5)	12.6924(7)	12.6535(5)	12.6281(6)	12.5928(5)	12.5648(5)	12.5485(5)	12.5190(5)	12.4922(5)	12.4708(15)	12.4584(5)
β/°	99.233(2)	98.705(2)	98.876(2)	98.839(2)	98.987(2)	98.976(3)	99.039(2)	99.143(3)	99.083(2)	99.094(2)	99.151(2)	99.121(2)	99.185(2)	99.221(3)	99.177(2)
V/Å^3	1906.94(16)	2075.92(17)	2045.73(14)	2020.29(20)	2003.14(14)	1977.70(20)	1960.53(14)	1948.88(16)	1934.17(13)	1916.83(13)	1911.05(13)	1896.79(13)	1883.68(13)	1870.2(4)	1866.98(13)
Z	8	8	8	8	8	8	8	8	8	8	8	8	8	8	8
Space group	$C2/c$	$C2/c$	$C2/c$	$C2/c$	$C2/c$	$C2/c$	$C2/c$	$C2/c$	$C2/c$	$C2/c$	$C2/c$	$C2/c$	$C2/c$	$C2/c$	$C2/c$
T, °C	23	23	23	23	23	23	23	23	23	23	23	23	23	23	23
λ(Mo Kα), Å	0.71073	0.71073	0.71073	0.71073	0.71073	0.71073	0.71073	0.71073	0.71073	0.71073	0.71073	0.71073	0.71073	0.71073	0.71073
D_{calc}, g cm^{-3}	2.223	2.362	2.404	2.440	2.483	2.556	2.589	2.641	2.672	2.721	2.746	2.783	2.814	2.864	2.883
μ(Mo Kα), cm^{-1}	61.5	41.4	44.8	48.5	52.1	59.7	64.3	68.4	73.4	78.3	83.1	88.8	94.5	100.33	106.08
$R_1{}^a$	0.0196	0.0150	0.0152	0.0160	0.0156	0.0163	0.0207	0.0240	0.0133	0.0139	0.0166	0.0187	0.0157	0.0193	0.0147
$wR_2{}^b$	0.0519	0.0372	0.0386	0.0417	0.0387	0.0384	0.0537	0.0479	0.0322	0.0322	0.0404	0.0489	0.0357	0.0489	0.0367

[a] $R_1 = \sum \| F_o | - | F_c \| / \sum | F_o |$. [b] $wR_2 = [\sum w(F_o^2 - F_c^2)^2 / \sum w(F_o^2)^2]^{1/2}$, $w = 1/[\sigma^2(F_o^2) + (aP)^2 + bP]$, $P = [\max(F_o^2, 0) + 2(F_c)^2]/3$.

Table 2 Selected bond lengths (Å) for $Nd(C_4O_4)_{1.5}(C_2H_6O_2)$ (compound **5**)

Nd(1)–O(6)^a	2.3416(15)	Nd(1)–O(5)	2.3569(16)
Nd(1)–O(3)	2.3700(14)	Nd(1)–O(4)^b	2.3739(16)
Nd(1)–O(2)^a	2.4811(15)	Nd(1)–O(8)	2.4760(19)
Nd(1)–O(1)	2.5111(13)	Nd(1)–O(7)	2.5639(18)
C(1)–O(1)	1.253(2)	C(2)-O(2)	1.257(2)
C(3)–O(3)	1.247(2)	C(4)–O(4)	1.258(3)
C(5)–O(5)	1.244(2)	C(6)–O(6)	1.244(2)
C(7)–O(7)	1.430(3)	C(8)–O(8)	1.426(3)
C(1)–C(2)	1.466(3)	C(3)–C(4)	1.457(3)
C(5)–C(6)	1.454(3)	C(5)–C(5)^b	1.463(4)
C(6)–C(6)^b	1.448(4)	C(7)–C(8)	1.486(4)
C(7)–H(7A)	0.99(4)	C(7)–H(7B)	0.99(3)
C(8)–H(8A)	1.01(3)	C(8)–H(8B)	1.06(3)
O(7)–H(7O)	0.72(3)	O(8)–H(8O)	0.70(4)

Symmetry codes:^{a} $-x+1/2,y+1/2,-z+1/2$; ^{b} $-x+1,y,-z+1/2$.

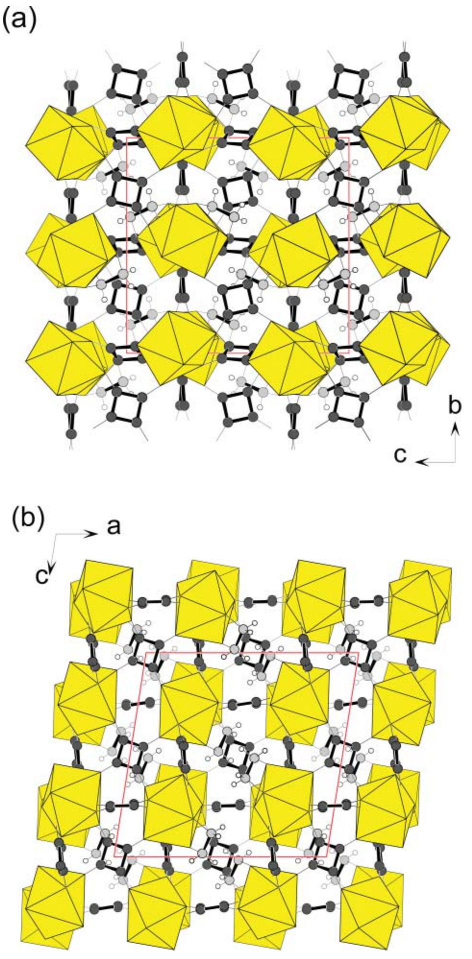

Fig. 3 Structure of **5** viewed along the *a*-axis. The polyhedra are NdO_8 dodecahedra. Black circles, C atoms of the $C_4O_4^{2-}$ ligands; gray circles, C atoms of the ethylene glycol ligands; open circles, H atoms. (b) Structure of **5** viewed along the *b*-axis. The H atoms of the OH groups in the ethylene glycol ligands are not shown for clarity.

metal complexes containing ethylene glycol chelates have been reported.[11] Many of the metal ethylene glycol complexes are appropriate precursors for oxide ceramics.[12] The title compounds are the first mixed hybrids based on the association of anionic squarate and neutral ethylene glycol ligands.

^{13}C CPMAS NMR

Four resonances at 62.6, 198.0, 199.4 and 203.3 ppm are observed in the ^{13}C CPMAS NMR spectrum of the La compound (Fig. 4). The strongest peak at 62.6 ppm belongs to the carbon nuclei of the ethylene glycol molecule. The other three resonances can be assigned to the carbon nuclei in the three distinct squarate ligands as indicated from crystal structure analysis. These values agree well with the chemical shift ranges found for ethylene glycol and squarate compounds reported in the literature.[13,14] For example, a signal at 61.5 ppm is observed for the sodium glycostannate $Na_2Sn(OCH_2CH_2O)_3$,[13a] and one signal at 203.9 ppm for $K_2C_4O_4$.[14b] The three resonances in Fig. 4 can be classified into two groups by their chemical shifts, namely, the two resonances at 198.0 and 199.4 ppm and the resonance at 203.3 ppm.

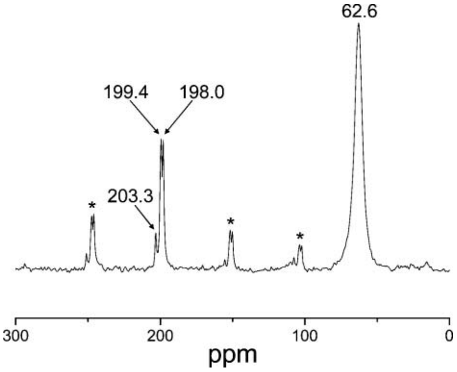

Fig. 4 ^{13}C CPMAS NMR spectrum of **2** acquired at a spinning speed of 6 kHz. Asterisks denote spinning sidebands.

The difference in ^{13}C signal intensity obtained from CP generally indicates different values of cross-relaxation time between ^1H and ^{13}C spins for the corresponding carbon nuclei. The cross-relaxation time is related to the strength of the dipolar coupling between ^1H and ^{13}C nuclei. The relatively stronger resonances at 198.0 and 199.4 ppm indicate that the carbon atoms have nearby proton spins that are close enough to cause such efficient CP signal transfer. On the basis of the H···C distances (d(H(8A)···C(2)) = 3.34 Å, d(H(8B)···C(1)) = 3.47 Å; d(H(8A)···C(3)) = 3.28 Å, d(H(8A)···C(4)) = 2.81 Å; d(H(7A)···C(5)) = 3.14 Å, d(H(7A)···C(6)) = 3.08 Å, d(H(7B)···C(5)) = 3.18 Å, d(H(7B)···C(6)) = 2.85 Å), the resonance at 203.3 ppm is, therefore, assigned to $C(1)_2C(2)_2O_4$, and the other two resonances to $C(3)_2C(4)_2O_4$ and $C(5)_2C(6)_2O_4$.

Absorption spectroscopy

Some 4f–4f transitions in the electronic spectra are 'hypersensitive' to changes in the symmetry and strength of the ligand field. It is most marked for the $^4I_{9/2} \rightarrow {}^2H_{9/2}, {}^4F_{5/2}$ transitions in the case of the Nd^{3+} ion.[15] Karraker *et al.* demonstrated that the coordination of the Nd^{3+} ion could be inferred from the shape of the absorption bands.[16] Fig. 5 shows the absorption spectrum of the $^4I_{9/2} \rightarrow {}^2H_{9/2}$, $^4F_{5/2}$ transitions of solid compound **5** which resembles that of $Nd_2(SO_4)_3{\cdot}8H_2O$, where the Nd^{3+} ion is known from a single-crystal X-ray study to be coordinated to eight water molecules. The spectral measurement results suggest that an 8-coordinate

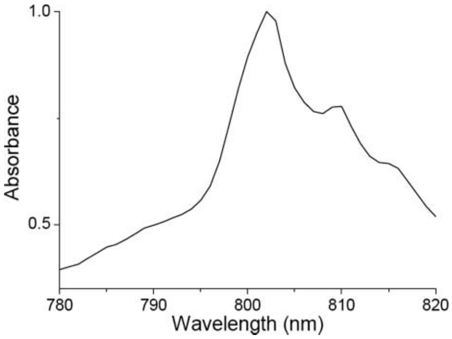

Fig. 5 Absorption spectrum of the Nd^{3+} $^4I_{9/2} \rightarrow {}^2H_{9/2}, {}^4F_{5/2}$ transitions for **5**.

Nd^{3+} is present in **5**, which is in agreement with the result from crystal structure analysis.

Magnetic susceptibility

The free-ion ground state of Nd^{3+} is $^4I_{9/2}$, with the next higher state ($^4I_{11/2}$) at approximately 1900 cm^{-1} higher.[17] The Zeeman factor, g_J, is 8/11 and the theoretical value of $\chi_M T$ for a mononuclear species is 1.64 cm^3 K/mol. The $\chi_M T$ *versus* T and $1/\chi_M$ *versus* T curves for **5** are shown in Fig. 6. At room temperature, $\chi_M T$ is equal to 1.66 cm^3 K/mol Nd, which is close to the theoretical value. $\chi_M T$ decreases continuously as T decreases and reaches a value of 0.72 cm^3 K/mol Nd at 2 K. In the 100–300 K range, the magnetic data follows the Curie–Weiss law $\chi_M = C/(T - \theta)$ with $C = 1.90$ cm^3 K/mol Nd and $\theta = -42.9$ K. The deviation of the magnetic susceptibility with respect to the Curie law results from the crystal field splitting of the $^4I_{9/2}$ state into five doublets. As temperature decreases, the Kramer doublets of higher energy are progressively depopulated and the magnetic susceptibility does not follow the Curie law, and only one doublet is populated at 20 K or below. Therefore, Nd^{3+} has an effective doublet ground state. The magnetic interactions between the Nd^{3+} ions in the structure are expected to be small.

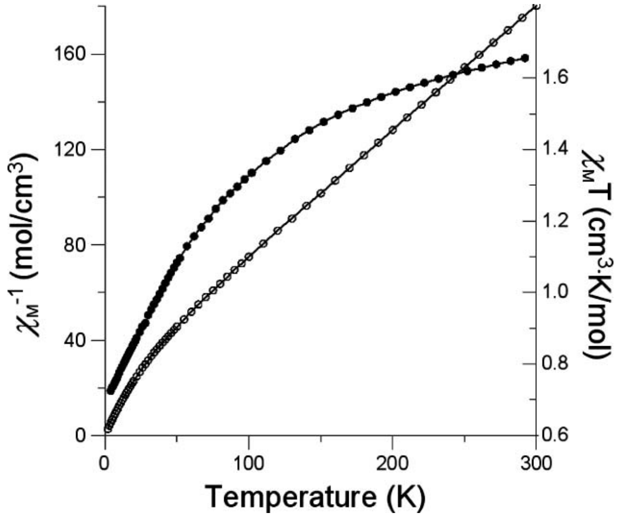

Fig. 6 $\chi_M T$ *vs* T (●) and $1/\chi_M$ *vs* T (○) for **5**.

In summary, we have synthesized fifteen isostructural rare earth metal squarates incorporating ethylene glycol ligand by a hydrothermal method and determined their structures by single-crystal X-ray diffraction. Each RE^{3+} cation is bonded to six squarate anions and one neutral ethylene glycol chelate, and each $C_4O_4^{2-}$ anion coordinates to four RE^{3+} cations such that a new 3-D framework structure is formed. These compounds are the first examples of organic–inorganic hybrids which contain both squarate and ethylene glycol ligands. They have also been characterized by TGA, ^{13}C CPMAS NMR, absorption spectroscopy and magnetic susceptibility. A variable-temperature *in situ* powder X-ray diffraction study on the Ce compound showed that the framework structure is retained up to 300 °C. The photoluminescence properties of these compounds are worth studying. Lanthanide-containing materials emit the entire spectral range from near infrared to blue. With the judicious selections of emitting ions doped in an inert host material, it is possible to design phosphors which emit across the entire visible spectrum with high color purity. The structure of the title compounds may allow simultaneous incorporation of a second (or even a third) type of lanthanide ion in the framework and, therefore, the fine-tuning of their photoluminescence properties. Further research on this theme is in progress.

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References

1 (*a*) B. Moulton and M. J. Zaworotko, *Curr. Opin. Solid State Mater. Sci.*, 2002, **6**, 117; (*b*) S. Kitagawa, R. Kitaura and S.-i. Noro, *Angew. Chem., Int. Ed.*, 2004, **43**, 2334; (*c*) H. K. Chae, D. Y. Siberio-Pérez, J. Kim, Y. B. Go, M. Eddaoudi, A. J. Matzger, M. O'Keeffe and O. M. Yaghi, *Nature*, 2004, **427**, 523; (*d*) U. Mueller, M. Schubert, F. Teich, H. Puetter, K. Schierle-Arndt and J. Pastré, *J. Mater. Chem.*, 2006, **16**, 626; (*e*) S. R. Batten, S. M. Neville, and D. R. Turner, *Coordination Polymers*, RSC Publishing, Cambridge, 2008 and references cited therein.

2 (*a*) H.-M. Lin, K.-H. Lii, Y.-C. Jiang and S.-L. Wang, *Chem. Mater.*, 1999, **11**, 519; (*b*) Z. A. D. Lethbridge and P. Lightfoot, *J. Solid State Chem.*, 1999, **143**, 58; (*c*) A. Choudhury, S. Natarajan and C. N. R. Rao, *J. Solid State Chem.*, 1999, **146**, 538; (*d*) J. Do, R. P. Bontchev and A. J. Jacobson, *Chem. Mater.*, 2001, **13**, 2601; (*e*) C. T. S. Choi, E. V. Anokhina, C. S. Day, Y. Zhao, F. Taulelle, C. Huguenard, Z. Gan and A. Lachgar, *Chem. Mater.*, 2002, **14**, 4096; (*f*) L.-H. Huang, H.-M. Kao and K.-H. Lii, *Inorg. Chem.*, 2002, **41**, 2936; (*g*) Y.-C. Jiang, S.-L. Wang, K.-H. Lii, N. Nguyen and A. Ducouret, *Chem. Mater.*, 2003, **15**, 1633; (*h*) Y.-C. Jiang, S.-L. Wang, S.-F. Lee and K.-H. Lii, *Inorg. Chem.*, 2003, **42**, 6154; (*i*) T. Loiseau, G. Férey, M. Haousa and F. Taulelle, *Chem. Mater.*, 2004, **16**, 5318; (*j*) C. N. R. Rao, S. Natarajan and R. Vaidhyanathan, *Angew. Chem., Int. Ed.*, 2004, **43**, 1466; (*k*) C.-Y. Sheu, S.-F. Lee and K.-H. Lii, *Inorg. Chem.*, 2006, **45**, 1891; (*l*) C.-M. Wang, Y.-Y. Wu, Y.-W. Chang and K.-H. Lii, *Chem. Mater.*, 2008, **20**, 2857.

3 F. A. Cotton, G. Wilkinson, C. A. Murillo and M. Bochmann, *Advanced Inorganic Chemistry*, 6th ed; John Wiley & Sons, 1999, New York, p. 486 and references therein.

4 (*a*) J. A. C. Van Ooijen, J. Reedijk and A. L. Spek, *Inorg. Chem.*, 1979, **18**, 1184; (*b*) X. Solans, M. Aguiló, A. Gleizes, J. Faus, M. Julve and M. Verdaguer, *Inorg. Chem.*, 1990, **29**, 775; (*c*) A. Bouayad, C. Brouca-Cabarrecq, J.-C. Trombe and A. Gleizes, *Inorg. Chim. Acta*, 1992, **195**, 193; (*d*) C.-R. Lee, C.-C. Wang, and Y. Wang, *Acta Crystallogr. Sect. B*, 1996, 52, 966; (*e*) K.-J. Lin and K.-H. Lii, *Angew. Chem., Int. Ed. Engl.*, 1997, **36**, 2076; (*f*) E. Huskowska and J. Legendziewicz, *J. Alloys Compd.*, 2000, **300–301**, 303; (*g*) P. Millet, L. Sabadié, J. Galy and J. C. Trombe, *J. Solid State Chem.*, 2003, **173**, 49; (*h*) M. Dan, K. Sivashankar, A. K. Cheetham and C. N. R. Rao, *J. Solid State Chem.*,

2003, **174**, 60; (*i*) J. Legendziewicz, P. Gawryszewska, J. Cybińska and G. Oremek, *J. Alloys Compd.*, 2004, **380**, 389; (*j*) C. Brouca-Cabarrecq, A. Mohanu, P. Millet and J. C. Trombe, *J. Solid State Chem.*, 2004, **177**, 2575; (*k*) N. Mahé and T. Bataille, *Inorg. Chem.*, 2004, **43**, 8379.

5 S. Konar, M. Corbella, E. Zangrando, J. Ribas and N. R. Chaudhuri, *Chem. Commun.*, 2003, 1424.

6 H. Akkari, P. Bénard-Rocherullé, H. Mérazig, T. Roisnel and J. Rocherullé, *Solid State Sci.*, 2006, **8**, 704.

7 B.-P. Yang and J.-G. Mao, *Inorg. Chem.*, 2005, **44**, 566.

8 C.-M. Wang and K.-H. Lii, *Inorg. Chem.*, 2009, **48**, 6335.

9 G. M. Sheldrick, *SHELXTL Programs, version 5.1*, Bruker AXS GmbH: Karlsruhe, Germany, 1998.

10 P. W. Selwood, *Magnetochemistry*, Interscience, New York, 1956.

11 (*a*) V. J. Scherle and F. A. Schröder, *Acta Crystallogr., Sect. B: Struct. Crystallogr. Cryst. Chem.*, 1974, **30**, 2772; (*b*) M. C. Cruickshank and L. S. D. Glasser, *Acta Crystallogr., Sect. C: Cryst. Struct. Commun.*, 1985, **41**, 1014; (*c*) A. Lehtonen and R. Sillanpää, *Polyhedron*, 1994, **13**, 2519; (*d*) O. Wichmann and A. Lehtonen, *Inorg. Chem. Commun.*, 2009, **12**, 15.

12 (*a*) A. R. Pico, C. S. Houk, T. J. R. Weakley and C. J. Page, *Inorg. Chim. Acta*, 1997, **258**, 155; (*b*) R. Köferstein, L. Jäger, V. Lorenz, H.-P. Abicht, J. Woltersdorf, E. Pippel and H. Görls, *Solid State Sci.*, 2005, **7**, 1280; (*c*) L. Jäger, V. Lorenz, C. Wagner, T. Müller and H.-P. Abicht, *Z. Kristallogr.*, 2005, **220**, 183.

13 (*a*) R. W. J. Scott, N. Coombs and G. A. Ozin, *J. Mater. Chem.*, 2003, **13**, 969; (*b*) X. Jiang, Y. Wang, T. Herricks and Y. Xia, *J. Mater. Chem.*, 2004, **14**, 695.

14 (*a*) W. Städeli, R. Hollenstein and W. von Philipsborn, *Helv. Chim. Acta*, 1977, **60**, 948; (*b*) G. Cerioni, R. Janoschek, Z. Rappoport and T. T. Tidwell, *J. Org. Chem.*, 1996, **61**, 6212; (*c*) A. N. Klymachyov and N. S. Datal, *Z. Phys. B: Condens. Matter*, 1997, **104**, 651.

15 S. Cotton, *Lanthanide and Actinide Chemistry*, John Wiley & Sons, West Sussex, England, 2007.

16 D. G. Karraker, *Inorg. Chem.*, 1968, **7**, 473.

17 M. Andruh, E. Bakalbassis, O. Kahn, J. C. Trombe and P. Porcher, *Inorg. Chem.*, 1993, **32**, 1616.