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FULL PAPER

Synthesis, structure and magnetic properties of the 2,2′-oxydiacetato-bridged Cu(II)–Ln(III) complexes $[\{Cu_3Ln_2(oda)_6(H_2O)_6\}\cdot 12H_2O]_n$ (Ln = Y, Gd, Eu, Nd, Pr)

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Heterometallic compounds comprising copper(II) and rare-earth cations with carboxylate groups of the 2,2′-oxydiacetato as the connecting ligands, have been investigated. Five isostructural polymers $[\{Cu_3Ln_2(oda)_6(H_2O)_6\}\cdot 12H_2O]_n$ (Ln = Y (**1**), Gd (**2**), Eu (**3**), Nd (**4**) and Pr (**5**)) have been obtained and their structures determined by X-ray diffraction methods. The Ln(III) cations in **1** to **5** are coordinated by six carboxy and three ether oxygen atoms in the tricapped trigonal prism arrangement and the Cu(II) cations are bonded to four carboxy oxygens and two apical aqua ligands in a distorted octahedral geometry. The magnetic behaviors of these complexes show very weak antiferromagnetic interaction in the solid.

Introduction

The study of heterometallic complexes containing copper(II) and rare-earth(III) cations connected by bridging ligands is being actively pursued because of their relevance in solid-state technology[1–3] and as models for magnetic studies.[4–6] Interest has been essentially focused on the Cu(II)–Gd(III) couple, since it has been shown to present a ferromagnetic interaction in most dinuclear and polynuclear compounds with Cu_2Gd, Cu_4Gd, Cu_4Gd_2 or $(CuGd)_n$ cores, bridged by phenoxo or multidentate ligands with hetero-donating groups.[7–20] It may be noted, however, that structural studies on heterometallic Cu–Ln complexes bridged by carboxylate groups only, are scarce. Reported cases involve a linear pentanuclear Cu_3Gd_2 compound bridged by chloroacetates,[21] tetranuclear Cu_2Ln_2 compounds (Ln = La, Ce, Gd, Sm) bridged by betaine ($Me_3N^+CH_2CO_2^-$),[22] CuLn (Ln = La, Nd) and pentanuclear Cu_3Nd_2 compounds bridged by pyridinioacetate ($C_5H_5N^+$-$CH_2CO_2^-$).[23]

Our previous work on the complexing properties of 2,2′-oxydiacetato [oda = $O(CH_2CO_2)_2^{2-}$] towards yttrium(III) and lanthanide(III) elements has highlighted its versatility as a connecting ligand in various homo- and hetero-metallic extended solids, with the metal centers bridged by carboxylate ligands only.[24–26] The design strategy of combining the $[Ln(oda)_3]^{3-}$ building blocks with tripositive Ln^{3+} metal ions is now used with divalent Cu(II) to obtain the Cu(II)–Ln(III) heterometallic complexes $[\{Cu_3Ln_2(oda)_6(H_2O)_6\}\cdot 12H_2O]_n$ (Ln = Y, Gd, Eu, Nd, Pr). Recent studies by Mao *et al.*[27–29] reported on the characterization of the similar polymers $Cu_3Ln_2(oda)_6(H_2O)_6\cdot nH_2O$ (Ln = Nd,[27] Gd,[28] $n = 3$; Er,[27] Yb,[29] $n = 0$). However, disagreement in the crystal data that it gives for the Cu(II)–Gd(II) complex and differences in the hydration number of the Cu(II)–Gd(II) and Cu(II)–Nd(II) compounds prompted us to further investigate this interesting series.

We report the preparation of heterometallic copper(II)–yttrium(III) (**1**), –gadolinium(III) (**2**), –europium(III) (**3**), –neodymium(III) (**4**) and –praseodymium(III) (**5**) complexes with the 2,2′-oxydiacetato ligand. Polymers **1** to **5** form a series of isostructural compounds which allows a comparative study, herein presented, on the structures and thermal and magnetic properties as the rare-earth element changes along the series. The X-ray structures of compounds **1, 2** and **3** have appeared in a preliminary communication.[30]

Experimental

Materials and methods

All starting materials were purchased from Aldrich and were used without further purification. Elemental analyses (C,H) were performed on a Carlo Erba EA 1108 instrument. Copper content was determined on a Shimadzu AA6501 spectrophotometer and Gd in the Cu–Gd compound **2** by ICP-atomic emission spectroscopy. Infrared spectra were recorded on a Nicolet FT-IR 510 P spectrophotometer using the KBr pellet technique. Thermogravimetric analyses were recorded on a Mettler TG-50 thermal analyzer under an atmosphere of air at a heating rate of 5 °C min^{-1}. Powder X-ray diffraction (XRD) data were collected using monochromated Cu-Kα radiation on a Phillips X'Pert diffractometer. Temperature dependent magnetic susceptibilities of solid samples were recorded on a SHE 906 SQUID susceptometer in the range 5–300 K with an applied field of 1 kOe (10^3 A m^{-1}). Pascal's

Table 1 Crystallographic data for compounds **1**, **2**, **3**, **4** and **5**

	1	**2**	**3**	**4**	**5**
Formula	$C_{24}H_{60}Cu_3O_{48}Y_2$	$C_{24}H_{60}Cu_3Gd_2O_{48}$	$C_{24}H_{60}Cu_3Eu_2O_{48}$	$C_{24}H_{60}Cu_3Nd_2O_{48}$	$C_{24}H_{60}Cu_3O_{48}Pr_2$
M	1485.16	1621.84	1611.26	1595.82	1589.16
a,b/Å	14.595(2)	14.717(2)	14.872(1)	15.064(2)	15.199(2)
c/Å	15.267(3)	15.169(3)	15.019(2)	14.751(3)	14.584(3)
U/Å^3	2816.2(8)	2845.3(6)	2876.6(5)	2899.2(7)	2917.9(8)
D_c/g cm^{-3}	1.75	1.89	1.86	1.83	1.81
F(000)	1506	1606	1602	1590	1586
μ/cm^{-1}	3.27	3.52	3.35	2.95	2.83
Reflections (unique)	875	890	896	902	906
Reflections $[F^2 > 2\sigma(F^2)]$	533	684	730	722	773
Parameters refined	86	84	70	80	81
$R1$ [a] $[F^2 > 2\sigma(F^2)]$	0.038, 0.080	0.024, 0.054	0.035, 0.100	0.030, 0.105	0.031, 0.105
$wR2$ [b]	0.081, 0.094	0.037, 0.060	0.042, 0.106	0.040, 0.114	0.036, 0.110
Max, min $\Delta\rho$/e Å^{-3}	0.37, −0.45	0.30, −0.31	0.86, −0.97	0.78, −0.49	0.66, −0.49

Features in common: $T = 23$ °C; system: hexagonal; $Z = 2$; space group: *P6/mcc* (No. 192); crystals: greenish-blue polyhedra; absorption corrections: semiempirical (ψ-scan). [a] $R1 : \Sigma\big||F_o| - |F_c|\big|/\Sigma|F_o|$. [b] $wR2$: $\{\Sigma[w(F_o^2 - F_c^2)^2]/\Sigma[w(F_o^2)^2]\}^{\frac{1}{2}}$.

constants were used to estimate the correction for the underlying diamagnetism of the sample.

Synthesis

$[\{Cu_3Y_2(oda)_6(H_2O)_6\}\cdot 12H_2O]_n$ 1. Compound **1** was prepared by adding to a water solution (250 mL) of 2,2′-oxydiacetic acid (1.0 g, 7.5 mmol) a mixture of $[Y\{Hoda\}_3\cdot H_2oda\cdot H_2O]$ (1.0 g, 2.0 mmol) prepared as reported previously[26] and copper acetate monohydrate (0.6 g, 3.0 mmol). The mixture was heated under reflux for 4 h and the compound was collected by filtration as a polycrystalline powder, washed with ethanol and dried in air. Yield: (0.80 g, 70%). (Found: C, 19.5; H, 4.2; Cu, 12.5. Calc. for $C_{24}H_{60}Cu_3O_{48}Y_2$: C, 19.4; H, 4.1; Cu, 12.8%). Single crystals of **1** suitable for crystallographic work separated out from the filtered solution after standing for three weeks. IR (KBr, cm^{-1}): 3430vs, br, 1599vs, 1478s, 1441vs, 1370m, 1318vs, 1248w, 1132s, 1063s, 1009w, 972m, 945m, 625s, br, 386m.

$[\{Cu_3Gd_2(oda)_6(H_2O)_6\}\cdot 12H_2O]_n$ 2. To a solution of 2,2′-oxydiacetic acid (1.0 g, 7.5 mmol) in water (350 mL) was added Gd_2O_3 (0.35 g, 1 mmol) and CuO (0.25 g, 3.1 mmol). The reaction mixture was heated under reflux for 8 h under continuous stirring. A blue solution was formed which was concentrated to *ca*. 150 mL on a rotary evaporator and passed through a glass filter. After standing in a stoppered flask for two weeks well-shaped blue single crystals of compound **2** separated out. The crystals were filtered, washed with cold water, and dried in air. Yield: (1.10 g, 75%). (Found: C, 17.8; H, 3.8; Cu, 11.8; Gd, 19.0. Calc. for $C_{24}H_{60}Cu_3Gd_2O_{48}$: C, 17.7; H, 3.7; Cu, 11.5; Gd, 19.4%). The IR spectrum was similar within ±5 cm^{-1} to that for **1** above.

$[\{Cu_3Eu_2(oda)_6(H_2O)_6\}\cdot 12H_2O]_n$ 3, $[\{Cu_3Nd_2(oda)_6(H_2O)_6\}\cdot 12H_2O]_n$ 4 and $[\{Cu_3Pr_2(oda)_6(H_2O)_6\}\cdot 12H_2O]_n$ 5. These compounds were obtained following the method described above for the Cu–Gd compound. The yields were about 75% for the three compounds based on the amount of Ln_2O_3 used. **3** (Found: C, 17.8; H, 3.8; Cu, 11.5. Calc. for $C_{24}H_{60}Cu_3Eu_2O_{48}$: C, 17.9; H, 3.75; Cu, 11.8%). **4** (Found: C, 18.1; H, 3.9; Cu, 12.1. Calc. for $C_{24}H_{60}Cu_3Nd_2O_{48}$: C, 18.1; H, 3.8; Cu, 11.9%). **5** (Found: C, 18.2; H, 3.7; Cu, 12.4. Calc. for $C_{24}H_{60}Cu_3O_{48}Pr_2$: C, 18.1; H, 3.8; Cu, 12.0%). The IR spectra are very similar to those above, with absorption bands within ±5 cm^{-1}.

Crystallography

A summary of crystal parameters and data collection and refinement details is given in Table 1. Data were collected on a Siemens R3m diffractometer equipped with a graphite-monochromated Mo-Kα ($\lambda = 0.71073$ Å) radiation. The unit cell parameters were determined by least-squares refinement of 25 reflections in the range $15° \le 2\theta \le 25°$. Intensity data were collected in the range $3° \le 2\theta \le 50°$ by the $\omega/2\theta$-scan technique and corrected for Lorentz and absorptions effects (ψ-scan). Two standard reflections were monitored every 98, and showed no systematic changes. The structures were solved by a combination, of direct methods and difference Fourier syntheses. Refinement was performed by full-matrix least-squares in F^2, with anisotropic thermal parameters for the non-hydrogen atoms.

The thermogravimetric analyses of single crystals indicated the presence of 18 water molecules per formula unit. The six molecules apically coordinated to copper could be identified on successive Fourier maps and were found to remain stable along anisotropic least-squares refinement; their hydrogen atoms were refined with constrained O–H and H · · · H distances in order to prevent drifts. Those attached to carbon were placed in their ideal positions (C–H = 0.96 Å) and allowed to ride on their host atoms. Hydration water molecules appeared elusive in all five structures and only a few of them, heavily disordered, could be located. Computer programs used in this study were SHELXL-97 and SHELXTL/PC software packages,[31,32] and PARST.[33]

CCDC reference number 186/1961.

See http://www.rsc.org/suppdata/dt/a9/a909544f/ for crystallographic files in .cif format.

Results and discussion

The reaction of aqueous solutions of 2,2′-oxydiacetic acid with Ln_2O_3 and CuO led to the formation of $[\{Cu_3Ln_2(oda)_6(H_2O)_6\}\cdot 12H_2O]_n$ complexes (where Ln = Gd, Eu, Nd or Pr) in high purity and yield. Only the yttrium complex could not be obtained from the oxides and was prepared from a mixture of $[Y\{Hoda\}_3\cdot H_2oda\cdot H_2O]$[26] and copper acetate monohydrate. Compounds **1** to **5** can be obtained as beautiful deep blue crystals and stored in air for extended periods of time. The IR spectra are almost identical within ±5 cm^{-1} suggesting similar structures for the compounds. The strong COO^- bands centered at *ca*. 1595, 1475 and 1440 cm^{-1} support the presence of bridging carboxylate groups.

The results from thermogravimetric analysis performed on air-dried crystals of compounds **1** to **5** are very similar. Typically, Fig. 1 shows the weight losses for compound **1**. The first mass loss of 21.8% in the range 50–150 °C corresponds to all the eighteen water molecules per formula unit. Two steps with maxima at 101 and 145 °C are seen to overlap in the dehydration process with a peak area ratio of 2 : 1. This can be accounted for by considering that the lower temperature event

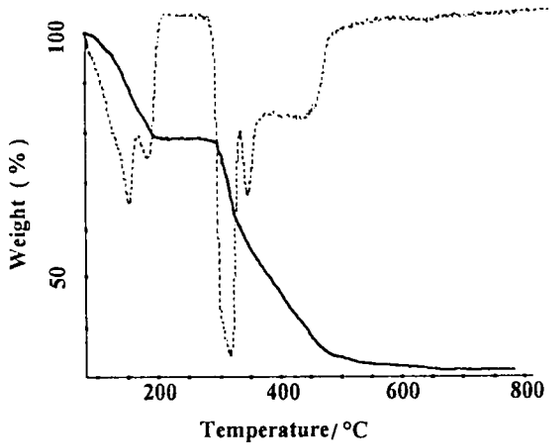

Fig. 1 TGA diagram of compound **1** (under an atmosphere of air). The first mass loss to 78% represents **1** − 18(H_2O). Dashed lines represent the negative values of the first derivatives (% $°C^{-1}$).

is the loss of the twelve water molecules in the interlayer region, and the higher temperature event is the loss of the six water molecules coordinated to the copper atoms. The process is easily reversible and rehydration occurs in a few hours under atmospheric conditions, as confirmed by TGA and XRD. Thermal gravimetric analysis performed on different microcrystalline phases showed, that the water content of the samples can be highly variable. The present is a rare example where the host structure is not destroyed when all the water molecules, including those coordinated to the Cu atoms, are completely removed. It is likely that the flexibility of the oda ligands prevent collapse of the structure upon departure of the enclathrated water. An example of reversible loss of water at temperatures below 200 °C has been reported for Y_2Cu_8-(μ_4-O)(μ-PyO)$_{12}$(μ-Cl)$_2$(NO_3)$_4$(H_2O)$_2$.[34] The onset temperature in Fig. 1 at *ca.* 250 °C should correspond to removal of the organic part of the material. No attempts were made to identify intermediate products during these thermolyses.

Crystal structures

Compounds [{Cu_3Ln_2(oda)$_6$(H_2O)$_6$}·12H_2O]$_n$ (Ln = Y (**1**), Gd (**2**), Eu (**3**), Nd (**4**), Pr (**5**)) crystallize in the hexagonal crystal system, space group *P6/mcc* (No. 192). The crystal structure is built up from two distinct types of building blocks, LnO_9 and CuO_6 illustrated in Fig. 2. The Ln atom lies on the intersection of a three- and two-fold axis (space group site *c*, site symmetry 32) and coordinates to the two carboxylate oxygens O1 and O1′ and to the ether oxygen O3 of three symmetry related oda ligands. The overall coordination geometry around the Ln atoms in the series conforms most closely to tricapped trigonal prismatic (TCTP).[35] Each Cu atom lies on the intersection of a twofold axis and a mirror plane (crystallographic site g, symmetry 2/*m*) and coordinates to the outer carboxylate oxygens O2 and O2′ of four oda ligands at the equatorial plane. Coordination is completed by two aqua ligands at the apical sites to form a highly elongated octahedral geometry (Jahn–Teller distortion). The fact that all the outer carboxylate oxygens link to copper atoms determines that each Ln atom is surrounded by six Cu atoms as nearest neighbors, while the Cu atoms have four Ln atoms in their vicinity, as expected from the Cu/Ln molar relationship. As a result of this connectivity pattern, the Ln polyhedra create a 2D planar honeycomb structure parallel to (001) at *z* heights of *ca.* 0.25 and 0.75. Each pair of polyhedra at one side of the hexagonal motif is connected with its homologous pair one layer below (above) *via* a copper atom bonded to four outer carboxylate oxygens (two from above and two from below). As a result of the translational symmetry along *z*, the 2D structure develops into a 3D honeycomb structure with columnar channels of nearly 6 Å diameter,

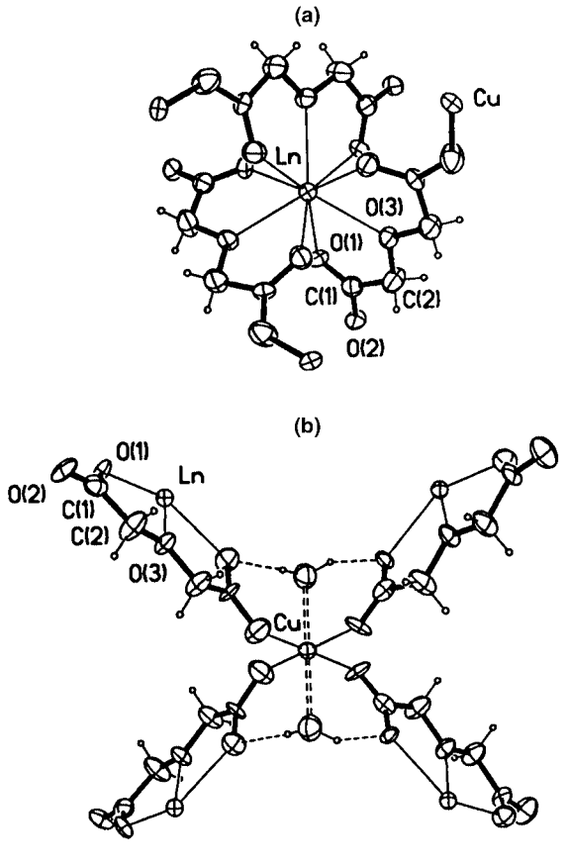

Fig. 2 Diagrams (50% thermal ellipsoids) showing the two building units (*a*) and (*b*) with atom labels of the Cu–Ln series.

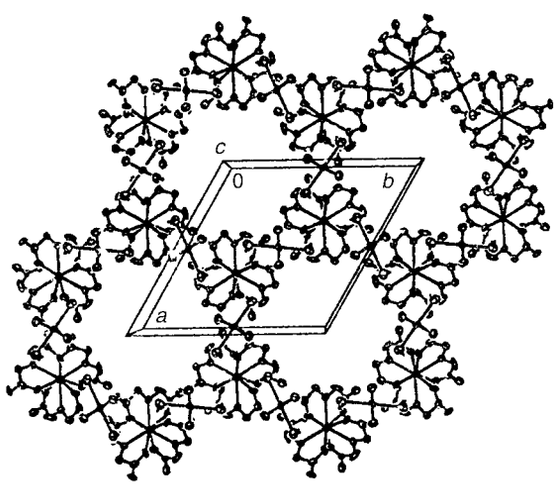

Fig. 3 View of a [001] projection of the extended solids of the Cu–Ln series accentuating the column channels. H atoms and water molecules are omitted for clarity.

Fig. 3. It should be emphasized that the latter are partially filled by the H atoms of the methylene groups and the lattice water molecules. This type of structure is by itself an interesting object to look into in terms of possible inclusion and enclathration activities and results from the particular *anti-anti* type of bridging of the carboxylate groups in the series. Each Ln atom in the extended structure is, connected to the six nearest Cu atoms *via* single *anti-anti* μ-carboxylato-*O*,*O*′ bridges with Cu · · · Ln distances across the carboxylate bridges ranging from 5.685(1) to 5.705(1) Å depending on the nature of Ln(III). This type of connection has also been found in polymeric rare-earth oxydiacetates.[24–26] It is noteworthy that in the chloroacetate complex Cu_3Gd_2(O_2CCH_2Cl)$_{12}$(H_2O)$_8$·2H_2O, the central Cu atom is connected to two Gd atoms *via syn-anti*

Table 2 Selected bond distances (Å) and angles (°) for compounds **1**, **2**, **3**, **4** and **5**[a]

	1	**2**	**3**	**4**	**5**
Ln–O(1)	2.371(3)	2.412(3)	2.424(4)	2.456(4)	2.467(3)
Ln–O(3)	2.455(4)	2.483(3)	2.492(5)	2.533(5)	2.557(7)
Cu–O(2)	1.954(3)	1.955(3)	1.951(4)	1.954(4)	1.955(3)
Cu–O(1w)^{i}	2.504(6)	2.510(5)	2.512(7)	2.542(8)	2.566(7)
O(1)–Ln–O(1)^{ii}	85.9(1)	85.3(2)	84.5(2)	83.2(2)	82.8(1)
O(1)–Ln–O(1)^{iii}	79.3(1)	80.0(1)	80.7(1)	81.8(1)	82.1(2)
O(1)–Ln–O(1)^{iv}	146.3(2)	147.1(1)	147.3(2)	147.8(2)	147.9(2)
O(1)–Ln–O(1)^{v}	127.5(1)	126.2(1)	125.4(2)	123.9(2)	122.9(2)
O(1)–Ln–O(3)	63.75(7)	63.11(6)	62.71(8)	61.93(8)	61.44(7)
O(1)–Ln–O(3)^{iii}	73.17(7)	73.54(6)	73.63(9)	73.89(9)	73.96(8)
O(1)–Ln–O(3)^{vi}	137.04(7)	137.4(6)	137.75(9)	138.42(9)	138.98(8)
O(3)–Ln–O(3)^{iii}	120.0	120.0	120.0	120.0	120.0
O(2)–Cu–O(2)^{vii}	91.3(2)	91.4(2)	91.1(3)	91.5(3)	91.5(2)
O(2)–Cu–O(2)^{viii}	180.0	180.0	180.0	180.0	180.0
O(2)–Cu–O(1w)^{i}	85.5(1)	84.1(1)	84.3(2)	83.0(2)	82.7(1)

[a] Symmetry codes: (i) $x - y + 1, -y + 1, -z + 1/2$; (ii) $x, x - y, -z + 1/2$; (iii) $-x + y + 1. -x + 1, z$; (iv) $-y + 1, -x + 1, -z + 1/2$; (v) $-x + y + 1, y, -z + 1/2$; (vi) $-y + 1, x, -y, z$; (vii) $-x + 2, -y + 1, z$; (viii) $-x + 2, -y + 1, -z + 1$.

Table 3 Hydrogen-bond distances (Å) and angles (°) involving the coordinated water molecules for compounds **1**, **2**, **3**, **4** and **5**[a]

Cu–Ln	Ow–Hw···O	Ow–Hw	Hw···O	Ow···O	Ow–Hw···O
1 Cu–Y	O1w–H1w···O1^{i}	1.00(5)	1.84(5)	2.800(4)	162(4)
	O1w–H1w···O2^{i}	1.00(5)	2.77(6)	3.295(6)	114(3)
2 Cu–Gd	O1w–H1w···O1^{i}	0.91(5)	1.91(5)	2.802(4)	166(5)
	O1w–H1w···O2^{i}	0.91(5)	2.82(6)	3.336(5)	118(4)
3 Cu–Eu	O1w–H1w···O1^{i}	1.06(7)	1.77(7)	2.793(5)	164(6)
	O1w–H1w···O2^{i}	1.06(7)	2.65(8)	3.330(7)	122(5)
4 Cu–Nd	O1w–H1w···O1^{i}	0.91(7)	1.92(6)	2.794(5)	164(7)
	O1w–H1w···O2^{i}	0.91(7)	2.92(8)	3.390(8)	114(5)
5 Cu–Pr	O1w–H1w···O1^{i}	0.93(8)	1.89(8)	2.799(5)	165(8)
	O1w–H1w···O2^{i}	0.93(8)	2.91(9)	3.419(7)	116(6)

[a] Symmetry codes: (i) $-x + y + 1, +y, -z + 1/2$.

Table 4 Selected geometrical parameters for the Cu(II)–Ln(III) compounds

Compound	*a*/Å	*c*/Å	*c*/*a*	Ln–O/Å	$r(Ln^{3+})$[a]/Å	Reference
Cu–Yb	14.344(3)	15.470(7)	1.0785	2.357(9)/2.414(6)	1.18	29
Cu–Er	14.516(4)	15.279(7)	1.0526	2.361(5)/2.417(3)	1.202	27
1 Cu–Y	14.595(2)	15.267(3)	1.0460	2.372(3)/2.453(5)	1.215	This work
2 Cu–Gd	14.717(2)	15.169(3)	1.0307	2.412(3)/2.493(3)	1.247	This work
2′ Cu–Gd	14.769(1)	15.098(3)	1.022	2.409(3)/2.483(5)	1.247	This work
3 Cu–Eu	14.872(1)	15.019(2)	1.0099	2.424(3)/2.493(5)	1.26	This work
4 Cu–Nd	15.064(2)	14.751(3)	0.9792	2.457(4)/2.537(5)	1.303	This work
Cu–Nd	15.091(4)	14.710(3)	0.9748	2.448(3)/2.520(5)	1.303	27
5 Cu–Pr	15.199(2)	14.584(3)	0.9592	2.470(5)/2.566(12)	1.319	This work
?(Cu–Gd)	15.126(3)	14.690(8)	0.9712	2.448(2)/2.522(2)	?	28

[a] Ionic radii according to Huheey, ref. 37.

μ-carboxylato-*O*,*O′* bridges with Cu···Gd distances of 4.662(1) Å. In addition each terminal Cu is quadruply connected to Gd(III) by four *syn-syn* μ-carboxylato-*O*,*O′* bridges with Cu···Gd distances of 3.561(1) Å.[21] Similar quadruple carboxylate bridges with Cu···Gd separations of 3.595(1) Å have been reported in the Cu_2Gd_2 betaine complex.[22] In complexes **1** to **5** the shortest Ln···Ln and Cu···Cu separations range from 7.3 to 7.6 Å, depending on the nature of the Ln(III) cation. Selected bond lengths and angles for the five isostructural complexes are summarized in Table 2. All metric parameters are normal and within the reported ranges for similar bonds.[36]

Hydrogen bonding plays an important role in the stabilization of the extended structure. Each aqua ligand bonded to Cu(II) is linked through two hydrogen bonds to neighboring carboxylate oxygens bonded to Ln atoms. The characteristics of the hydrogen bond network are given in Table 3. The hydration water molecules which occupy the columnar gaps are mostly disordered and the hydrogen atomic positions could not be found.

Selected geometrical parameters for compounds **1** to **5** together with the corresponding values for the related compounds in references[27–29] are collected in Table 4. Analysis of the data shows that the cell parameters ratio *c*/*a* as well as the Ln–O bonds vary in a smooth and continuous way with increasing cation radii $r(Ln^{3+})$. The Cu–O distances, however, are identical for all the compounds in Table 2. The compound reported as **2′** was obtained from the reaction of a mixture of gadolinium and copper nitrates with H_2oda at pH = 7 following the method described by Mao *et al.*[28] Our values for bond distances and angles in **2** and **2′** differ by less than 3σ and both are within experimental error to those reported for the tris-chelated $[Gd(oda)_3]^{3-}$ core in $[\{LaGd(oda)_3(H_2O)_3{\cdot}6H_2O\}_n]$.[25] The rather large differences in the repeat distances along *a* and *c* (*ca.*

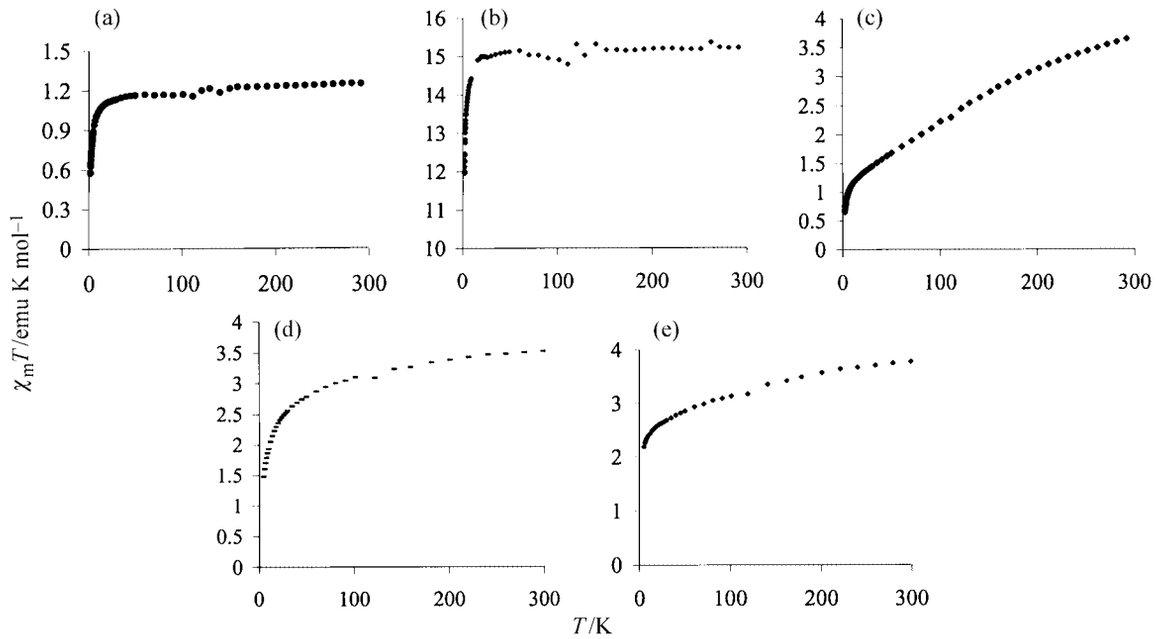

Fig. 4 Plots of molar susceptibility *versus* temperature for compounds **1** to **5**: (a) Cu–Y (**1**), (b) Cu–Gd (**2**), (c) Cu–Eu (**3**), (d) Cu–Nd (**4**) and (e) Cu–Pr (**5**).

50σ) may be ascribed to the different number of hydration water molecules in the solids. Though all compounds in Table 4 clearly belong to the same family, the Gd–O bond distances for the reported Cu–Gd compound[28] are significantly longer than our data for **2** and **2′** (*ca.* 10σ higher). We also note that the results for the *c*/*a* factor and particularly those for the Gd–O bond distances fit closer into the entire body of data in Table 4 if we assume that a lanthanide with a larger cation radius was actually the compound described in the reference paper. Obviously if this is correct, the X-ray data that it gives should correspond to an earlier lanthanide (or mixture of lanthanides), as suggested by the smooth changes in the bond distances along the isostructural series. It appears that the near identity of the crystallographic data for both the Cu–Gd and the Cu–Nd compounds has been overlooked in the references.[27,28] The correctness of the data given here for the Cu(II)–Gd(III) compound **2** is further supported by analytical data and by the magnetic measurements below.

Magnetic properties

The temperature dependencies of the magnetic susceptibility for compounds **1** to **5** were measured in the temperature range 5–300 K, with an applied field of 1 kOe. The plots of $\chi_m T$ *versus* T for these five compounds are shown in Fig. 4 with χ_m being the molar magnetic susceptibility corrected for the diamagnetic contribution and T the temperature.

For compound **1** $\chi_m T$ is practically constant from room temperature down to 50 K ($\chi_m T = 1.25$ emu K mol^{-1}). This high temperature value corresponds to that expected for three non-interacting $S = 1/2$ spins, belonging to the copper(II) ions, since no contribution is expected from the nonmagnetic yttrium ions. This value of $\chi_m T = 1.25$ emu K mol^{-1} allows us to calculate a magnetic moment of 1.83 μ_B per copper atom. On further lowering the temperature below 50 K, $\chi_m T$ decreases abruptly to a value of 0.60 emu K mol^{-1} at 5 K (μ_{eff} = 1.26 μ_B per copper atom). Since the closest interatomic Cu · · · Cu distance is greater than 7 Å, the possibility of an exchange between the copper centers is remote, and the decrease in the magnetic moment below 50 K should be attributed to weak lattice interactions. The results for compound **1** should be of use in the interpretation of the interactions which might exist in the rest of the isostructural complexes **2** to **5**, when non-magnetic Y(III) is replaced by magnetic Ln(III) ions.

For compound **2** $\chi_m T$ is quite constant from 300 K to 20 K and, weak bulk antiferromagnetic exchange interactions become evident at lower temperatures. The room temperature value of $\chi_m T$ is 15.21 emu K mol^{-1}. Considering that the three non-interacting copper(II) ions will contribute 1.25 emu K mol^{-1} to the bulk $\chi_m T$ value, a magnetic moment of 7.5 μ_B per gadolinium center can be calculated by using the difference of both magnetic susceptibilities ($\Delta = (\chi_m T)_2 - (\chi_m T)_1$). This value is fairly close to the expected value of 7.94 μ_B for a well isolated non-interacting gadolinium(III) ion. Magnetic studies on Cu(II)–Gd(III) complexes containing heterodonor ligands (N and O as donating atoms) bonded to the metal centers have been shown to display an overall ferromagnetic behavior.[13,18,38,39] However, the magnetic behaviors of carboxylate-bridged Cu(II)–Gd(III) complexes show that at low temperature the strongest interaction present is antiferromagnetic.[22] Our data for compound **2** are in line with these results.

The plot of $\chi_m T$ *vs.* T for compound **3** is shown in Fig. 4c. The room temperature value of $\chi_m T$ is 3.82 emu K mol^{-1}, larger than the 1.25 emu K mol^{-1} of the copper(II)-only value in spite of the non-magnetic character of the $^7F_0$ ground state of Eu(III). This effect is obviously due to the van Vleck behavior of the europium ions. A monotonical decrease of $\chi_m T$ is observed as the temperature is lowered, due to the thermal depopulation of the excited state $^7F_1$. The sharp decrease of $\chi_m T$ below 20 K should then correspond to a combined effect of depopulation and intermolecular antiferromagnetism, as observed for the above compounds.

Figs. 4d and 4e show the magnetic behavior of compounds **4** and **5**. The same feature is observed in both cases, that is, a decrease in the values of $\chi_m T$ as the temperature is lowered. The room temperature values of $\chi_m T$ are 3.77 and 3.53 emu K mol^{-1} for compounds **4** and **5**, respectively. These values allow us to calculate a magnetic moment of 3.2 and 3.1 μ_B per neodymium and praseodymium atom respectively, which correspond to their expected free-ion moments. If the Nd(III) and Pr(III) ions are exchange-coupled with copper(II), the temperature dependence of $\chi_m T$ is due both to this interaction and to the thermal population of the rare-earth ion Stark components.[40] Thus, the magnetic data for complexes **2** to **5** show that the calculated

magnetic moments for the lanthanide ions at room temperature correspond fairly well to the expected free-ion values (except for Eu, which is a van Vleck ion). A slight decrease of the magnetic moment at lower temperatures, can be attributed to both an antiferromagnetic coupling between the 4f electrons of the lanthanide(III) ions and the copper(II) 3d electrons and also to crystal field effects due to the intrinsic nature of the lanthanide series. At temperatures below 20 K, the Cu–Cu antiferromagnetic interactions dominate the magnetic behavior, as clearly seen in the case of complex **1**. Our results coincide with those reported for the Cu_2Ln_2 betaine clusters with carboxylate bridges in *syn-anti* conformation.[22]

In conclusion, the main results described here have shown (i) new members of the Cu(II)–Ln(III) isostructural series of Cu_3Ln_2 cores bonded by carboxylate groups in *anti-anti* conformation and (ii) very weak antiferromagnetic exchanges dominating in these *anti-anti* carboxylate-bridged compounds.

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