Structural trends in a series of isostructural lanthanide–copper metallacrown sulfates (Ln^{III} = Pr, Nd, Sm, Eu, Gd, Dy and Ho): hexaaquapentakis[μ_3-glycinehydroxamato(2−)]sulfatopentacopper(II)lanthanide(III) heptaaquapentakis[μ_3-glycinehydroxamato(2−)]sulfatopentacopper(II)lanthanide(III) sulfate hexahydrate

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The seven isostructural complexes, $[Cu_5Ln(C_2H_4N_2O_2)_5(SO_4)(H_2O)_{6.5}]_2(SO_4)\cdot6H_2O$, where Ln^{III} = Pr, Nd, Sm, Eu, Gd, Dy and Ho, are representatives of the 15-metallacrown-5 family. Each dianion of glycinehydroxamic acid (GlyHA) links two Cu^{II} cations forming a cyclic $[CuGlyHA]_5$ frame. The Ln^{III} cations are located at the centre of the $[CuGlyHA]_5$ rings and are bound by the five hydroxamate O atoms in the equatorial plane. Five water molecules are coordinated to Cu^{II} cations, and one further water molecule, located close to an inversion centre between two adjacent $[Cu_5Ln(GlyHA)_5]^{2+}$ cations, is disordered around this inversion centre and coordinated to a Cu^{II} cation of either the first or second metallacrown ether. Another water molecule and one of the two crystallographically independent sulfate anions are coordinated, the latter in a bidentate fashion, to the Ln^{III} cation in the axial positions. The second sulfate anion is not coordinated to the cation, but is located in an interstitial position on a crystallographic inversion centre, thus leading to disorder of the O atoms around the centre of inversion. The Ln—O bond distances follow the trend of the lanthanide contraction. The apical Ln—O bond distances are very close to the sums of the ionic radii. However, the Ln—O distances within the metallacrown units are slightly compressed and the Ln^{III} cations protrude

significantly from the plane of the otherwise flat metallacrown ligand, thus indicating that the cavity is somewhat too small to accommodate the Ln^{III} ions comfortably. This effect decreases with the size of the lanthanide cation from complex (I) (Ln^{III} = Pr; 0.459 Å) to complex (VII) (Ln^{III} = Ho; 0.422 Å), which indicates that the smaller lanthanide cations fit the cavity of the pentacopper metallacrown ring better than the larger ones. The diminished contraction of Ln—O distances within the metallacrown planes leads to an aniostropic contraction of the unit-cell parameters, with a, c and V following the trend of the lanthanide contraction. The b axes, which are mostly aligned with the rigid planes of the metallacrown units, show only a little variation between the seven compounds.

Comment

Mixed 3d–4f metal complexes continue to attract attention due to their potentially important properties, such as non-trivial magnetic behaviour (Benelli & Gatteschi, 2002), catalytic activity (Shibasaki et al., 2008), luminescence (Sakamoto et al., 2001), and others. Magnetic ordering has been found in several 3d–4f heterometallic compounds (Novitchi et al., 2009), thus stimulating research in this area. 15-Metallacrown-5 complexes containing 3d and lanthanide metals are ideally suited for investigations of the influence of structure on magnetic properties, since complete series of these compounds

(I) Ln = Pr   (V) Ln = Gd
(II) Ln = Nd   (VI) Ln = Dy
(III) Ln = Sm   (VII) Ln = Ho
(IV) Ln = Eu
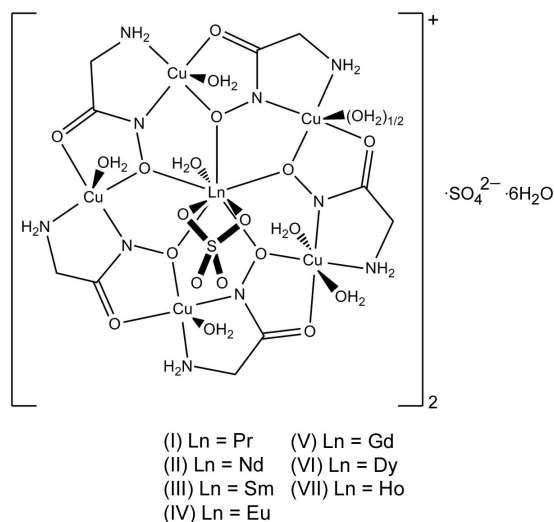
that differ only in the nature of the lanthanide can be synthesized with relative ease. Complexes of this type can be used as sensors (Tegoni et al., 2009), as building blocks for coordination polymers and for the construction of supramolecular assemblies (Cutland et al., 2001), so the synthesis and characterization of new metallacrown complexes are of interest. Here, we report the structures of a series of isostructural heterohexanuclear copper–lanthanide complexes, $\{[Cu_5Ln(GlyHA)_5(SO_4)(H_2O)_{6.5}]\}_2(SO_4)\cdot6H_2O$, where Ln^{III} = Pr in (I), Nd in (II), Sm in (III), Eu in (IV), Gd in (V), Dy in (VI) and Ho in (VII), derived from the dianion of glycinehydroxamic acid, $H_2N–CH_2–C(O)–NHOH$ or GlyHA.

Compounds (I)–(VII) reported here (Fig. 1, and Tables 1, 3, 5, 7, 9, 11 and 13) are isostructural in the space group $P\bar{1}$. Thus,
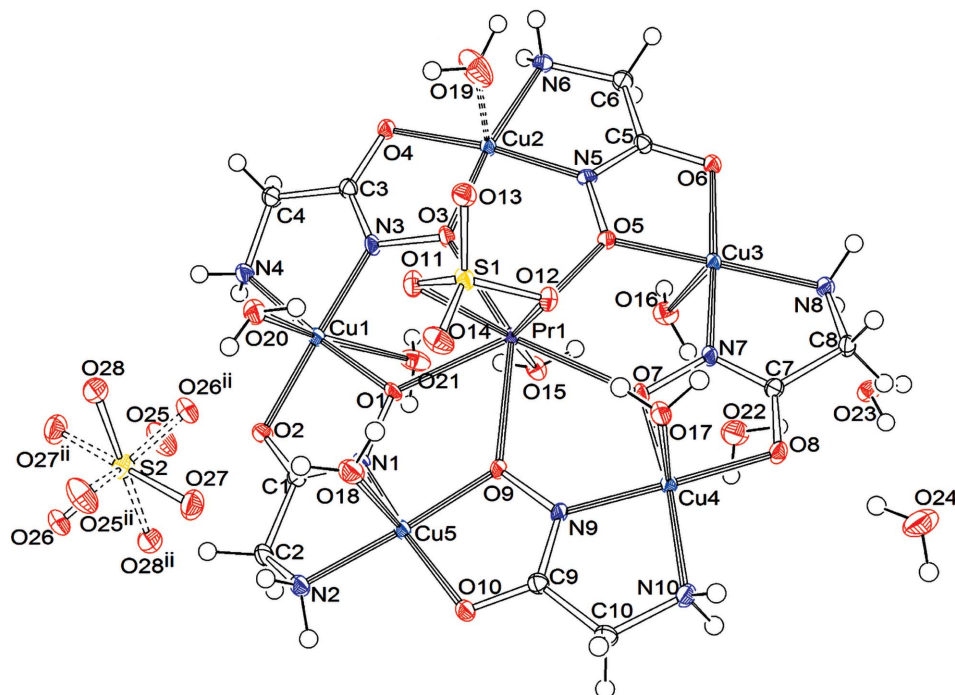
Figure 1
The crystal structure of (I), showing the atom-numbering scheme. Displacement ellipsoids are drawn at the 50% probability level. Dashed lines indicate disorder of the noncoordinated sulfate anion and of the half-occupied water molecule (O19). [Symmetry code: (ii) $-x$, $-y$, $-z + 1$.]

the structure will be described in general and only significant differences between the structures will be specifically noted. A common atom-numbering scheme was used for all the complexes.

Each unit cell contains two hexanuclear metallacrown cations, each with six coordinated water molecules, and one further coordinated water molecule (O19). This water molecule is disordered over two positions with occupation factors of 0.5, close to an inversion centre in between two different Cu_5Ln cations, and is coordinated to Cu2 of one of the two hexanuclear cations. Thus, the compounds contain $[Cu_5Ln(GlyHA)_5(SO_4)(H_2O)_6]^+$ and $[Cu_5Ln(GlyHA)_5(SO_4)(H_2O)_7]^+$ cations in a 1:1 ratio in each unit cell. Since the two cations are crystallographically identical (they are related through the above-mentioned inversion centre), they will herein be referred to simply as $[Cu_5Ln(GlyHA)_5(SO_4)(H_2O)_{6.5}]^+$. In addition, the unit cell contains one charge-compensating noncoordinated sulfate dianion (0.5 per Cu_5Ln cation) and six noncoordinated water molecules.

Each of the $[Cu_5Ln(GlyHA)_5(SO_4)(H_2O)_{6.5}]^+$ cations consists of a cyclic pentacopper core, formed from five Cu^{II} cations and five doubly deprotonated $GlyHA^{2-}$ dianions (Fig. 2). Each $GlyHA^{2-}$ dianion is linked to two Cu^{2+} cations, and in turn each Cu^{2+} cation is bound by two hydroxamates. The coordination modes of all five $GlyHA^{2-}$ dianions are similar. The bonds that do not involve metal cations vary insignificantly (both within the different complexes and between different ligands in one complex). The bond-length ranges for complexes (I)–(VII) are 1.388 (3)–1.399 (4) Å for N—O, 1.288 (6)–1.301 (4) Å for C—N(hydroxamate), 1.495 (7)–1.515 (4) Å for C—C, 1.476 (6)–1.493 (3) Å for C—N(amino) and 1.286 (5)–1.304 (4) Å for C═O. The deviation of the

N—O bonds from the highest value within one compound in all complexes varies between 0.27 and 0.79%. The deviation is 0.39–1.00% for C—N(hydroxamate) bonds, 0.60–1.19% for C—C, 0.47–1.00% for C—N(amino) and 0.08–1.00% for C═O. In contrast with the nonmetal bonds, the variation within similar coordination bonds is higher, both between and within the seven complexes, the ranges being 1.992 (4)–2.021 (2) Å for Cu—N(amino), 1.887 (3)–1.926 (2) Å for Cu—N(hydroxamate), 1.931 (3)–1.972 (2) Å for Cu—O(carboxylate) and 1.915 (2)–1.946 (2) Å for Cu—O(hydroxamate).
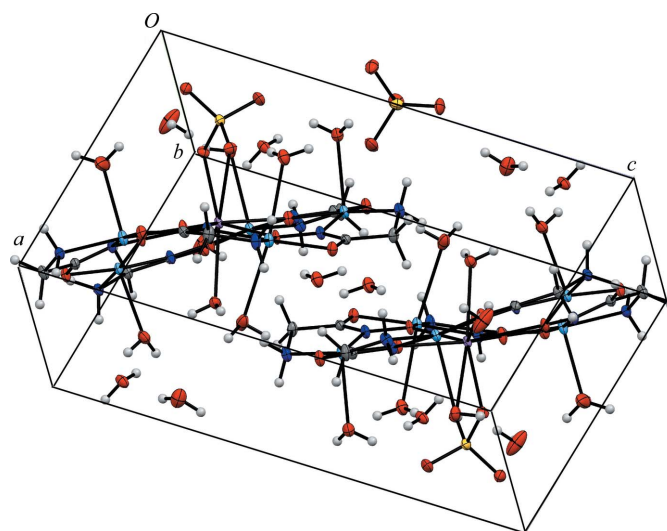

Figure 2
A view of the complete unit cell of the crystal structure of (I). Disorder of the sulfate O atoms and of the partially occupied water molecule has been omitted for clarity.

All the GlyHA^{2-} dianions in (I)–(VII) are almost flat. The deviations of the C atoms from the mean planes of the GlyHA^{2-} dianions (as defined by all non-H atoms) are generally greater than the deviations of the hydroxamate O and N atoms, but even the largest deviation from its corresponding mean plane does not exceed 0.163 (2) Å [for atom C2 in compound (V)].

The Ln^{III} cations are located in the centre of the [CuGlyHA]$_5$ ring and are bound by five O atoms of the hydroxamate ligands. All bond distances and angles in the [Cu$_5$Ln(GlyHA)$_5$(SO$_4$)(H$_2$O)$_{6.5}$]$^+$ cations of (I)–(VII) are in the ranges typical for metallacrowns (Stemmler et al., 1999). The Cu^{II} cations have, to a first approximation, a square-planar coordination which is augmented by more loosely coordinated water molecules in one or both of the axial positions of the Cu^{II} cations. The equatorial coordination environment of the Cu^{II} cations is made up of two N atoms (one from the amino group and one from the doubly deprotonated hydroxamate group) and two O atoms (one from the N—O group and one carbonyl O atom). The Cu—O and Cu—N distances range between 1.891 (3) and 2.016 (3) Å. In previously reported 15-MC-5 metallacrown complexes based on glycine hydroxamate, [Eu(NO$_3$)$_2$OH{15-MC$_{Cu^{II}N(GlyHA)}$-5}-(H$_2$O)$_4$]·4H$_2$O (Stemmler et al., 1999) and [Gd(NO$_3$)(H$_2$O)$_2$-{15-MC$_{Cu^{II}N(GlyHA)}$-5}(NO$_3$)(H$_2$O)$_4$]NO$_3$·5H$_2$O (Parac-Vogt et al., 2006), in which Eu^{III} and Gd^{III} cations are encapsulated in the centre of the [Cu$_5$(GlyHA)$_5$] cation, the lengths of the equatorial Cu—O and Cu—N bonds are in the ranges 1.877 (1)–2.022 (2) Å for the Eu^{III} complex and 1.875 (1)–2.033 (2) Å for the Gd^{III} complex, in good agreement with the values found for (I)–(VII). Hence, the influence, if any, of the counter-ion (sulfate or nitrate) on the bond lengths within the hexanuclear core is not significant.

Three of the five Cu^{II} cations in (I)–(VII), viz. Cu3, Cu4 and Cu5, are in addition coordinated by a water molecule in their apical positions (O16, O17 and O18, respectively), which completes the coordination environments of these three cations to square-pyramidal, with an N$_2$O$_3$ donor set. These axial Cu—O bonds are significantly longer than the equatorial Cu—O bonds, evidencing a Jahn–Teller-like distortion [for example, in compound (II), Cu3—O16 = 2.505 (2) Å, Cu4—O17 = 2.470 (2) Å and Cu5—O18 = 2.380 (2) Å]. One of the Cu^{II} cations, Cu1, is coordinated by two water molecules (atoms O20 and O21) in both its apical positions and thus has a distorted octahedral N$_2$O$_4$ coordination environment. These Cu—O bonds are again longer than the Cu—O bonds within the equatorial plane [for example, in (II), Cu1—O20 = 2.591 (2) Å and Cu1—O21 = 2.732 (2) Å]. The last Cu^{II} cation, Cu2, again possesses a coordinated water molecule in one of its apical positions, but it is only half occupied due to the disorder of this molecule across the nearby inversion centre, so that 50% of the Cu2 cations are square-planar and 50% have a square-pyramidal environment [for example, in (II), Cu2—O19 = 2.370 (4) Å].

The coordination environments of the Ln^{III} cations (Pr1, Nd1, Sm1, Eu1, Gd1, Dy1 and Ho1) contain five hydroxamate O atoms in their equatorial plane; the Ln1—O bond lengths
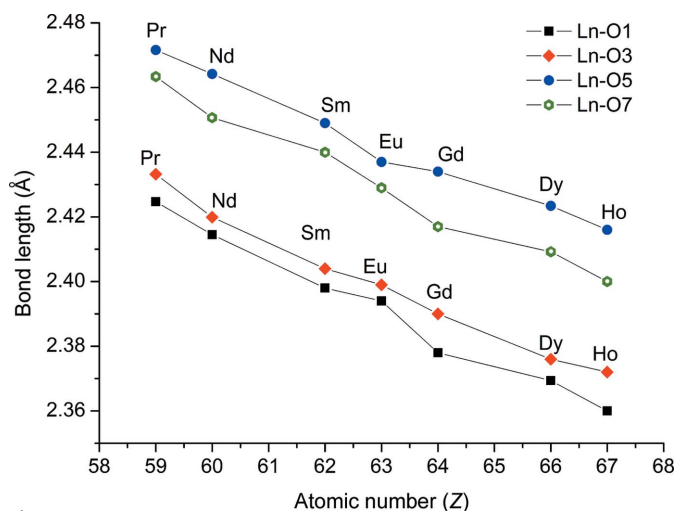

Figure 3
The dependence of the Ln—O1, Ln—O3, Ln—O5 and Ln—O7 bond lengths on the atomic number of the lanthanide in (I)–(VII).
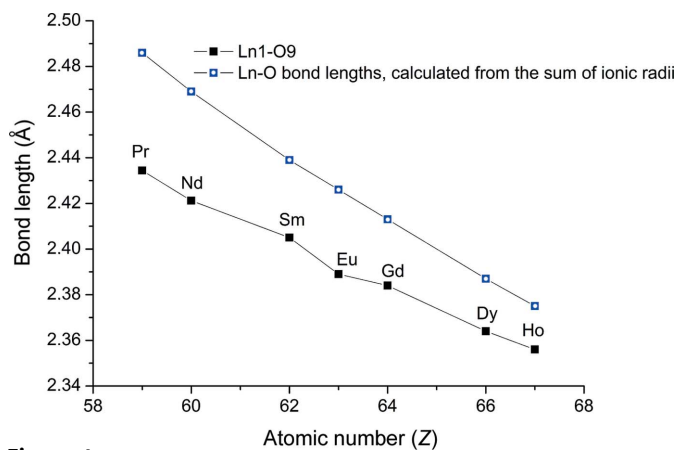

Figure 4
The dependence of the Ln—O9 bond lengths on the atomic number of the lanthanide in (I)–(VII), and expected values calculated from the sum of the ionic radii.

decrease consecutively from complex (I) to complex (VII) due to the change in ionic radius of the lanthanides [the Ln1—O bond lengths in the equatorial plane fall in the ranges 2.425 (2)–2.472 (2) Å for (I) (Pr^{III}), 2.415 (2)–2.464 (2) Å for (II) (Nd^{III}), 2.398 (4)–2.449 (3) Å for (III) (Sm^{III}), 2.389 (3)–2.437 (3) Å for (IV) (Eu^{III}), 2.378 (3)–2.434 (3) Å for (V) (Gd^{III}), 2.364 (2)–2.423 (2) Å for (VI) (Dy^{III}) and 2.356 (2)–2.416 (2) Å for (VII) (Ho^{III})] (Figs. 3 and 4). The equatorial Gd—O bonds in previously reported [Gd(NO$_3$)(H$_2$O)$_2${15-MC$_{Cu^{II}N(GlyHA)}$-5}(NO$_3$)(H$_2$O)$_4$]NO$_3$·5H$_2$O (Stemmler et al., 1999) are in the range 2.400 (1)–2.493 (1) Å, which is approximately 0.02–0.06 Å longer than in (V). Similarly, the Eu—O equatorial bonds in the earlier reported nitrate analogue, [Eu(NO$_3$)$_2$OH{15-MC$_{Cu^{II}N(GlyHA)}$-5}(H$_2$O)$_4$]·4H$_2$O [2.406 (1)–2.493 (1) Å; Parac-Vogt et al., 2006] are also longer by approximately 0.017–0.056 Å than in (IV). The higher degree of planarity found in the nitrate complexes compared with the sulfates (see below) might be one of the reasons for the longer equatorial Ln—O bonds in the former compounds

than the latter. The equatorial Ln—O bond lengths in (I)–(VII) are shorter than the sums of the ionic radii of O^{2-} and Ln^{III} (for a coordination number of 8; Shannon, 1976), which provides evidence for some strain caused by trying to fit the lanthanide cations into the metallacrown cavity (a similar situation was observed in the aforementioned nitrate analogues). This observation is further substantiated by the fact that the Ln^{III} cations are not perfectly in-plane with the metallacrown units but protrude significantly from this plane, thus indicating that the cavity is somewhat too small to accommodate the Ln^{III} cations comfortably (see below).

The coordination environment of the Ln1 cations is completed by O atoms from the sulfate anions and coordinated water molecules. One of the two crystallographically distinct sulfate dianions is coordinated to Ln1 through two O atoms, O11 and O12 [Ln1—O11 = 2.417 (2)–2.525 (2) Å and Ln1—O12 = 2.414 (2)–2.528 (2) Å]. The coordination polyhedron of Ln1 is completed by atom O15 of a coordinated water molecule [Ln1—O15 = 2.357 (2)–2.495 (2) Å], so that the sulfate anion and water molecule are mutually *trans* and the coordination number of Ln^{III} is 8. Similar to the Ln—O bonds in the equatorial plane, the Ln1—O11, Ln—O12 and Ln—O15 bond lengths decrease consecutively from (I) to (VII), so that the lowest values in the above ranges correspond to (VII) and the highest to (I) (Fig. 5). The values of the apical Ln—O bond distances are very close to the sums of the ionic radii of O^{2-} and Ln^{III} (for a coordination number of 8; Shannon, 1976). This indicates that, in contrast with the equatorial Ln—O bonds, there are no spatial restrictions for the sulfate coordination, as the SO_4^{2-} anions can be located at any distance from the Ln^{III} cation.

The separations between Ln1 and the Cu^{II} cations, and between adjacent Cu^{II} cations, in complexes (I)–(VII) are given in Table 16. Both Ln···Cu and Cu···Cu separations decrease consecutively from (I) to (VII), again evidencing the lanthanide contraction (Table 16). However, the overall shape of the whole $Cu_5(GlyHA)_5$ metallacrown unit depends some-

what on the size of the Ln^{III} cation. Opposite the sulfate anion, all the Cu_5 crowns are noticeably bowed. The metallacrown fragments $[Cu_5Ln(GlyHA)_5(SO_4)(H_2O)_{6.5}]^+$ in (I)–(VII) are not planar but are slightly distorted, in that the Ln1 cations deviate from the mean plane of the five Cu^{II} cations. The amount by which the Ln^{III} cations protrude from the mean plane of the Cu^{II} cations decreases consecutively with the size of the Ln^{III} cation from (I) (0.459 Å) to (VII) (0.422 Å), which indicates that the smaller lanthanide cations better fit the cavity of the pentacopper metallacrown ring than the larger ones.

In the previously reported nitrate analogues, $[Eu(NO_3)_2$-OH{15-MC$_{Cu^{II}N(GlyHA)}$-5}(H_2O)_4]·4H_2O$ (Stemmler *et al.*, 1999) and $[Gd(NO_3)(H_2O)_2$\{15-MC$_{Cu^{II}N(GlyHA)}$-5\}(NO_3)(H_2O)_4]$-NO_3·5H_2O$ (Parac-Vogt *et al.*, 2006), the deviations of the Ln^{III} cations from the mean planes of the Cu^{II} cations are 0.351 (for Eu^{III}) and 0.405 Å (for Gd^{III}), which are lower by 0.088 and 0.025 Å than the deviations of the Ln^{III} cations from the Cu_5 planes in (IV) and (V), respectively. The coordination of the sulfate anion to the $Cu_5Ln(GlyHA)_5^{3+}$ cation thus seems to be leading to somewhat greater distortion of the metallacrown cation from planarity than in the above-mentioned nitrate analogues, despite the similar coordination modes of SO_4^{2-} and NO_3^-. Possible reasons may include the different sizes of sulfate and nitrate, and especially the different charges of these anions.

The largest deviation among non-H atoms from the mean plane of the five Cu^{II} cations is observed for atom O2; from (I) to (VII), this value increases systematically from 0.978 to 1.055 Å. The values for the Ln1 and O2 deviations from the pentacopper plane are given in Table 15 and the dependence of these values on the ionic radii of the lanthanides (for coordination number 8) are presented in Figs. 6 and 7. The r.m.s. deviations of the non-H atoms from the metallacrown plane of all non-H atoms increase consecutively from (I) (0.400 Å) to (VII) (0.421 Å).

The variations in geometry of (I)–(VII) that accompany the change in ionic radius of the lanthanides are not limited to the individual compexes, but also affect the unit-cell geometries and volumes. The b axes of (I)–(VII) are mostly aligned with the plane of the metallacrown units (the angles between the b axes and the mean planes of the five Cu^{2+} ions of the cations range from 18.73 to 19.08°). As a consequence the lengths of the b axes are largely independent of the atomic number and they fluctuate around 11.57 Å. The a and c axes, on the other hand, are partially aligned with the axial Ln—O bonds and consequently follow the trend of the axial lanthanide bond lengths (see above). Except for the Eu metallacrown, (IV), the unit-cell parameters a and c decrease when going from the lightest lanthanide in the series [Pr, (I)] to the heaviest [Ho, (VII)], and decrease consecutively from 9.6649 (17) to 9.5859 (8) Å, and from 16.279 (3) to 16.1967 (14) Å, respectively (Fig. 8). The unit-cell volumes follow the trend of the a and c axes and decrease in the series (I)–(VII) (Fig. 9).

The crystal structures of (I)–(VII) also contain one non-coordinated sulfate dianion per pair of $[Cu_5Ln(GlyHA)_5$-$(SO_4)(H_2O)_{6.5}]^+$ complex cations and interstitial uncoordi-
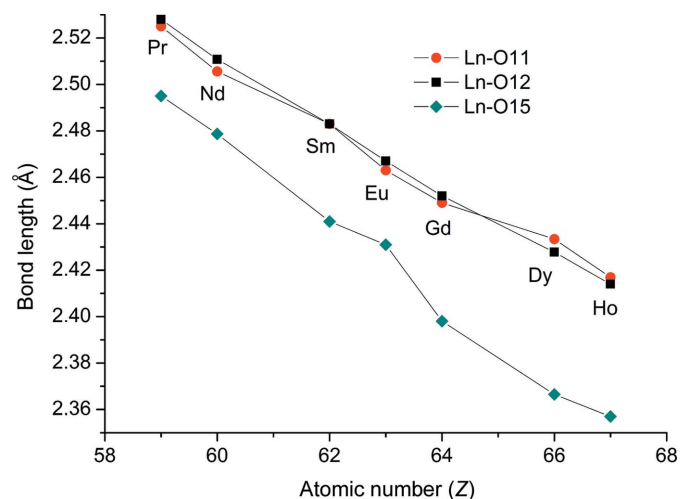

Figure 5
The dependence of the Ln—O11, Ln—O12 and Ln—O15 bond lengths on the atomic number of the lanthanide in (I)–(VII).
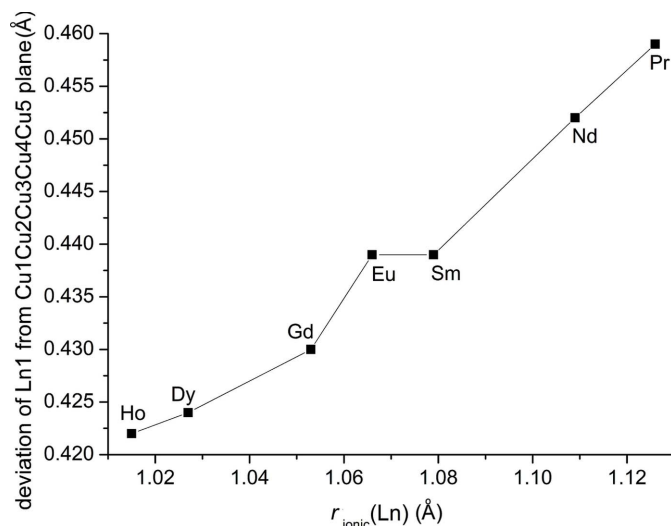
Figure 6
The dependence of the deviation of Ln1 from the Cu1/Cu2/Cu3/Cu4/Cu5 plane on the ionic radii of the lanthanide (for coordination number 8) in (I)–(VII).
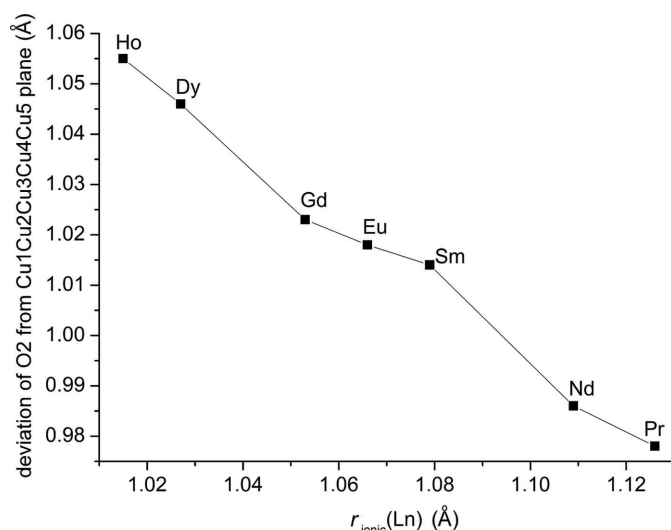

Figure 7
The dependence of the deviation of O2 from the Cu1/Cu2/Cu3/Cu4/Cu5 plane on the ionic radii of the lanthanide (for coordination number 8) in (I)–(VII).
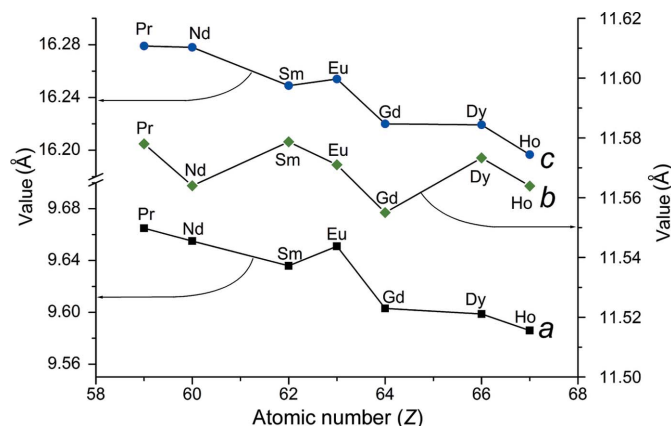

Figure 8
Plots of unit-cell parameters a, b and c (Å) versus lanthanide atomic number Z in (I)–(VII). Solid lines are to guide the eye.

nated water molecules. Both the sulfate anion and the water molecules are bound to the complex cation *via* a network of strong O—H···O hydrogen bonds (see hydrogen-bond Tables 2, 4, 6, 8, 10, 12 and 14 for numeric details). The sulfate anion is located on an inversion centre and its O atoms are disordered between two mutually exclusive positions with occupancy factors of 0.5.

In all the complexes (I)–(VII), the metallacrown units are monomeric and not bound to each other *via* covalent bonds. In particular, the formation of polymers or stacks (dimers or trimers) is not observed. This seems to be typical behaviour for 15-MC-5 systems. For the nitrate-containing europium complex $[Eu(NO_3)_2OH\{15\text{-}MC_{Cu^{II}N(GlyHA)}\text{-}5\}(H_2O)_4]\cdot 4H_2O$ (Stemmler *et al.*, 1999) and the gadolinium analogue $[Gd(NO_3)(H_2O)_2\{15\text{-}MC_{Cu^{II}N(GlyHA)}\text{-}5\}(NO_3)(H_2O)_4]NO_3\cdot 5H_2O$ (Parac-Vogt *et al.*, 2006) of the metallacrowns based on glycinehydroxamic acid, for example, no such aggregation of neighbouring cations *via* covalent bonds was observed. In contrast, the formation of dimers (Gaynor *et al.*, 2001) or trimers (Pavlishchuk *et al.*, 2010) from metallacrown units, as well as their aggregation into one-dimensional chains (Kurzak *et al.*, 1991), have been described for 12-MC-4 systems. For 15-MC-5 cations, only a few examples of aggregation *via* covalent bonds have been reported. One of the few examples is the Sm^{III}–Cu^{II} complex obtained from phenylalanine hydroxamic acid, $[\{Sm(NO_3)\}\{15\text{-}MC_{Cu^{II}N(L\text{-}pheHA)}\text{-}5\}](NO_3)$, in which neighbouring metallacrown units are bound through equatorial and apical Cu—O contacts (Cutland-Van Noord *et al.*, 2002). In (I)–(VII), neighbouring $[Cu_5Ln(GlyHA)_5(SO_4)(H_2O)_{6.5}]^+$ complex cations are connected *via* an extended system of strong hydrogen bonds (O6···H17B, O10···H21B, O12···H8B, O15···H2A, O17···H16A, O18···H21A and O20···H10A; for the corresponding bond distances and symmetry codes, see hydrogen-bond geometry Tables 2, 4, 6, 8, 10, 12 and 14). These strong hydrogen bonds between the heptanuclear $[Cu_5Ln(GlyHA)_5(SO_4)(H_2O)_{6.5}]^+$ cations and the noncoordinated sulfate dianions, and the electrostatic
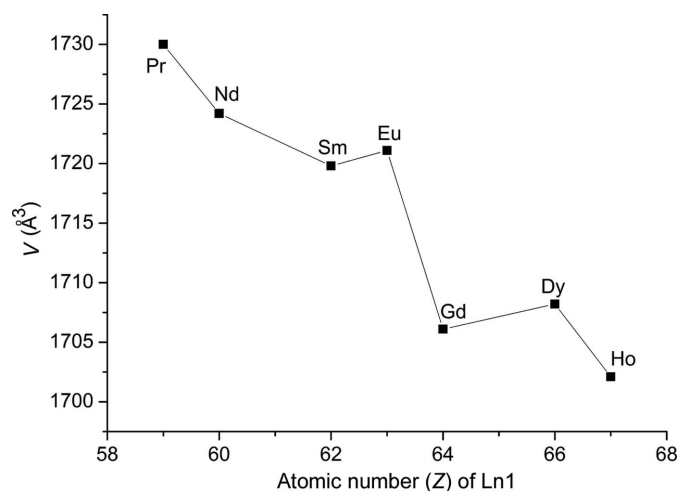
Figure 9
The dependence of the unit-cell volume V (Å^3) on the atomic number Z of the lanthanide in (I)–(VII).

metal-organic compounds

interactions between cations and anions, govern the packing of complexes (I)–(VII). The total solvent-accessible volume in (I)–(VII), as estimated using the program *PLATON* (Spek, 2009), is between 15.5 and 16.5% (267–285 Å^3) of the unit-cell volumes for a probe molecule with $r = 1.4$ Å (all non-coordinated and coordinated water molecules were removed). This volume is completely occupied by water. In particular, there are three noncoordinated water molecules per $[Cu_5Ln-(GlyHA)_5(SO_4)(H_2O)_{6.5}]^+$ complex cation in (I)–(VII), which occupy about 4.6–4.8% of the cell volume (79–84 Å^3, calculated as above).

In summary, a series of isostructural lanthanide–copper complexes, $[Cu_5Ln(GlyHA)_5(SO_4)(H_2O)_{6.5}]_2(SO_4)·6H_2O$ (where GlyHA is the dianion of doubly deprotonated glycinehydroxamic acid and Ln^{III} = Pr, Nd, Sm, Eu, Gd, Dy and Ho), were isolated and their crystal structures determined. The values of the unit-cell parameters (a, c and V) and the Ln—O bond lengths were found to be governed by lanthanide contraction. The complex metallacrown cation is not planar, with the lanthanide cation protruding from the plane of the metallacrown ligand. The degree of deviation from planarity was found to be governed by the radius of the lanthanide cation.

Experimental

All compounds were prepared by the following general method. Copper(II) sulfate pentahydrate (2.49 g, 10 mmol) was dissolved in water (10 ml) and mixed with a solution of $Ln(NO_3)_3·xH_2O$ (2 mmol) in water (5 ml), followed by the addition of a solution of the sodium salt of glycinehydroxamic acid, $C_2H_5O_2N_2Na$ (1.12 g, 10 mmol), in water (10 ml) with stirring. Slow evaporation resulted in the formation of dark-blue crystals. The masses of $Ln(NO_3)_3·xH_2O$ used in the syntheses, the yields of (I)–(VII) and data for the elemental analyses are given in Table 15.

Compound (I)

Crystal data

$[Cu_5Pr(C_2H_4N_2O_2)_5(SO_4)-(H_2O)_{6.5}]_2(SO_4)·6H_2O$	$\beta = 91.296$ (2)°
$M_r = 2428.56$	$\gamma = 105.156$ (2)°
Triclinic, $P\bar{1}$	$V = 1730.0$ (5) Å^3
$a = 9.6649$ (17) Å	$Z = 1$
$b = 11.578$ (2) Å	Mo $K\alpha$ radiation
$c = 16.279$ (3) Å	$\mu = 4.60$ mm^{-1}
$\alpha = 99.518$ (2)°	$T = 100$ K
	$0.43 \times 0.41 \times 0.10$ mm

Data collection

Bruker SMART APEX CCD area-detector diffractometer	34050 measured reflections
	10309 independent reflections
Absorption correction: multi-scan (*APEX2*; Bruker, 2009)	8778 reflections with $I > 2\sigma(I)$
$T_{min} = 0.499$, $T_{max} = 0.746$	$R_{int} = 0.042$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.029$	H atoms treated by a mixture of independent and constrained refinement
$wR(F^2) = 0.069$	
$S = 1.05$	
10309 reflections	$\Delta\rho_{max} = 1.64$ e Å^{-3}
562 parameters	$\Delta\rho_{min} = -1.29$ e Å^{-3}
20 restraints	

Table 1
Selected bond lengths (Å) for (I).

Cu1—O1	1.9157 (19)	Cu4—O8	1.9458 (18)
Cu1—N3	1.926 (2)	Cu4—N10	2.009 (2)
Cu1—O2	1.9716 (19)	Cu5—N1	1.903 (2)
Cu1—N4	1.995 (2)	Cu5—O9	1.9268 (18)
Cu2—N5	1.912 (2)	Cu5—O10	1.9520 (19)
Cu2—O3	1.9165 (19)	Cu5—N2	2.006 (2)
Cu2—O4	1.9463 (19)	Cu5—O18	2.386 (2)
Cu2—N6	2.013 (2)	Pr1—O1	2.4247 (18)
Cu2—O19	2.364 (6)	Pr1—O3	2.4332 (19)
Cu3—N7	1.908 (2)	Pr1—O9	2.4344 (18)
Cu3—O5	1.9400 (18)	Pr1—O7	2.4634 (19)
Cu3—O6	1.9510 (19)	Pr1—O5	2.4716 (18)
Cu3—N8	2.007 (2)	Pr1—O15	2.495 (2)
Cu4—N9	1.898 (2)	Pr1—O11	2.525 (2)
Cu4—O7	1.9328 (19)	Pr1—O12	2.528 (2)

Table 2
Hydrogen-bond geometry (Å, °) for (I).

D—H···A	D—H	H···A	D···A	D—H···A
N2—H2A···O15^i	0.92	2.03	2.929 (3)	164
N2—H2B···O27	0.92	2.56	3.434 (5)	159
N2—H2B···O28^{ii}	0.92	2.07	2.855 (5)	142
N4—H4B···O2^{iii}	0.92	2.26	3.124 (5)	156
N4—H4A···O25^{iii}	0.92	1.98	2.769 (5)	143
N4—H4A···O27^{iv}	0.92	2.18	3.041 (5)	155
N6—H6A···O13^{iv}	0.92	2.17	3.082 (3)	174
N6—H6B···O24^v	0.92	2.17	2.951 (4)	142
N8—H8B···O12^v	0.92	2.03	2.942 (3)	169
N8—H8A···O23	0.92	2.15	2.999 (3)	153
N10—H10A···O20^{vi}	0.92	2.18	2.957 (3)	142
N10—H10B···O22^{vii}	0.92	2.12	2.908 (3)	144
O15—H15B···O16	0.84 (2)	1.87 (2)	2.706 (3)	174 (4)
O15—H15A···O21	0.82 (2)	1.85 (2)	2.661 (3)	169 (4)
O16—H16A···O17^{iv}	0.83 (2)	1.94 (2)	2.774 (3)	178 (4)
O16—H16B···O22	0.83 (2)	1.91 (2)	2.720 (3)	169 (4)
O17—H17B···O6^v	0.82 (2)	1.91 (2)	2.727 (3)	178 (4)
O17—H17A···O12	0.81 (2)	2.09 (2)	2.874 (3)	162 (4)
O18—H18B···O14	0.82 (2)	1.91 (2)	2.731 (3)	176 (4)
O18—H18A···O26^{ii}	0.82 (2)	2.08 (2)	2.859 (5)	159 (4)
O18—H18A···O27	0.82 (2)	1.88 (2)	2.638 (5)	153 (4)
O19—H19B···O24^v	0.85 (2)	2.14 (7)	2.878 (6)	146 (11)
O19—H19A···O24^{viii}	0.84 (2)	1.76 (5)	2.547 (6)	155 (11)
O20—H20B···O11	0.84 (2)	2.13 (2)	2.954 (5)	169 (4)
O20—H20A···O25	0.81 (2)	1.94 (2)	2.723 (5)	162 (4)
O20—H20A···O26^{ii}	0.81 (2)	2.17 (3)	2.897 (5)	150 (4)
O21—H21B···O10^i	0.84 (2)	1.88 (2)	2.714 (3)	173 (4)
O21—H21A···O18^{iv}	0.83 (2)	1.94 (2)	2.763 (3)	173 (4)
O22—H22B···O23	0.84 (2)	1.89 (2)	2.694 (3)	162 (4)
O22—H22A···O26^i	0.84 (2)	2.17 (2)	2.982 (5)	165 (4)
O22—H22A···O28^{ix}	0.84 (2)	1.97 (3)	2.728 (5)	151 (4)
O23—H23A···O4^{vi}	0.82 (2)	1.91 (2)	2.725 (3)	173 (4)
O23—H23B···O13^{ix}	0.82 (2)	2.05 (2)	2.843 (3)	163 (4)
O24—H24B···O8	0.83 (2)	1.97 (2)	2.794 (3)	173 (5)
O24—H24A···O11^{vi}	0.83 (2)	2.19 (3)	2.969 (3)	156 (5)

Symmetry codes: (i) $-x+1, -y+1, -z+1$; (ii) $-x, -y, -z+1$; (iii) $-x+1, -y, -z+1$; (iv) $x+1, y, z$; (v) $-x+1, -y+1, -z$; (vi) $x, y+1, z$; (vii) $x-1, y, z$; (viii) $x, y-1, z$; (ix) $x+1, y+1, z$.

Compound (II)

Crystal data

$[Cu_5Nd(C_2H_4N_2O_2)_5(SO_4)-(H_2O)_{6.5}]_2(SO_4)·6H_2O$	$\beta = 91.304$ (2)°
$M_r = 2435.08$	$\gamma = 105.236$ (2)°
Triclinic, $P\bar{1}$	$V = 1724.2$ (6) Å^3
$a = 9.655$ (2) Å	$Z = 1$
$b = 11.564$ (2) Å	Mo $K\alpha$ radiation
$c = 16.278$ (3) Å	$\mu = 4.71$ mm^{-1}
$\alpha = 99.697$ (2)°	$T = 100$ K
	$0.55 \times 0.21 \times 0.10$ mm

Data collection

Bruker SMART APEX CCD area-
  detector diffractometer
Absorption correction: multi-scan
  (*APEX2*; Bruker, 2009)
  $T_{min} = 0.443$, $T_{max} = 0.746$

30967 measured reflections
10271 independent reflections
9453 reflections with $I > 2\sigma(I)$
$R_{int} = 0.029$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.022$
$wR(F^2) = 0.071$
$S = 1.12$
10271 reflections
562 parameters
22 restraints

H atoms treated by a mixture of
  independent and constrained
  refinement
$\Delta\rho_{max} = 1.19$ e Å^{-3}
$\Delta\rho_{min} = -1.25$ e Å^{-3}

Compound (III)

Crystal data

$[Cu_5Sm(C_2H_4N_2O_2)_5(SO_4)(H_2O)_{6.5}]_2(SO_4)\cdot 6H_2O$
$M_r = 2447.30$
Triclinic, $P\overline{1}$
$a = 9.6359\ (15)$ Å
$b = 11.5787\ (18)$ Å
$c = 16.249\ (3)$ Å
$\alpha = 99.676\ (2)°$

$\beta = 91.446\ (2)°$
$\gamma = 105.230\ (2)°$
$V = 1719.8\ (5)$ Å^3
$Z = 1$
Mo $K\alpha$ radiation
$\mu = 4.92$ mm^{-1}
$T = 100$ K
$0.43 \times 0.41 \times 0.10$ mm

Data collection

Bruker SMART APEX CCD area-
  detector diffractometer
Absorption correction: multi-scan
  (*APEX2*; Bruker, 2009)
  $T_{min} = 0.369$, $T_{max} = 0.746$

18813 measured reflections
9817 independent reflections
8537 reflections with $I > 2\sigma(I)$
$R_{int} = 0.040$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.051$
$wR(F^2) = 0.137$
$S = 1.02$
9817 reflections
562 parameters
20 restraints

H atoms treated by a mixture of
  independent and constrained
  refinement
$\Delta\rho_{max} = 5.55$ e Å^{-3}
$\Delta\rho_{min} = -2.56$ e Å^{-3}

Compound (IV)

Crystal data

$[Cu_5Eu(C_2H_4N_2O_2)_5(SO_4)(H_2O)_{6.5}]_2(SO_4)\cdot 6H_2O$
$M_r = 2450.68$
Triclinic, $P\overline{1}$
$a = 9.651\ (3)$ Å
$b = 11.571\ (3)$ Å
$c = 16.254\ (4)$ Å
$\alpha = 99.720\ (4)°$

$\beta = 91.000\ (4)°$
$\gamma = 105.398\ (4)°$
$V = 1721.1\ (8)$ Å^3
$Z = 1$
Mo $K\alpha$ radiation
$\mu = 5.03$ mm^{-1}
$T = 100$ K
$0.20 \times 0.20 \times 0.08$ mm

Data collection

Bruker SMART APEX CCD area-
  detector diffractometer
Absorption correction: multi-scan
  (*APEX2*; Bruker, 2009)
  $T_{min} = 0.524$, $T_{max} = 0.746$

19621 measured reflections
10033 independent reflections
8634 reflections with $I > 2\sigma(I)$
$R_{int} = 0.027$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.038$
$wR(F^2) = 0.092$
$S = 1.05$
10033 reflections
562 parameters
22 restraints

H atoms treated by a mixture of
  independent and constrained
  refinement
$\Delta\rho_{max} = 2.67$ e Å^{-3}
$\Delta\rho_{min} = -1.53$ e Å^{-3}

Table 3
Selected bond lengths (Å) for (II).

Cu1—O1	1.9229 (16)	Cu4—O8	1.9417 (17)
Cu1—N3	1.9234 (19)	Cu4—N10	2.0118 (19)
Cu1—O2	1.9702 (17)	Cu5—N1	1.9008 (19)
Cu1—N4	1.994 (2)	Cu5—O9	1.9337 (16)
Cu2—N5	1.9091 (19)	Cu5—O10	1.9509 (16)
Cu2—O3	1.9226 (16)	Cu5—N2	2.004 (2)
Cu2—O4	1.9433 (16)	Cu5—O18	2.3803 (19)
Cu2—N6	2.0156 (19)	Nd1—O1	2.4145 (16)
Cu2—O19	2.369 (4)	Nd1—O3	2.4199 (16)
Cu3—N7	1.9072 (19)	Nd1—O9	2.4212 (16)
Cu3—O5	1.9437 (16)	Nd1—O7	2.4507 (16)
Cu3—O6	1.9497 (16)	Nd1—O5	2.4642 (16)
Cu3—N8	2.007 (2)	Nd1—O15	2.4787 (18)
Cu4—N9	1.898 (2)	Nd1—O11	2.5056 (17)
Cu4—O7	1.9346 (16)	Nd1—O12	2.5108 (17)

Table 4
Hydrogen-bond geometry (Å, °) for (II).

D—H$\cdots A$	D—H	H$\cdots A$	$D\cdots A$	D—H$\cdots A$
N2—H2A$\cdots$O15^i	0.92	2.03	2.924 (3)	163
N2—H2B$\cdots$O27	0.92	2.55	3.425 (4)	159
N2—H2B$\cdots$O28^{ii}	0.92	2.06	2.846 (4)	143
N4—H4B$\cdots$O2^{iii}	0.92	2.27	3.134 (3)	155
N4—H4A$\cdots$O25^{iii}	0.92	1.97	2.766 (4)	143
N4—H4A$\cdots$O27^{iv}	0.92	2.18	3.036 (5)	155
N6—H6A$\cdots$O13^{iv}	0.92	2.18	3.095 (3)	175
N6—H6B$\cdots$O24^v	0.92	2.18	2.952 (3)	141
N8—H8B$\cdots$O12^v	0.92	2.03	2.940 (3)	168
N8—H8A$\cdots$O23	0.92	2.15	3.000 (3)	153
N10—H10A$\cdots$O20^{vi}	0.92	2.18	2.954 (3)	141
N10—H10B$\cdots$O22^{vii}	0.92	2.11	2.904 (3)	144
O15—H15B$\cdots$O16	0.82 (2)	1.90 (2)	2.705 (3)	170 (3)
O15—H15A$\cdots$O21	0.84 (2)	1.84 (2)	2.662 (3)	169 (3)
O16—H16A$\cdots$O17^{iv}	0.84 (2)	1.95 (2)	2.780 (3)	176 (4)
O16—H16B$\cdots$O22	0.83 (2)	1.89 (2)	2.711 (3)	175 (4)
O17—H17B$\cdots$O6^v	0.82 (2)	1.91 (2)	2.724 (2)	178 (4)
O17—H17A$\cdots$O12	0.82 (2)	2.09 (2)	2.867 (3)	159 (3)
O18—H18B$\cdots$O14	0.81 (2)	1.93 (2)	2.734 (3)	175 (4)
O18—H18A$\cdots$O26^{ii}	0.83 (2)	2.04 (2)	2.850 (4)	166 (3)
O18—H18A$\cdots$O27	0.83 (2)	1.91 (3)	2.638 (4)	146 (3)
O19—H19B$\cdots$O24^v	0.84 (2)	2.37 (11)	2.876 (5)	119 (10)
O19—H19A$\cdots$O24^{viii}	0.84 (2)	1.82 (5)	2.557 (5)	146 (9)
O20—H20B$\cdots$O11	0.82 (2)	2.16 (2)	2.954 (3)	163 (3)
O20—H20A$\cdots$O25	0.82 (2)	1.95 (2)	2.724 (4)	159 (4)
O20—H20A$\cdots$O26^{ii}	0.82 (2)	2.15 (2)	2.896 (3)	152 (3)
O21—H21B$\cdots$O10^i	0.83 (2)	1.89 (2)	2.713 (3)	173 (4)
O21—H21A$\cdots$O18^{iv}	0.82 (2)	1.95 (2)	2.758 (3)	167 (4)
O22—H22B$\cdots$O23	0.82 (2)	1.89 (2)	2.700 (3)	167 (4)
O22—H22A$\cdots$O26^i	0.83 (2)	2.18 (2)	2.977 (4)	160 (4)
O22—H22A$\cdots$O28^{ix}	0.83 (2)	1.95 (2)	2.729 (4)	155 (4)
O23—H23A$\cdots$O4^{vi}	0.83 (2)	1.89 (2)	2.719 (2)	175 (3)
O23—H23B$\cdots$O13^{ix}	0.84 (2)	2.02 (2)	2.838 (2)	164 (3)
O24—H24B$\cdots$O8	0.83 (2)	2.00 (2)	2.800 (3)	164 (4)
O24—H24A$\cdots$O11^{vi}	0.82 (2)	2.18 (2)	2.967 (3)	162 (4)

Symmetry codes: (i) $-x+1, -y+1, -z+1$; (ii) $-x, -y, -z+1$; (iii) $-x+1, -y, -z+1$; (iv) $x+1, y, z$; (v) $-x+1, -y+1, -z$; (vi) $x, y+1, z$; (vii) $x-1, y, z$; (viii) $x, y-1, z$; (ix) $x+1, y+1, z$.

Compound (V)

Crystal data

$[Cu_5Gd(C_2H_4N_2O_2)_5(SO_4)(H_2O)_{6.5}]_2(SO_4)\cdot 6H_2O$
$M_r = 2461.10$
Triclinic, $P\overline{1}$
$a = 9.603\ (3)$ Å
$b = 11.555\ (3)$ Å
$c = 16.220\ (5)$ Å
$\alpha = 99.700\ (4)°$

$\beta = 91.472\ (5)°$
$\gamma = 105.356\ (4)°$
$V = 1706.1\ (8)$ Å^3
$Z = 1$
Mo $K\alpha$ radiation
$\mu = 5.18$ mm^{-1}
$T = 100$ K
$0.12 \times 0.12 \times 0.04$ mm

Table 5
Selected bond lengths (Å) for (III).

Cu1—O1	1.918 (4)	Cu4—O8	1.942 (4)
Cu1—N3	1.923 (4)	Cu4—N10	2.005 (4)
Cu1—O2	1.972 (3)	Cu5—N1	1.900 (4)
Cu1—N4	1.998 (5)	Cu5—O9	1.935 (3)
Cu2—N5	1.907 (4)	Cu5—O10	1.951 (4)
Cu2—O3	1.926 (3)	Cu5—N2	2.004 (4)
Cu2—O4	1.944 (4)	Cu5—O18	2.378 (4)
Cu2—N6	2.015 (4)	Sm1—O1	2.398 (3)
Cu2—O19	2.369 (11)	Sm1—O9	2.405 (3)
Cu3—N7	1.907 (4)	Sm1—O3	2.405 (3)
Cu3—O5	1.946 (4)	Sm1—O7	2.440 (4)
Cu3—O6	1.948 (3)	Sm1—O15	2.441 (4)
Cu3—N8	2.008 (4)	Sm1—O5	2.450 (3)
Cu4—N9	1.900 (4)	Sm1—O12	2.484 (4)
Cu4—O7	1.942 (4)	Sm1—O11	2.484 (4)

Table 7
Selected bond lengths (Å) for (IV).

Cu1—N3	1.911 (4)	Cu4—O8	1.940 (3)
Cu1—O1	1.917 (3)	Cu4—N10	2.009 (4)
Cu1—O2	1.966 (3)	Cu5—N1	1.896 (3)
Cu1—N4	1.996 (4)	Cu5—O9	1.934 (3)
Cu2—N5	1.904 (3)	Cu5—O10	1.944 (3)
Cu2—O3	1.922 (3)	Cu5—N2	2.008 (3)
Cu2—O4	1.942 (3)	Cu5—O18	2.385 (3)
Cu2—N6	2.013 (3)	Eu1—O9	2.389 (3)
Cu2—O19	2.397 (10)	Eu1—O1	2.394 (3)
Cu3—N7	1.902 (3)	Eu1—O3	2.399 (3)
Cu3—O6	1.941 (3)	Eu1—O7	2.429 (3)
Cu3—O5	1.945 (3)	Eu1—O15	2.431 (3)
Cu3—N8	2.003 (3)	Eu1—O5	2.437 (3)
Cu4—N9	1.896 (3)	Eu1—O11	2.463 (3)
Cu4—O7	1.938 (3)	Eu1—O12	2.467 (3)

Table 6
Hydrogen-bond geometry (Å, °) for (III).

D—H$\cdots A$	D—H	H$\cdots A$	$D\cdots A$	D—H$\cdots A$
N2—H2A$\cdots$O15[i]	0.92	2.04	2.935 (6)	163
N2—H2B$\cdots$O27	0.92	2.54	3.420 (9)	159
N2—H2B$\cdots$O28[ii]	0.92	2.05	2.843 (9)	143
N4—H4B$\cdots$O2[iii]	0.92	2.29	3.151 (6)	156
N4—H4A$\cdots$O25[iii]	0.92	1.97	2.763 (9)	143
N4—H4A$\cdots$O27[iv]	0.92	2.16	3.016 (10)	155
N6—H6A$\cdots$O13[iv]	0.92	2.20	3.112 (6)	174
N6—H6B$\cdots$O24[v]	0.92	2.18	2.950 (6)	141
N8—H8B$\cdots$O12[v]	0.92	2.04	2.942 (5)	168
N8—H8A$\cdots$O23	0.92	2.17	3.015 (6)	152
N10—H10A$\cdots$O20[vi]	0.92	2.22	2.980 (6)	139
N10—H10B$\cdots$O22[vii]	0.92	2.12	2.917 (6)	144
O15—H15B$\cdots$O16	0.84 (2)	1.87 (2)	2.708 (5)	176 (8)
O15—H15A$\cdots$O21	0.84 (2)	1.85 (3)	2.651 (6)	161 (7)
O16—H16A$\cdots$O17[iv]	0.83 (2)	1.95 (2)	2.774 (5)	173 (8)
O16—H16B$\cdots$O22	0.84 (2)	1.89 (3)	2.719 (7)	170 (8)
O17—H17B$\cdots$O6[v]	0.84 (2)	1.89 (2)	2.721 (5)	171 (8)
O17—H17A$\cdots$O12	0.84 (2)	2.11 (4)	2.874 (5)	152 (7)
O18—H18B$\cdots$O14	0.83 (2)	1.89 (2)	2.725 (5)	173 (8)
O18—H18A$\cdots$O26[ii]	0.84 (2)	2.03 (3)	2.857 (9)	168 (8)
O18—H18A$\cdots$O27	0.84 (2)	1.93 (5)	2.637 (9)	142 (7)
O19—H19A$\cdots$O24[viii]	0.84 (2)	1.74 (6)	2.560 (12)	165 (20)
O19—H19B$\cdots$O24[v]	0.84 (2)	2.25 (19)	2.878 (11)	131 (22)
O20—H20B$\cdots$O11	0.83 (2)	2.12 (2)	2.946 (5)	172 (8)
O20—H20A$\cdots$O25	0.83 (2)	1.96 (4)	2.730 (9)	154 (8)
O20—H20A$\cdots$O26[ii]	0.83 (2)	2.12 (4)	2.899 (9)	156 (8)
O21—H21B$\cdots$O10[i]	0.84 (2)	1.89 (3)	2.718 (5)	167 (8)
O21—H21A$\cdots$O18[iv]	0.83 (2)	1.93 (2)	2.762 (6)	172 (8)
O22—H22B$\cdots$O23	0.84 (2)	1.89 (3)	2.701 (5)	161 (9)
O22—H22A$\cdots$O26[i]	0.84 (2)	2.17 (4)	2.962 (9)	157 (8)
O22—H22A$\cdots$O28[ix]	0.84 (2)	1.94 (4)	2.725 (9)	155 (9)
O23—H23A$\cdots$O4[vi]	0.84 (2)	1.90 (2)	2.729 (5)	170 (8)
O23—H23B$\cdots$O13[ix]	0.85 (2)	2.00 (2)	2.841 (5)	170 (8)
O24—H24B$\cdots$O8	0.83 (2)	1.99 (4)	2.801 (6)	164 (10)
O24—H24A$\cdots$O11[vi]	0.83 (2)	2.21 (5)	2.973 (6)	153 (10)

Symmetry codes: (i) $-x+1, -y+1, -z+1$; (ii) $-x, -y, -z+1$; (iii) $-x+1, -y, -z+1$; (iv) $x+1, y, z$; (v) $-x+1, -y+1, -z$; (vi) $x, y+1, z$; (vii) $x-1, y, z$; (viii) $x, y-1, z$; (ix) $x+1, y+1, z$.

Table 8
Hydrogen-bond geometry (Å, °) for (IV).

D—H$\cdots A$	D—H	H$\cdots A$	$D\cdots A$	D—H$\cdots A$
N2—H2A$\cdots$O15[i]	0.92	2.04	2.935 (5)	163
N2—H2B$\cdots$O27	0.92	2.55	3.433 (8)	160
N2—H2B$\cdots$O28[ii]	0.92	2.04	2.845 (7)	145
N4—H4B$\cdots$O2[iii]	0.92	2.31	3.176 (5)	156
N4—H4A$\cdots$O25[iii]	0.92	1.99	2.781 (8)	142
N4—H4A$\cdots$O27[iv]	0.92	2.17	3.032 (8)	156
N6—H6A$\cdots$O13[iv]	0.92	2.23	3.145 (5)	176
N6—H6B$\cdots$O24[v]	0.92	2.22	2.975 (6)	139
N8—H8B$\cdots$O12[v]	0.92	2.03	2.930 (5)	167
N8—H8A$\cdots$O23	0.92	2.18	3.017 (5)	152
N10—H10A$\cdots$O20[vi]	0.92	2.22	2.977 (5)	140
N10—H10B$\cdots$O22[vii]	0.92	2.11	2.915 (5)	145
O15—H15B$\cdots$O16	0.84 (2)	1.87 (2)	2.695 (4)	171 (6)
O15—H15A$\cdots$O21	0.84 (2)	1.83 (2)	2.667 (5)	171 (6)
O16—H16A$\cdots$O17[iv]	0.83 (2)	1.95 (2)	2.775 (5)	174 (6)
O16—H16B$\cdots$O22	0.83 (2)	1.90 (2)	2.729 (5)	174 (6)
O17—H17B$\cdots$O6[v]	0.83 (2)	1.89 (2)	2.726 (4)	177 (6)
O17—H17A$\cdots$O12	0.83 (2)	2.16 (3)	2.917 (5)	152 (6)
O18—H18B$\cdots$O14	0.83 (2)	1.94 (3)	2.734 (5)	160 (6)
O18—H18A$\cdots$O26[ii]	0.84 (2)	2.00 (3)	2.820 (8)	167 (6)
O18—H18A$\cdots$O27	0.84 (2)	1.96 (4)	2.663 (8)	141 (6)
O19—H19A$\cdots$O24[viii]	0.84 (2)	1.69 (8)	2.486 (12)	156 (20)
O19—H19B$\cdots$O24[v]	0.84 (2)	2.11 (12)	2.872 (11)	150 (21)
O20—H20B$\cdots$O11	0.83 (2)	2.15 (2)	2.970 (5)	173 (7)
O20—H20A$\cdots$O25	0.83 (2)	1.98 (4)	2.752 (8)	154 (7)
O20—H20A$\cdots$O26[ii]	0.83 (2)	2.13 (4)	2.897 (8)	153 (6)
O21—H21B$\cdots$O10[i]	0.83 (2)	1.90 (2)	2.721 (5)	169 (7)
O21—H21A$\cdots$O18[iv]	0.83 (2)	1.94 (3)	2.754 (5)	164 (7)
O22—H22B$\cdots$O23	0.83 (2)	1.91 (3)	2.703 (5)	160 (7)
O22—H22A$\cdots$O26[i]	0.84 (2)	2.14 (3)	2.948 (8)	160 (6)
O22—H22A$\cdots$O28[ix]	0.84 (2)	1.95 (4)	2.733 (8)	155 (7)
O23—H23A$\cdots$O4[vi]	0.84 (2)	1.88 (2)	2.725 (4)	177 (6)
O23—H23B$\cdots$O13[ix]	0.85 (2)	2.03 (2)	2.859 (5)	165 (5)
O24—H24B$\cdots$O8	0.84 (2)	2.01 (3)	2.803 (5)	158 (7)
O24—H24A$\cdots$O11[vi]	0.85 (2)	2.18 (3)	2.988 (5)	160 (7)

Symmetry codes: (i) $-x+1, -y+1, -z+1$; (ii) $-x, -y, -z+1$; (iii) $-x+1, -y, -z+1$; (iv) $x+1, y, z$; (v) $-x+1, -y+1, -z$; (vi) $x, y+1, z$; (vii) $x-1, y, z$; (viii) $x, y-1, z$; (ix) $x+1, y+1, z$.

Data collection

Bruker SMART APEX CCD area-detector diffractometer	10795 independent reflections
Absorption correction: multi-scan (APEX2; Bruker, 2009)	8342 reflections with $I > 2\sigma(I)$
$T_{min} = 0.621$, $T_{max} = 0.746$	$R_{int} = 0.037$
20703 measured reflections	

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.038$	H atoms treated by a mixture of independent and constrained refinement
$wR(F^2) = 0.082$	
$S = 1.03$	
10795 reflections	$\Delta\rho_{max} = 1.53$ e Å^{-3}
562 parameters	$\Delta\rho_{min} = -1.42$ e Å^{-3}
20 restraints	

Table 9
Selected bond lengths (Å) for (V).

Cu1—N3	1.918 (3)	Cu4—O7	1.940 (3)
Cu1—O1	1.922 (3)	Cu4—N10	2.009 (3)
Cu1—O2	1.963 (3)	Cu5—N1	1.893 (3)
Cu1—N4	1.992 (3)	Cu5—O9	1.930 (3)
Cu2—N5	1.899 (3)	Cu5—O10	1.949 (3)
Cu2—O3	1.922 (3)	Cu5—N2	2.003 (3)
Cu2—O4	1.937 (3)	Cu5—O18	2.358 (3)
Cu2—N6	2.014 (3)	Gd1—O1	2.378 (3)
Cu2—O19	2.384 (9)	Gd1—O9	2.384 (3)
Cu3—N7	1.900 (3)	Gd1—O3	2.390 (3)
Cu3—O6	1.939 (3)	Gd1—O15	2.398 (3)
Cu3—O5	1.943 (3)	Gd1—O7	2.417 (3)
Cu3—N8	2.007 (3)	Gd1—O5	2.434 (3)
Cu4—N9	1.892 (3)	Gd1—O11	2.449 (3)
Cu4—O8	1.934 (3)	Gd1—O12	2.452 (3)

Table 11
Selected bond lengths (Å) for (VI).

Cu1—N3	1.9136 (19)	Cu4—O7	1.9408 (16)
Cu1—O1	1.9236 (16)	Cu4—N10	2.012 (2)
Cu1—O2	1.9610 (16)	Cu5—N1	1.8915 (19)
Cu1—N4	1.994 (2)	Cu5—O9	1.9388 (15)
Cu2—N5	1.8967 (19)	Cu5—O10	1.9462 (15)
Cu2—O3	1.9267 (16)	Cu5—N2	2.0064 (18)
Cu2—O4	1.9370 (16)	Cu5—O18	2.3623 (18)
Cu2—N6	2.0206 (19)	Dy1—O9	2.3640 (15)
Cu2—O19	2.384 (5)	Dy1—O15	2.3665 (17)
Cu3—N7	1.8963 (18)	Dy1—O1	2.3694 (15)
Cu3—O6	1.9412 (16)	Dy1—O3	2.3760 (16)
Cu3—O5	1.9462 (16)	Dy1—O7	2.4092 (16)
Cu3—N8	2.0097 (19)	Dy1—O5	2.4234 (15)
Cu4—N9	1.8908 (18)	Dy1—O12	2.4278 (16)
Cu4—O8	1.9357 (16)	Dy1—O11	2.4334 (17)

Table 10
Hydrogen-bond geometry (Å, °) for (V).

$D—H\cdots A$	$D—H$	$H\cdots A$	$D\cdots A$	$D—H\cdots A$
N2—H2A···O15[i]	0.92	2.05	2.934 (5)	162
N2—H2B···O27	0.92	2.53	3.406 (8)	159
N2—H2B···O28[ii]	0.92	2.04	2.835 (7)	144
N4—H4B···O2[iii]	0.92	2.31	3.165 (5)	155
N4—H4A···O25[iii]	0.92	1.97	2.765 (7)	143
N4—H4A···O27[iv]	0.92	2.15	3.007 (7)	155
N6—H6A···O13[iv]	0.92	2.21	3.127 (5)	174
N6—H6B···O24[v]	0.92	2.18	2.948 (5)	140
N8—H8B···O12[v]	0.92	2.03	2.933 (4)	168
N8—H8A···O23	0.92	2.17	3.008 (5)	152
N10—H10A···O20[vi]	0.92	2.22	2.969 (5)	138
N10—H10B···O22[vii]	0.92	2.12	2.914 (5)	145
O15—H15B···O16	0.84 (2)	1.87 (2)	2.700 (4)	170 (5)
O15—H15A···O21	0.83 (2)	1.85 (2)	2.663 (4)	166 (5)
O16—H16A···O17[iv]	0.83 (2)	1.95 (2)	2.767 (4)	170 (5)
O16—H16B···O22	0.84 (2)	1.87 (2)	2.702 (5)	173 (5)
O17—H17B···O6[v]	0.83 (2)	1.90 (2)	2.722 (4)	171 (5)
O17—H17A···O12	0.82 (2)	2.11 (3)	2.880 (4)	158 (5)
O18—H18B···O14	0.82 (2)	1.92 (2)	2.728 (4)	171 (5)
O18—H18A···O26[ii]	0.84 (2)	2.03 (2)	2.840 (7)	164 (5)
O18—H18A···O27	0.84 (2)	1.92 (4)	2.639 (7)	144 (5)
O19—H19A···O24[viii]	0.85 (2)	1.83 (10)	2.524 (10)	138 (13)
O19—H19B···O24[v]	0.84 (2)	2.28 (13)	2.879 (9)	128 (14)
O20—H20B···O11	0.84 (2)	2.12 (2)	2.947 (4)	172 (5)
O20—H20A···O25	0.83 (2)	1.94 (3)	2.720 (7)	156 (5)
O20—H20A···O26[ii]	0.83 (2)	2.13 (3)	2.903 (7)	154 (5)
O21—H21B···O10[i]	0.83 (2)	1.91 (2)	2.717 (4)	164 (6)
O21—H21A···O18[iv]	0.83 (2)	1.96 (3)	2.755 (4)	160 (6)
O22—H22B···O23	0.84 (2)	1.89 (3)	2.689 (5)	159 (6)
O22—H22A···O26[i]	0.84 (2)	2.19 (3)	2.974 (8)	157 (6)
O22—H22A···O28[ix]	0.84 (2)	1.93 (3)	2.729 (7)	159 (6)
O23—H23A···O4[vi]	0.83 (2)	1.89 (2)	2.723 (4)	178 (5)
O23—H23B···O13[ix]	0.83 (2)	2.04 (2)	2.845 (4)	162 (5)
O24—H24A···O11[vi]	0.83 (2)	2.19 (3)	2.993 (5)	161 (7)
O24—H24B···O8	0.83 (2)	2.00 (3)	2.802 (4)	163 (7)

Symmetry codes: (i) $-x+1, -y+1, -z+1$; (ii) $-x, -y, -z+1$; (iii) $-x+1, -y, -z+1$; (iv) $x+1, y, z$; (v) $-x+1, -y+1, -z$; (vi) $x, y+1, z$; (vii) $x-1, y, z$; (viii) $x, y-1, z$; (ix) $x+1, y+1, z$.

Compound (VI)

Crystal data

[Cu5Dy(C2H4N2O2)5(SO4)-(H2O)6.5]2(SO4)·6H2O	$\beta = 91.452$ (1)°
$M_r = 2471.74$	$\gamma = 105.290$ (1)°
Triclinic, $P\bar{1}$	$V = 1708.2$ (3) Å^3
$a = 9.5987$ (8) Å	$Z = 1$
$b = 11.5733$ (10) Å	Mo $K\alpha$ radiation
$c = 16.2193$ (14) Å	$\mu = 5.42$ mm^{-1}
$\alpha = 99.754$ (1)°	$T = 100$ K
	$0.43 \times 0.41 \times 0.10$ mm

Data collection

Bruker SMART APEX CCD area-detector diffractometer	19309 measured reflections
Absorption correction: multi-scan (*APEX2*; Bruker, 2009)	9894 independent reflections
$T_{min} = 0.401$, $T_{max} = 0.746$	9303 reflections with $I > 2\sigma(I)$
	$R_{int} = 0.030$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.024$	H atoms treated by a mixture of independent and constrained refinement
$wR(F^2) = 0.064$	
$S = 1.05$	
9894 reflections	$\Delta\rho_{max} = 1.83$ e Å^{-3}
562 parameters	$\Delta\rho_{min} = -1.69$ e Å^{-3}
20 restraints	

Compound (VII)

Crystal data

[Cu5Ho(C2H4N2O2)5(SO4)-(H2O)6.5]2(SO4)·6H2O	$\beta = 91.453$ (1)°
$M_r = 2476.46$	$\gamma = 105.284$ (1)°
Triclinic, $P\bar{1}$	$V = 1702.1$ (3) Å^3
$a = 9.5859$ (8) Å	$Z = 1$
$b = 11.5639$ (10) Å	Mo $K\alpha$ radiation
$c = 16.1967$ (14) Å	$\mu = 5.57$ mm^{-1}
$\alpha = 99.779$ (1)°	$T = 100$ K
	$0.43 \times 0.41 \times 0.10$ mm

Data collection

Bruker SMART APEX CCD area-detector diffractometer	20988 measured reflections
Absorption correction: multi-scan (*APEX2*; Bruker, 2009)	9744 independent reflections
$T_{min} = 0.459$, $T_{max} = 0.746$	8636 reflections with $I > 2\sigma(I)$
	$R_{int} = 0.029$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.031$	H atoms treated by a mixture of independent and constrained refinement
$wR(F^2) = 0.082$	
$S = 1.03$	
9744 reflections	$\Delta\rho_{max} = 3.27$ e Å^{-3}
562 parameters	$\Delta\rho_{min} = -2.35$ e Å^{-3}
20 restraints	

In each structure, one of the sulfate anions is located on an inversion centre and its O atoms are 1:1 disordered. One of the water molecules is disordered over two crystallographically equivalent positions in between two crystallographically equivalent neighbouring molecules and is bonded to one or the other *via* one of the Cu^{II} cations of the metalla-macrocycles.

Table 12
Hydrogen-bond geometry (Å, °) for (VI).

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
N2—H2A···O15^i	0.92	2.05	2.935 (3)	161
N2—H2B···O27	0.92	2.53	3.408 (4)	159
N2—H2B···O28^{ii}	0.92	2.05	2.847 (4)	144
N4—H4B···O2^{iii}	0.92	2.33	3.190 (3)	156
N4—H4A···O25^{iii}	0.92	1.98	2.766 (4)	143
N4—H4A···O27^{iv}	0.92	2.14	3.004 (4)	155
N6—H6A···O13^{iv}	0.92	2.24	3.155 (3)	174
N6—H6B···O24^v	0.92	2.20	2.957 (3)	140
N8—H8B···O12^v	0.92	2.03	2.938 (2)	168
N8—H8A···O23	0.92	2.18	3.023 (3)	152
N10—H10A···O20^{vi}	0.92	2.24	2.984 (3)	137
N10—H10B···O22^{vii}	0.92	2.11	2.906 (3)	145
O15—H15B···O16	0.82 (2)	1.89 (2)	2.696 (2)	171 (3)
O15—H15A···O21	0.82 (2)	1.86 (2)	2.665 (2)	167 (3)
O16—H16A···O17^{iv}	0.83 (2)	1.95 (2)	2.776 (2)	173 (3)
O16—H16B···O22	0.82 (2)	1.90 (2)	2.714 (3)	170 (3)
O17—H17B···O6^v	0.82 (2)	1.91 (2)	2.726 (2)	177 (3)
O17—H17A···O12	0.82 (2)	2.09 (2)	2.885 (3)	165 (3)
O18—H18B···O14	0.81 (2)	1.92 (2)	2.726 (2)	177 (4)
O18—H18A···O26^{ii}	0.84 (2)	2.03 (2)	2.855 (4)	169 (3)
O18—H18A···O27	0.84 (2)	1.94 (3)	2.644 (4)	140 (3)
O19—H19A···O24^{viii}	0.84 (2)	1.73 (3)	2.555 (5)	164 (10)
O19—H19B···O24^v	0.85 (2)	2.10 (5)	2.881 (5)	153 (10)
O20—H20B···O11	0.83 (2)	2.13 (2)	2.948 (2)	169 (3)
O20—H20A···O25	0.81 (2)	1.95 (2)	2.719 (4)	157 (4)
O20—H20A···O26^{ii}	0.81 (2)	2.15 (2)	2.898 (4)	154 (3)
O21—H21B···O10^i	0.84 (2)	1.89 (2)	2.720 (2)	171 (4)
O21—H21A···O18^{iv}	0.83 (2)	1.94 (2)	2.751 (3)	167 (4)
O22—H22B···O23	0.83 (2)	1.89 (2)	2.704 (3)	166 (4)
O22—H22A···O26^i	0.84 (2)	2.18 (2)	2.964 (4)	156 (4)
O22—H22A···O28^{ix}	0.84 (2)	1.93 (2)	2.727 (4)	158 (4)
O23—H23A···O4^{vi}	0.83 (2)	1.91 (2)	2.727 (2)	170 (3)
O23—H23B···O13^{ix}	0.83 (2)	2.02 (2)	2.847 (2)	172 (3)
O24—H24B···O8	0.84 (2)	1.99 (2)	2.805 (3)	162 (4)
O24—H24A···O11^{vi}	0.83 (2)	2.18 (2)	3.002 (3)	172 (5)

Symmetry codes: (i) $-x+1, -y+1, -z+1$; (ii) $-x, -y, -z+1$; (iii) $-x+1, -y, -z+1$; (iv) $x+1, y, z$; (v) $-x+1, -y+1, -z$; (vi) $x, y+1, z$; (vii) $x-1, y, z$; (viii) $x, y-1, z$; (ix) $x+1, y+1, z$.

Table 14
Hydrogen-bond geometry (Å, °) for (VII).

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
N2—H2A···O15^i	0.92	2.06	2.940 (4)	160
N2—H2B···O27	0.92	2.52	3.397 (6)	159
N2—H2B···O28^{ii}	0.92	2.04	2.839 (6)	145
N4—H4B···O2^{iii}	0.92	2.34	3.195 (4)	155
N4—H4A···O25^{iii}	0.92	1.98	2.768 (6)	143
N4—H4A···O27^{iv}	0.92	2.14	2.999 (6)	155
N6—H6A···O13^{iv}	0.92	2.24	3.162 (4)	174
N6—H6B···O24^v	0.92	2.21	2.964 (4)	139
N8—H8B···O12^v	0.92	2.03	2.935 (3)	168
N8—H8A···O23	0.92	2.18	3.026 (4)	152
N10—H10A···O20^{vi}	0.92	2.24	2.980 (4)	137
N10—H10B···O22^{vii}	0.92	2.10	2.904 (4)	145
O15—H15B···O16	0.83 (2)	1.86 (2)	2.692 (3)	174 (4)
O15—H15A···O21	0.84 (2)	1.84 (2)	2.664 (4)	164 (5)
O16—H16A···O17^{iv}	0.83 (2)	1.94 (2)	2.768 (3)	176 (5)
O16—H16B···O22	0.83 (2)	1.90 (2)	2.716 (4)	171 (5)
O17—H17B···O6^v	0.83 (2)	1.90 (2)	2.724 (3)	177 (5)
O17—H17A···O12	0.82 (2)	2.10 (2)	2.886 (3)	160 (4)
O18—H18B···O14	0.83 (2)	1.90 (2)	2.722 (3)	174 (5)
O18—H18A···O26^{ii}	0.84 (2)	2.01 (2)	2.844 (6)	172 (5)
O18—H18A···O27	0.84 (2)	1.97 (4)	2.640 (6)	136 (4)
O19—H19A···O24^{viii}	0.84 (2)	1.76 (6)	2.559 (8)	157 (14)
O19—H19B···O24^v	0.84 (2)	2.16 (10)	2.875 (7)	142 (15)
O20—H20B···O11	0.83 (2)	2.13 (2)	2.942 (4)	167 (5)
O20—H20A···O25	0.83 (2)	1.89 (2)	2.714 (6)	169 (5)
O20—H20A···O26^{ii}	0.83 (2)	2.19 (3)	2.896 (5)	143 (4)
O21—H21B···O10^i	0.83 (2)	1.90 (2)	2.721 (3)	172 (5)
O21—H21A···O18^{iv}	0.83 (2)	1.93 (2)	2.750 (3)	168 (5)
O22—H22B···O23	0.84 (2)	1.88 (2)	2.697 (4)	165 (5)
O22—H22A···O26^i	0.84 (2)	2.15 (3)	2.961 (6)	163 (5)
O22—H22A···O28^{ix}	0.84 (2)	1.95 (3)	2.725 (6)	153 (5)
O23—H23A···O4^{vi}	0.83 (2)	1.91 (2)	2.731 (3)	168 (5)
O23—H23B···O13^{ix}	0.84 (2)	2.02 (2)	2.849 (4)	173 (5)
O24—H24B···O8	0.84 (2)	2.00 (3)	2.803 (4)	158 (6)
O24—H24A···O11^{vi}	0.84 (2)	2.18 (2)	3.003 (4)	167 (6)

Symmetry codes: (i) $-x+1, -y+1, -z+1$; (ii) $-x, -y, -z+1$; (iii) $-x+1, -y, -z+1$; (iv) $x+1, y, z$; (v) $-x+1, -y+1, -z$; (vi) $x, y+1, z$; (vii) $x-1, y, z$; (viii) $x, y-1, z$; (ix) $x+1, y+1, z$.

Table 13
Selected bond lengths (Å) for (VII).

Cu1—N3	1.909 (3)	Cu4—O7	1.941 (2)
Cu1—O1	1.922 (2)	Cu4—N10	2.011 (3)
Cu1—O2	1.959 (2)	Cu5—N1	1.887 (3)
Cu1—N4	1.993 (3)	Cu5—O9	1.938 (2)
Cu2—N5	1.893 (3)	Cu5—O10	1.944 (2)
Cu2—O3	1.921 (2)	Cu5—N2	2.005 (3)
Cu2—O4	1.931 (2)	Cu5—O18	2.360 (3)
Cu2—N6	2.016 (3)	Ho1—O9	2.356 (2)
Cu2—O19	2.384 (7)	Ho1—O15	2.357 (2)
Cu3—N7	1.897 (3)	Ho1—O1	2.360 (2)
Cu3—O6	1.936 (2)	Ho1—O3	2.372 (2)
Cu3—O5	1.945 (2)	Ho1—O7	2.400 (2)
Cu3—N8	2.007 (3)	Ho1—O12	2.414 (2)
Cu4—N9	1.891 (3)	Ho1—O5	2.416 (2)
Cu4—O8	1.934 (2)	Ho1—O11	2.417 (2)

Methylene and amine H atoms were placed in calculated positions and were refined as riding on their respective parent atoms, with C—H = 0.99 Å and N—H = 0.92 Å, and with $U_{iso}(H) = 1.2U_{eq}(C,N)$. Water H atoms were located in difference density Fourier maps and refined with the O—H distances restrained to 0.84 (2) Å and with $U_{iso}(H) = 1.5U_{eq}(O)$.

For all seven compounds, data collection: *APEX2* (Bruker, 2009); cell refinement: *APEX2*; data reduction: *APEX2*; program(s) used to solve structure: *SHELXTL* (Version 6.14; Sheldrick, 2008); program(s) used to refine structure: *SHELXTL*; molecular graphics: *SHELXTL* and *Mercury* (Macrae *et al.*, 2008); software used to prepare material for publication: *SHELXTL* and *publCIF* (Westrip, 2010).

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Table 15
Details of synthetic procedures.

Salt used	Mass (g)	Empirical formula of product	Yield, mass of product (g)	Calculated CHN (%)	Experimental CHN (%)
$Pr(NO_3)_3 \cdot 6H_2O$	0.870	$C_{20}H_{78}Cu_{10}N_{20}Pr_2O_{51}S_3$	66%, 3.21	C 9.89, H 3.24, N 11.54	C 10.13, H 3.82, N 11.61
$Nd(NO_3)_3 \cdot 6H_2O$	0.877	$C_{20}H_{78}Cu_{10}N_{20}Nd_2O_{51}S_3$	65%, 3.16	C 9.87, H 3.23, N 11.50	C 9.96, H 3.76, N 11.58
$Sm(NO_3)_3 \cdot 6H_2O$	0.889	$C_{20}H_{78}Cu_{10}N_{20}Sm_2O_{51}S_3$	68%, 3.33	C 9.82, H 3.21, N 11.45	C 9.78, H 3.64, N 11.34
$Eu(NO_3)_3 \cdot 5H_2O$	0.856	$C_{20}H_{78}Cu_{10}N_{20}Eu_2O_{51}S_3$	63%, 3.09	C 9.80, H 3.21, N 11.43	C 10.26, H 2.87, N 11.37
$Gd(NO_3)_3 \cdot 6H_2O$	0.903	$C_{20}H_{78}Cu_{10}N_{20}Gd_2O_{51}S_3$	67%, 3.30	C 9.76, H 3.19, N 11.38	C 9.45, H 3.6, N 11.4
$Dy(NO_3)_3 \cdot 5H_2O$	0.877	$C_{20}H_{78}Cu_{10}N_{20}Dy_2O_{51}S_3$	71%, 3.51	C 9.72, H 3.18, N 11.33	C 9.51, H 2.83, N 11.42
$Ho(NO_3)_3 \cdot 5H_2O$	0.882	$C_{20}H_{78}Cu_{10}N_{20}Ho_2O_{51}S_3$	70%, 3.47	C 9.70, H 3.17, N 11.31	C 9.36, H 2.89, N 11.27

Table 16
Additional structural parameters for (I)–(VII).

Complex	Ln$\cdots$Cu	Ln$\cdots$Cu separation range (Å)	Cu$\cdots$Cu separation range (Å)	Deviation of Ln^{III} from the Cu1/Cu2/Cu3/Cu4/Cu5 plane (Å)	Relative change of Ln1 deviation (%)	Deviation of O2 from the Cu1/Cu2/Cu3/Cu4/Cu5 plane (Å)
(I)	Pr$\cdots$Cu	3.862 (3)–3.923 (2)	4.530 (2)–4.604 (2)	0.459	100	0.978
(II)	Nd$\cdots$Cu	3.862 (3)–3.915 (4)	4.524 (4)–4.598 (5)	0.452	98.47	0.986
(III)	Sm$\cdots$Cu	3.8539 (9)–3.9083 (8)	4.518 (1)–4.592 (1)	0.439	95.64	1.014
(IV)	Eu$\cdots$Cu	3.844 (7)–3.899 (8)	4.504 (8)–4.585 (9)	0.439	95.64	1.018
(V)	Gd$\cdots$Cu	3.838 (7)–3.897 (9)	4.501 (8)–4.578 (11)	0.430	93.68	1.023
(VI)	Dy$\cdots$Cu	3.834 (2)–3.889 (2)	4.493 (2)–4.573 (2)	0.424	92.37	1.046
(VII)	Ho$\cdots$Cu	3.827 (2)–3.884 (2)	4.485 (2)–4.565 (2)	0.422	91.94	1.055

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