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Formation of Coordination Polymers or Discrete Adducts via Reactions of Gadolinium(III)−Copper(II) 15-Metallacrown-5 Complexes with Polycarboxylates: Synthesis, Structures and Magnetic Properties

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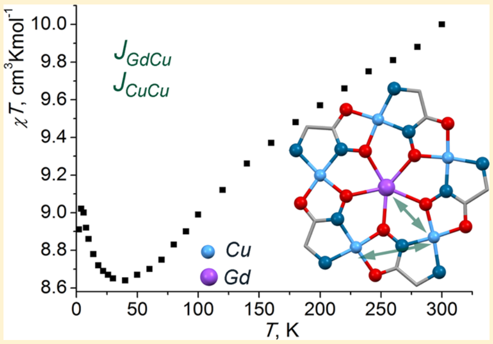
S Supporting Information



ABSTRACT: Reactions of the copper(II)−gadolinium(III) 15-metallacrown-5 complex $[GdCu_5(Glyha)_5(NO_3)_2(H_2O)_6](NO_3)$ ($Glyha^{2-}$ = dianion of glycinehydroxamic acid) with different di/tricarboxylates (1,3-phthalate, 1,4-phthalate, biphenyl-4,4′-dicarboxylate, citrate) resulted in formation of different types of products: $\{[(GdCu_5(Glyha)_5(H_2O)_2)(GdCu_5(Glyha)_5(H_2O)_3)(1,3\text{-bdc})_3]\cdot 16H_2O\}_n$ (**1**), $\{[(GdCu_5(Glyha)_5(H_2O)_3)_2(1,4\text{-bdc})_2](1,4\text{-bdc})\cdot 8H_2O\}_n$ (**2**), $\{[(GdCu_5(Glyha)_5(H_2O)_4)_2(1,4\text{-bdc})_3]\cdot 8H_2O\}_n$ (**3**), $[GdCu_5(Glyha)_5(Citr)(H_2O)_4]\cdot 7H_2O$ (**4**), $\{[GdCu_5(Glyha)_5(H_2O)_5](\mu_2\text{-}CO_3)[Cu(Fgg)]\}\cdot 7H_2O$ (**5**) and $[Cu(Gly)_2(H_2O)]_n$ (**6**) (where bdc^{2-} is the corresponding phthalate (benzenedicarboxylate), $Citr^{3-}$ is citrate, Fgg^{3-} is the trianion of [(*N*-formylaminoacetyl)amino]acetic acid and Gly^- is glycinate). Complexes **1**−**5** contain the $[GdCu_5(Glyha)_5]^{3+}$ cation. Complexes **2** and **3** possess the same composition but differ by the mode of *p*-phthalate coordination to the $[GdCu_5(Glyha)_5]^{3+}$ unit. In compounds **1**−**3**, metallacrown cations are linked by the corresponding phthalates in 1D, 1D and 2D polymers, respectively, whereas **4** and **5** are discrete molecules. Compound **5** is the product of a multistep reaction, which finally involves atmospheric CO_2 capture. Hydrolysis of hydroxamate in this reaction is confirmed by isolation of a mononuclear copper glycine complex 6. The $\chi_M T$ vs T data for **1** were fitted using a model based on the Hamiltonian $\hat{H}$ $(GdCu_5) = -2J_1(S_1 \times S_{Gd} + S_2 \times S_{Gd} + S_3 \times S_{Gd} + S_4 \times S_{Gd} + S_5 \times S_{Gd}) - 2J_2(S_1 \times S_2 + S_2 \times S_3 + S_3 \times S_4 + S_4 \times S_1 + S_5 \times S_1$. The best fit corresponded to $J_1 = +0.60(2)$ cm^{-1}, $J_2 = -61.0(5)$ cm^{-1} and $zJ' = -0.035(4)$ cm^{-1}. Complex **1** is the first example of a 15-metallacrown-5 system, for which numerical values of exchange parameters have been reported. The isotherm for methanol absorption by compound **1** at 293 K was typical for microporous sorbents, whereas ethanol sorption was negligibly small.

■ INTRODUCTION

Metallacrown (MC) complexes are polynuclear assemblies, based in the majority of cases, on hydroxamates.[1,2] Interest in this class of coordination compounds has been stimulated by their interesting properties, such as selective recognition of cations, anions and molecules,[3] potential bioactivity,[4] catalytic activity,[5] etc.

Polynuclear complexes can themselves be used as suitable "building blocks" for the construction of larger coordination polymers.[6] It has been shown that the magnetic properties of such assemblies can be controlled by the magnetic properties of the starting polynuclear blocks, which can open the way for construction of polymers with predetermined, tailored properties. Many examples of coordination polymers have been reported where polynuclear cores were formed by self-assembly from mononuclear precursors.[7] Compounds formed by such self-assembly often possess unexpected or noteworthy properties, but the outcome of such reactions is frequently unpredictable. Metallacrowns, due to their stability in solution and the presence of vacant or labile coordination sites, are

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suitable moieties for generation of coordination polymers and supramolecular assemblies.

The aim of this study was to examine the outcomes of combining the previously described $[GdCu_5(Glyha)_5]^{3+}$ metallacrown cation ($Glyha^{2-}$ = dianion of glycinehydroxamic acid) with polycarboxylates of different types and to determine the various conditions leading to formation of different coordination polymers.

A number of papers have noted the magnetic properties of compounds of this class,[8,9] and several examples of metallacrowns with single molecular magnet (SMM) behavior have been reported.[10,11] However, to the best of our knowledge, numerical values of exchange parameters have not been determined for any representative of the 15-metallacrown-5 family. Quantitative characterization of exchange interactions in $LnCu_5$ systems is clearly essential for ultimately understanding the factors that govern the magnetic properties of such systems. An additional aim of this work was thus to develop a model that could be used for exchange parameter estimation using magnetic data for 15-MC-5 complexes, and apply it to determining numerical values of exchange integrals in this $GdCu_5$ system.

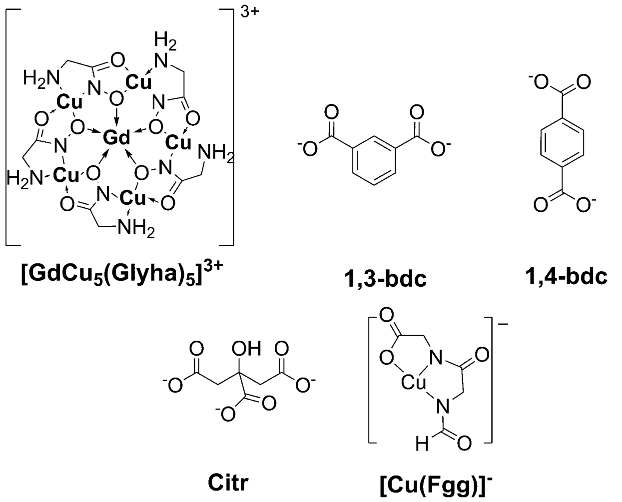
As a source for the metallacrown building block, we have used the previously reported copper(II)−gadolinium(III) complex $[GdCu_5(Glyha)_5(NO_3)_2(H_2O)_6](NO_3)\cdot 5H_2O$, which was synthesized according to the published procedure.[12] The choice of polycarboxylates as potential linkers was stimulated by their ability to coordinate to metal ions in metallacrowns,[3] along with their negative charge, favoring combination with cationic blocks to form complex lattices.

In this paper, we report the synthesis, structures and properties of three coordination polymers: $\{[(GdCu_5(Glyha)_5(H_2O)_2)(GdCu_5(Glyha)_5(H_2O)_3)(1,3\text{-}bdc)_3]\cdot 16H_2O\}_n$ (1), $\{[(GdCu_5(Glyha)_5(H_2O)_3)_2(1,4\text{-}bdc)_2](1,4\text{-}bdc)\cdot 8H_2O\}_n$ (2) and $\{[(GdCu_5(Glyha)_5(H_2O)_4)_2(1,4\text{-}bdc)_3]\cdot 8H_2O\}_n$ (3), and of the discrete complexes $[GdCu_5(Glyha)_5(Citr)(H_2O)_4]\cdot 7H_2O$ (4) and $\{[GdCu_5(Glyha)_5(H_2O)_5](\mu_2\text{-}CO_3)[Cu(Fgg)]\}\cdot 7H_2O$ (5) (where Fgg^{3-} = (trianion of [(*N*-formylaminoacetyl)amino]-acetic acid). In addition, Cu^{II} glycinate $[Cu(Gly)_2(H_2O)]_n$ (6) was isolated, which supports our suppositions regarding the possibility of hydrolysis of glycinehydroxamate in some of the reaction media. The interaction of $[(GdCu_5(Glyha)_5]^{3+}$ with 1,3-phthalate in water−methanol solutions was investigated using ESI mass spectrometry, and the magnetic and sorption properties of compound 1 were studied.

■ EXPERIMENTAL SECTION

Materials and Measurements. Commercially available reagents and solvents (Merck and Aldrich) were used without further purification. The sodium salt of glycine hydroxamic acid was synthesized as described previously.[13] $[GdCu_5(Glyha)_5(NO_3)_2(H_2O)_6](NO_3)\cdot 5H_2O$ was prepared using a previously reported procedure.[12] C, H and N analyses were carried out on a Carlo Erba 1106 instrument. Single-crystal X-ray diffraction was performed at 100 K on a Smart Apex diffractometer with Apex2 software using graphite-monochromated Mo Kα radiation of wavelength 0.710 73 Å, whereas powder data were measured on a Bruker X9 diffractometer (radiation of wavelength 1.540 56 Å). Crystals suitable for X-ray data collection were taken directly from the reaction mixtures. CCDC 950109, 950110, 950111, 950112, 950113 and 950114.

Scheme 1. Structural Formula for $[GdCu_5(Glyha)_5]^{3+}$, 1,3- and 1,4-bdc, Citr and $[Cu(Fgg)]^-$



Variable-temperature magnetic data (2−300 K) were obtained using a Quantum Design MPMS5S SQUID magnetometer with field strengths in the range of 0.1 to 1.0 T. Samples were prepared in gelatin capsules, mounted inside straws, and then fixed to the end of the sample transport rod. Background corrections for the sample holder assembly were applied. Susceptibility data were corrected for diamagnetism using Pascal's constants,[14] $Co[Hg(SCN)_4]$ being used as a calibration standard.

Thermogravimetric analysis (TGA) was performed with the samples in air with an MOM Q1500 instrument at a heating rate of 10 °C min^{-1}, over the range 20−670 °C. For gravimetric sorption measurements (at 293 K), samples were first activated at 130 °C in vacuo at 10^{-2} Torr, followed by temperature equilibration and introduction of sorbate vapor. Each point on the sorption and desorption isotherms corresponds to equilibrium conditions (constant sample weight at a given P/P_S value).

Synthesis of $\{[(GdCu_5(Glyha)_5(H_2O)_2)(GdCu_5(Glyha)_5(H_2O)_3)(1,3\text{-}bdc)_3]\cdot 16H_2O\}_n$ (1). $[GdCu_5(Glyha)_5(NO_3)_2(H_2O)_6](NO_3)\cdot 5H_2O$ (25 mg, 0.019 mmol) was dissolved in hot DMF (1.5 mL, 100 °C), and the solution was added to a stirred solution of disodium 1,3-phthalate (6 mg, 0.029 mmol) in water (3 mL). After 2 days, violet platelets were obtained. The crystals were filtered off and air-dried (16 mg, 62% yield). Anal. Calcd for $Gd_2Cu_{10}C_{44}H_{94}N_{20}O_{53}$: C, 19.6; H, 3.48; N, 10.4. Found: C, 19.9; H, 3.82; N, 10.7.

Synthesis of $\{[(GdCu_5(Glyha)_5(H_2O)_3)_2(1,4\text{-}bdc)_2](1,4\text{-}bdc)\cdot 8H_2O\}_n$ (2) and $\{[(GdCu_5(Glyha)_5(H_2O)_4)_2(1,4\text{-}bdc)_3]\cdot 8H_2O\}_n$ (3) (the mixture). $[GdCu_5(Glyha)_5(NO_3)_2(H_2O)_6](NO_3)\cdot 5H_2O$ (25 mg, 0.019 mmol) was dissolved in hot DMF (1.5 mL), which was then added to a stirred solution of disodium 1,4-phthalate (6 mg, 0.029 mmol) in water (3 mL). After 2 days, a mixture containing two types of violet platelets was obtained. Attempts to produce only one complex (changes of solvents, concentrations and reagent ratios) were not successful. Note that although the two compounds differ in their crystal structures, their compositions (and expected microanalytical data) are very similar. Anal. Calcd for $Gd_2Cu_{10}C_{44}H_{81.79}N_{20}O_{46.90}$ (2): C, 20.4; H, 3.2; N, 10.8. Anal. Calcd for $GdCu_5C_{22}H_{42}N_{10}O_{24}$ (3): C, 20.2; H, 3.2; N, 10.7; Found: C, 20.3; H, 3.3; N, 10.4.

Synthesis of $[GdCu_5(Glyha)_5(Citr)(H_2O)_4]\cdot 7H_2O$ (4). $[GdCu_5(Glyha)_5(NO_3)_2(H_2O)_6](NO_3)\cdot 5H_2O$ (25 mg, 0.019 mmol) was dissolved in warm DMF (1.5 mL), which was added to a solution of trisodium citrate hydrate ($Na_3C_6H_5O_7\cdot 5.5H_2O$, 7 mg, 0.019 mmol) in water (3 mL). After several days, dark blue crystals were obtained (14 mg, 57% yield). Anal. Calcd for $GdCu_5C_{16}H_{47}N_{10}O_{28}$: C, 14.8; H, 3.64; N, 10.8; Found: C, 14.5; H, 3.92; N, 11.1.

Synthesis of $\{[GdCu_5(Glyha)_5(H_2O)_5](\mu_2\text{-}CO_3)[Cu(Fgg)]\}\cdot 7H_2O$ (5) and $[Cu(Gly)_2(H_2O)]_n$ (6). Biphenyl-4,4′-dicarboxylic acid (7 mg, 0.029 mmol) was dissolved in an aqueous solution of tetraethylammonium hydroxide (2 mL 20%, 0.066 mmol) plus water (3 mL). To this was added a solution of $[GdCu_5(Glyha)_5(NO_3)_2(H_2O)_6](NO_3)\cdot$

Table 1. Single-Crystal Data and Structure Refinement Details for Complexes 1−6

	complex 1	complex 2	complex 3	complex 4	complex 5	complex 6
formula	$Gd_2Cu_{10}C_{44}H_{96.61}N_{20}O_{54.305}$	$Gd_2Cu_{10}C_{44}H_{81.79}N_{20}O_{46.90}$	$GdCu_5C_{22}H_{42}N_{10}O_{24}$	$GdCu_5C_{16}H_{46.50}N_{10}O_{27.73}$	$GdCu_6C_{16}H_{49}N_{12}O_{29}$	$CuC_4H_{10}N_2O_5$
M/g mol^{-1}	2724.89	2591.43	1305.60	1297.85	1412.16	229.68
crystal system	Triclinic	Triclinic	Triclinic	Triclinic	Triclinic	Orthorhombic
space group	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$	$P2_12_12_1$
a, Å	13.6625(14)	9.6089(13)	9.7320(15)	10.5647(11)	10.665(4)	5.1685(19)
b, Å	15.7784(16)	14.0914(19)	13.686(2)	11.8928(12)	10.890(4)	10.586(4)
c, Å	19.959(2)	14.990(2)	14.923(2)	16.0985(17)	17.845(8)	13.538(5)
α, deg	90.3970(10)	105.517(2)	87.433(2)	86.4170(10)	82.102(7)	90.00
β, deg	100.9860(10)	97.625(3)	77.622(2)	74.0700(10)	87.238(4)	90.00
γ, deg	102.700(2)	100.234(3)	76.958(3)	77.4340(10)	79.426(5)	90.00
volume, Å^3	4115.1(7)	1889.5(4)	1891.3(5)	1898.4(3)	2017.6(13)	740.7(5)
Z	2	2	2	2	2	4
T, K	100(2)	100(2)	100(2)	100(2)	100(2)	100(2)
range of data collection	1.325° < 2θ < 30.769°	1.436° < 2θ < 28.280°	1.397° < 2θ < 28.278°	1.754° < 2θ < 32.119°	1.152° < 2θ < 26.730°	2.44° < 2θ < 31.97°
ρcalc, g·cm^{-3}	2.199	2.277	2.293	2.270	2.325	2.060
absorption coefficient, mm^{-1}	4.234	4.598	4.595	4.584	4.835	2.934
μ (Mo Kα)	0.71073	0.71073	0.71073	0.71073	0.71073	0.71073
F(000)	2706.1	1279	1290	1286.7	1398	468
collected reflections	46572	18776	30432	42297	18661	8825
reflections unique	23962	9218	9197	12236	8486	2446
R_{int}	0.0574	0.0352	0.0572	0.0227	0.0595	0.0258
GOF on F^2	1.014	1.027	1.119	1.048	1.050	0.999
$R_1[I > 2\sigma(I)]^a$	0.0489	0.0445	0.0476	0.0298	0.0705	0.0175
$wR_2[I > 2\sigma(I)]^b$	0.0949	0.1086	0.1015	0.0642	0.1834	0.0428

$^aR_1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$ $^bwR_2 = \{\Sigma[w(F_o^2 - F_c^2)^2]/\Sigma[w(F_o^2)^2]\}^{1/2}$

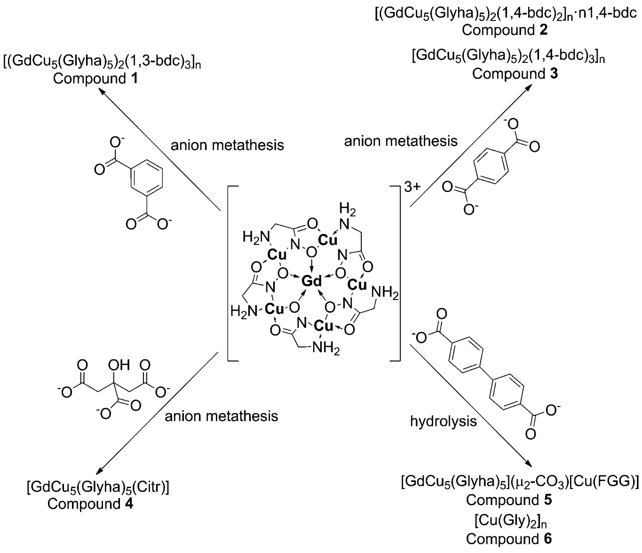
$5H_2O$ (25 mg, 0.019 mmol) in warm DMF (1.5 mL). After several weeks, two types of crystals (dark blue (5) and light blue (6)) formed.

Crystal data, data collection parameters and structure refinement details for complexes 1−6 are given in Table 1.

■ RESULTS AND DISCUSSION

Synthesis. Complexes 1−3 were obtained from metathesis reactions between $[GdCu_5(Glyha)_5(NO_3)_2(H_2O)_6](NO_3)$ and sodium salts of the corresponding phthalates in DMF−water mixtures. Complex 1 was isolated as a single product, whereas complexes 2 and 3 crystallized as a mixture from a single reaction system. These complexes have polymeric structures, vide infra. Formation of 1−3 can be considered as "normal" metathesis reactions, in which NO_3^- was replaced by phthalate dianions, the lower solubility of the products appearing to be the driving force for the reaction (Scheme 2). Attempts to confirm the presence of adducts of $[GdCu_5(Glyha)_5]^{3+}$ generated in solution with 1,3-phthalate using ESI mass spectrometry were not gainful (see Figure S1, Supporting Information).

Scheme 2. Formation of Compounds 1−6[a]

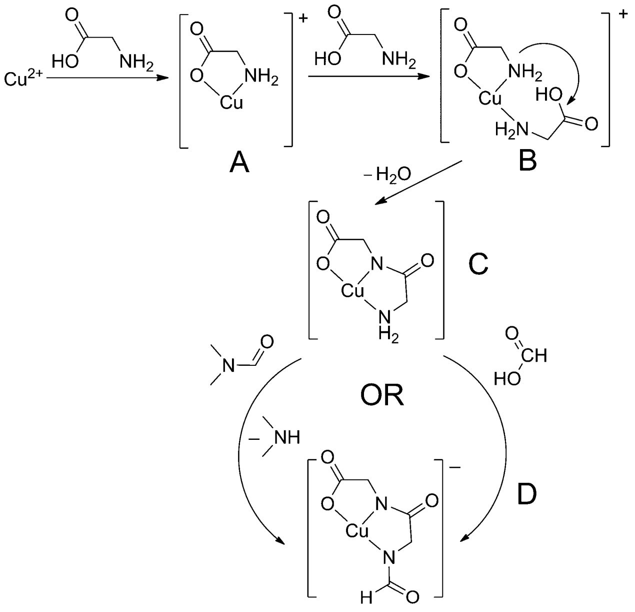


[a]Solvent molecules in formula are omitted for clarity of presentation.

Complex 4 was obtained by reaction of $[GdCu_5(Glyha)_5(NO_3)_2(H_2O)_6](NO_3)$ with citrate in a DMF/water mixture, with the formation of discrete complexes rather than coordination polymers presumably encouraged electrostatically by the large cationic and anionic charges (+3 and −3).

The reaction of $[GdCu_5(Glyha)_5(NO_3)_2(H_2O)_6](NO_3)$ with biphenyl-4,4′-dicarboxylate was performed in DMF by adding an aqueous solution of the acid's tetraethylammonium salt. For the syntheses of 1−3 and 5 50% excess of dicarboxylates was used. However, in the reaction with biphenyl-4,4′-dicarboxylate, instead of the intended 2:3 adduct, a mixture of copper(II) glycinate (6) was isolated, along with the heptanuclear complex $\{[GdCu_5(Glyha)_5(H_2O)_5](\mu_2\text{-}CO_3)[Cu(Fgg)]\}\cdot 7H_2O$ (5). Complex 5 contains the original $[GdCu_5(Glyha)_5]^{3+}$ metallacrown unit, and the mononuclear Cu^{II} complex $[Cu(Fgg)]^-$, attached to this $GdCu_5$ block through a bridging carbonate (see X-ray structure description). The formation of the $[Cu(Fgg)]^-$ anion (Fgg^{3-} is the trianion of [(*N*-formylaminoacetyl)amino]acetic acid) is presumed to arise from the hydrolysis of glycinehydroxamate, leading to formation of free glycine and cleavage of the parent metallocycle (Scheme 3).

Scheme 3. Scenario for $[Cu(Fgg)]^-$ Anion Formation[a]



[a]See text.

Formation of $[Cu(Fgg)]^-$ must involve hydrolysis of glycinehydroxamate, followed by condensation to give GlyGly (presumably metal-promoted or base-catalyzed). The N-formylation step required for $[Cu(Fgg)]^-$ production likely involves a DMF-derived formyl moiety, atmospheric CO_2 is inevitably the CO_3^{2-} source.[15−17] Complexes 1−4 have not yielded products of these kinds, likely due to the longer reaction times in solution required for the synthesis of compounds 5 and 6, because of their greater solubilities in the reaction solvents.

Solid State Structures. *Compound 1.* The polymeric 1D chain of compound 1 contains two types of crystallographically independent $[GdCu_5(Glyha)_5]^{3+}$ cations (Figure 1). Except for the atoms in axial positions, the molecular structures of these two types of $[GdCu_5(Glyha)_5]^{3+}$ metallacrown blocks are almost the same. As required for charge balancing, there are three 1,3-phthalates per two metallacrown cations.

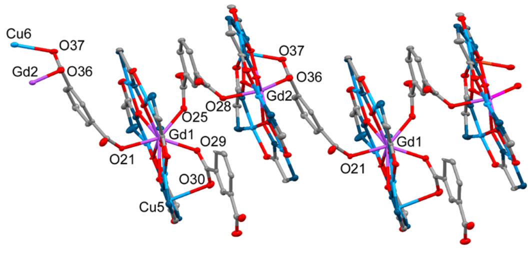


Figure 1. Fragment of the crystal structure of complex 1. Hydrogen atoms and water molecules (including the one coordinated to Gd2 and several coordinated to Cu^{II} ions, as well as all noncoordinated waters) are omitted for clarity of presentation. Complete metal ion coordination spheres are shown in Figures 2 and 3

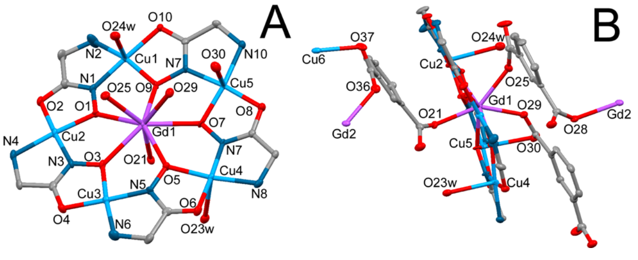


Figure 2. First type of crystallographically independent $[GdCu_5(Glyha)_5]^{3+}$ cation in the crystal structure of 1 (A) and a different projection (B) of the same cation, showing the modes of 1,3-phthalate binding. Hydrogen atoms are omitted for clarity.

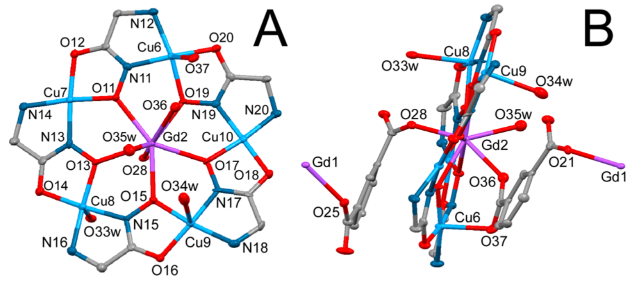


Figure 3. Second type of crystallographically independent $[GdCu_5(Glyha)_5]^{3+}$ cation in the crystal structure of 1 (A) and a different projection (B) of the same cation, showing the modes of 1,3-phthalate binding. Hydrogen atoms are omitted for clarity.

The structures of the $[GdCu_5(Glyha)_5]^{3+}$ metallacrown units in compounds 1−5 are similar, so the structure of this building block will be described in detail only for compound 1, and for the other complexes, only significant differences will be noted. Each $[GdCu_5(Glyha)_5]^{3+}$ cation is constructed from five anions of doubly deprotonated glycinehydroxamic acid, five Cu^{II} ions and one Gd^{III} ion. Each $Glyha^{2-}$ anion links two neighboring Cu^{II} ions, and each Cu^{II} ion is in turn bound to two $Glyha^{2-}$ anions, forming a cyclic structure $[Cu_5(Glyha)_5]$, the center of which is occupied by the Gd^{III} ion (Figures 2 and 3). In each case, the Gd^{III} coordination involves five hydroxamate oxygen atoms in an equatorially oriented pentagonal plane with a single axial donor on one side of this plane. On the other side of the plane, two donor atoms are located, splayed symmetrically (equivalently) off the vertical axis. Each Cu^{II} ion has an N_2O_2 coordination environment in the equatorial plane, with nitrogen donors from hydroxamate and amino groups, and oxygen donors from carbonyl and hydroxamate groups (Table 2). In addition, the axial positions of the Cu5 and Cu6 ions (from two different independent $GdCu_5$ units) are occupied by oxygen atoms of 1,3-phthalates (Cu5−O30 = 2.636(5) Å, Cu6−O37 = 2.420(4) Å), whereas axial positions of Cu1, Cu4, Cu8 and Cu9 ions are occupied by water molecules O24w, O23w, O33w, O34w. (The “w” symbol is used in descriptions of structures, tables and figures to indicate water oxygen but is not used in the .cif files (Supporting Information)). The coordination polyhedra of these six Cu^{II} ions can thus be considered to be square pyramidal (τ values[18] are in Table 2), whereas all remaining Cu^{II} ions possess distorted square-planar geometries (Figures 2 and 3). The largest twist distortion of the donor set from square-planar is observed for Cu8 (i.e., the angle between the O13−Cu8−N15 and O14−Cu8−N16 planes is 14.6°), whereas the smallest angle is found for Cu2 (the O1−Cu2−N3 and O2−Cu2−N4 planes are twisted by only 1.7°). In general, τ values for the pentacoordinate copper(II) ions are small in all of 1−5 (from 0.06 to 0.23), thus indicating square-pyramidal coordination.

Both types of Gd^{III} ions in 1 are eight-coordinate, their coordination spheres containing five hydroxamate oxygens in the equatorial planes (Table 2). Additionally Gd1 is bound to three 1,3-phthalate carboxyl-oxygens (Gd1−O21 = 2.346(4) Å, Gd1−O25 = 2.399(4) Å, Gd1−O29 = 2.396(4) Å), whereas Gd2 involves two phthalate oxygens (Gd2−O28 = 2.347(4) Å, Gd2−O36 = 2.387(4) Å) and one water molecule O35w. All bond lengths and angles in $[GdCu_5(Glyha)_5]^{3+}$ are typical for metallacrowns;[8,12,19] selected bond parameters are given in Tables 2 and S1 (Supporting Information).

Two of the three 1,3-phthalates link two $[GdCu_5(Glyha)_5]^{3+}$ cations through coordination to Gd^{III}, one of the two acting as a “doubly monodentate” ligand (Figure 1), similarly to previously described cases.[3] The second 1,3-phthalate, also coordinated to two Gd^{III} ions from neighboring metallacrown units, is in addition coordinated to Cu^{II} ion via one of its carboxyl O atoms

Table 2. Selected Characteristics of Crystal Structures of 1−5

complex	1		2	3	4	5
	1st type of $GdCu_5$	2nd type of $GdCu_5$				
range of Gd−Cu separation, Å	3.833(1)−3.934(1)		3.8613(7)−3.9640(8)	3.878(1)−3.905(1)	3.7510(5)−3.9475(6)	3.860(2)−3.926(2)
range of Cu−Cu separation, Å	4.505(1)−4.581(1)		4.539(1)−4.595(1)	4.538(1)−4.587(1)	4.5339(6)−4.6051(5)	4.546(2)−4.594(2)
average $Gd-O_{equat}$, Å	2.430		2.451	2.435	2.499	2.427
average $Cu-O_{equat}$, Å	1.930		1.933	1.937	1.935	1.928
average $Cu-N_{equat}$, Å	1.950		1.952	1.954	1.952	1.949
range of τ values for pentacoordinate Cu(II) ions	0.01−0.19	0.02−0.18	0.03−0.12	0.04−0.09	0.002−0.06	
average deviation among non-hydrogen atoms from $GdCu_5$ plane[a], Å	0.26	0.36	0.18	0.20	0.21	0.23
largest deviation among non-hydrogen atoms from $GdCu_5$ plane[a], Å	0.63	1.18	0.55	0.61	0.66	0.69
deviation of Gd^{III} ion from Cu_5 plane[a], Å	0.46	0.33	0.43	0.32	0.36	0.18
BVS[b]	3.07	3.14	3.11	3.12	2.93	3.08

[a] Mean-square planes passing through indicated metal ions. [b] Bond valence sum for Gd^{III} ions in complexes 1−5.

and acts as an "overall" tridentate ligand (Figure 1). The third 1,3-phthalate is coordinated via one of its carboxylate groups to Gd^{III} and Cu^{II} ions of a $[GdCu_5(Glyha)_5]^{3+}$ cation. The second carboxylate group remains, however, noncoordinated (Figure 1) and instead is involved in hydrogen bonding interactions with water molecules.

Apart from the above-mentioned twist angles, minor distortions of the metallacrown units can be characterized by the average and largest deviations of non-hydrogen atoms from the $GdCu_5$ mean planes (Table 2). It can be concluded that the metallacrown cations in 1 are typically slightly distorted. The average and largest deviations are smaller in the $[GdCu_5(Glyha)_5]^{3+}$ fragment containing Gd1 than in the metallacrown cation containing Gd2 (Table 2). Compared to previously reported analogs, the deviation of the Gd1 ion from the mean plane of Cu1Cu2Cu3Cu4Cu5 (0.46 Å) is somewhat larger than in $\{Gd(NO_3)(H_2O)_2[15\text{-}MC_{Cu^{II}N(GlyHa)}\text{-}5](NO_3)(H_2O)_4\}NO_3\cdot 5H_2O$[12] and $\{[GdCu_5(Glyha)_5(SO_4)(H_2O)_{6.5}]\}_2(SO_4)\cdot 6H_2O$[19] (0.41 and 0.43 Å, respectively), whereas the corresponding value for Gd2 (0.33 Å) is less than in these two reference compounds. Metallacrown units in complexes 2–5 are also slightly distorted, as indicated by deviations of non-hydrogen atoms from the Cu_5Gd mean planes and deviations of Gd^{III} ions from the Cu_5 mean planes (Table 2). Compound 1 displays the largest deviations both of non-hydrogen atoms from the Cu_5Gd mean plane and of Gd^{III} from the Cu_5 mean plane (1.18 and 0.63 Å, respectively), making the Cu_5Gd metallacrown units in 1 the most distorted found here.

The space between the 1D chains in 1 is filled by water molecules, some of which are disordered and are involved in an extended system of hydrogen bonds. The total volume of solvent-accessible voids in 1 is 15.5%, corresponding to a void volume about 0.08 cm^3/g (calculated using PLATON[20] for a probe molecule with r = 1.4 Å; only noncoordinated water molecules were considered) assuming that the structure does not collapse upon desolvation.

Compound 2. This complex contains crystallographically equivalent $[GdCu_5(Glyha)_5]^{3+}$ units (Figure S2, Supporting Information), plus coordinated and noncoordinated 1,4-phthalate dianions and water molecules. The $[GdCu_5(Glyha)_5]^{3+}$ units are linked into 1D chains by bridging 1,4-phthalate dianions, which are coordinated through oxygen atoms O15 and O18 to the Gd^{III} ion in trans positions (Gd1–O15 = 2.332(4) Å and Gd1–O18 = 2.349(4) Å, Figure 4). In addition, there are noncoordinated 1,4-phthalate dianions (one for every two $[GdCu_5(Glyha)_5]^{3+}$ cations), which compensate the positive charge of the 1D chains (Figure S3, Supporting Information).

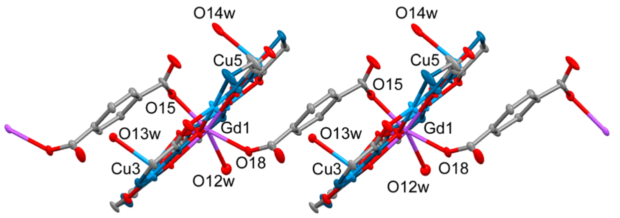


Figure 4. Fragment of the crystal structure of complex 2. Noncoordinated 1,4-phthalate, noncoordinated water molecules and hydrogen atoms are omitted for clarity.

The Gd^{III} ion in 2 is eight-coordinate, with five equatorial positions occupied by oxygen atoms of hydroxamates and two axial positions occupied by oxygen atoms of bridging 1,4-phthalate, whereas the eighth position is occupied by a coordinated water molecule O12w. The axial positions of the square pyramidal Cu1, Cu3 and Cu5 ions are occupied by oxygen atoms O11w, O13w and O14w of water molecules. The metallacrown unit in 2 is almost planar (Table 2). Selected bond lengths and angles are presented in Tables 2 S2 (Supporting Information).

Complex 3. This complex is built from $[GdCu_5(Glyha)_5]^{3+}$ units (Figure S3, Supporting Information), coordinated 1,4-phthalate dianions and water molecules (Figure 5). All the $[GdCu_5(Glyha)_5]^{3+}$ cations in 3 are crystallographically equivalent, but in a contrast to 2, all the 1,4-phthalates in 3 are coordinated. The apical position of Cu4 is occupied by oxygen atom O19 of a 1,4-phthalate dianion (Cu4–O19 = 2.584(5) Å), whereas the axial positions of Cu1, Cu3 and Cu5 are, respectively, occupied by oxygen atoms O20w, O11w and O13w of coordinated water molecules (τ values[18] for these essentially square-pyramidal Cu^{II} ions are in Table 2). The coordination number of the Gd^{III} ion is again eight; its equatorial coordination environment consists of five hydroxamate oxygen atoms (Table 2), whereas the three apical positions of the Gd^{III} are occupied by two oxygen atoms of different 1,4-phthalate dianions (Gd1–O14 = 2.315(5) Å and Gd1–O17 = 2.362(5) Å) and the oxygen atom of a coordinated water molecule O12w. There are three 1,4-phthalate dianions coordinated to each $[GdCu_5(Glyha)_5]^{3+}$ unit, and each 1,4-phthalate links in turn to two metallacrown cations. However, the coordination modes of these three phthalates are different (Figure 5). Two crystallographically equivalent 1,4-phthalates link the neighboring $[GdCu_5(Glyha)_5]^{3+}$ units, resulting in formation of infinite 1D chains. The third 1,4-phthalate links two Cu^{II} ions from two $[GdCu_5(Glyha)_5]^{3+}$ units, which belong to different 1D chains, via apical bonds Cu4–O19 (2.584(5) Å), thus leading to formation of a 2D polymer (Figure 6). The metallacrown block in 3 is again almost planar (Table 2). Selected bond lengths and angles are given in Table S3 (Supporting Information).

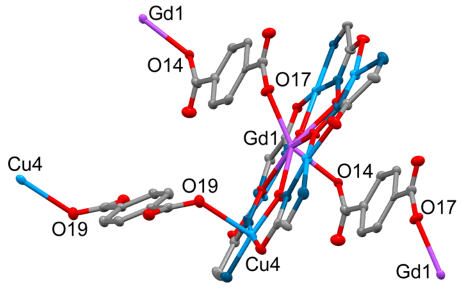


Figure 5. A fragment of the crystal structure of complex 3. Water molecules (both coordinated and noncoordinated) and hydrogen atoms are omitted for clarity.

Complex 4. This complex is built from discrete neutral molecules $[GdCu_5(Glyha)_5(Citr)(H_2O)_4]$ and noncoordinated solvent water molecules (Figure 7).

The structure of the metallacrown block $[GdCu_5(Glyha)_5]^{3+}$ in 4 is generally similar to the one in complexes 1–3 (Figures S5 and S6, Supporting Information). In $[GdCu_5(Glyha)_5(Citr)(H_2O)_4]$, the citrate anion is coordinated to $[GdCu_5(Glyha)_5]^{3+}$ via oxygen atoms O12, O14 and O16 of

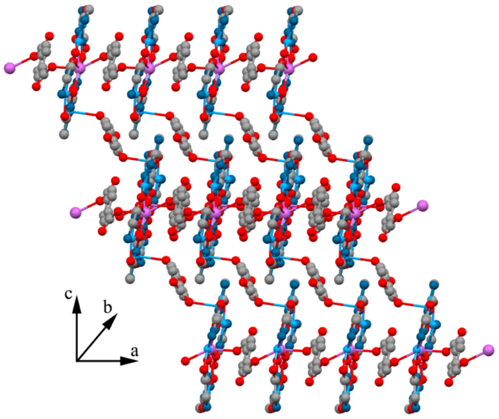


Figure 6. A fragment of the crystal structure of complex 3.

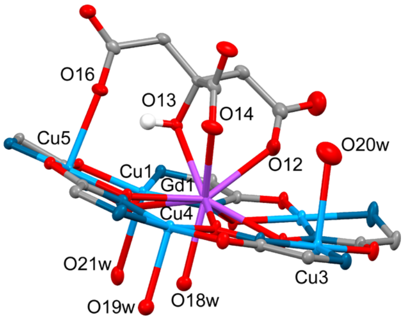


Figure 7. The structure of the neutral molecule $[GdCu_5(Glyha)_5(Citr)(H_2O)_4]$ in complex 4. Noncoordinated water molecules and hydrogen atoms except hydrogen on the alcoholic O13 are omitted for clarity.

three carboxyl groups and via O13 from a nondeprontated hydroxyl group. This last atom is coordinated to the Gd1 ion (Gd1−O13 = 2.4636(19) Å). Two of the carboxyl groups are coordinated via oxygen atoms O12 and O14 to the apical positions of Gd1 (Gd1−O12 = 2.511(2) Å and Gd1−O14 = 2.463(2) Å), whereas oxygen atom O16 of the third carboxyl group occupies an apical position at ion Cu5 (Cu5−O16 = 2.456(3) Å). The coordination sphere of Gd1 is completed by water oxygen O18w, trans to O12−O14, thus Gd1 is nine-coordinate. The average Gd−O apical distances in 4 are longer than the corresponding average values in 1−3 by 0.041−0.102 Å, which is consistent with the greater effective ionic radius of a nonacoordinate Gd^{III} ion vs an octacoordinate one (the difference is 0.054 Å[21]).

The apical positions of Cu1, Cu3 and Cu4 are occupied by ligating water oxygens O21w, O20w and O19w, which complete square pyramidal coordination for these Cu^{II} ions. Similar to 1−3, the metallacrown block in 4 is also essentially planar (Table 2). Selected bond lengths and angles for complex 4 are given in Table S4 (Supporting Information).

Complexes 5 and 6. Complex 5 (Figure 8) entails a metallacrown unit, a carbonate dianion and a mononuclear copper complex, formation of which can be rationalized as shown in Scheme 3.

Compound 5 can be formally considered as being built from two moieties: a hexanuclear metallacrown cation $[GdCu_5(Glyha)_5(H_2O)_5]^{3+}$ and an anion $[Cu(Fgg)]^-$, which are linked by a μ_2-CO_3^{2-} anion (probably captured from the air, vide supra).

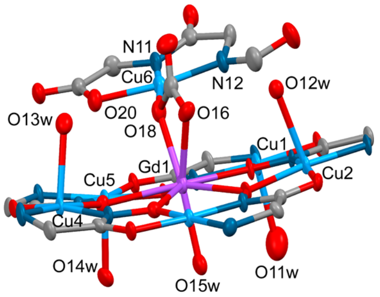


Figure 8. Molecular structure of $\{[GdCu_5(Glyha)_5(H_2O)_5](\mu_2\text{-}CO_3)[Cu(Fgg)]\}$ in compound 5. Hydrogen atoms and solvent molecules are omitted for clarity.

In the metallacrown unit $[GdCu_5(Glyha)_5(H_2O)_5]^{3+}$, the apical positions of atoms Cu1, Cu2, Cu4, Cu5 (Figure S7, Supporting Information) are occupied by oxygen atoms of coordinated water molecules O11w, O12w, O13w and O14w, respectively, which complete their square pyramidal coordination spheres (Table 2). The Gd^{III} ion is octacoordinate, with two oxygen atoms of carbonate (d(Gd−O16) = 2.391(9) Å and d(Gd1−O18) = 2.425(8) Å) and oxygen atom O15w of a water molecule trans to CO_3^{2-}. The axial Gd−O (carbonate) bonds (2.408 Å on average) are longer than the Gd−O (phthalate) bonds in compounds 1−3 (2.363 Å on average), and shorter than both the Gd−O (citrate carboxylate) bonds in compound 4 (2.4635 Å on average) and the Gd−O (sulfate) bonds (2.451 Å on average) and nitrate (2.703 Å on average) in $\{[GdCu_5(Glyha)_5(SO_4)(H_2O)_{6.5}]\}_2(SO_4)\cdot 6H_2O$[19] and $\{Gd(NO_3)(H_2O)_2[15\text{-}MC_{Cu^{II}N(GlyHa)}\text{-}5](NO_3)(H_2O)_4\}NO_3\cdot 5H_2O$.[12]

In the anion $[Cu(Fgg)]^-$ (Figure S8, Supporting Information) the nearly square-planar coordination environment of copper ion Cu6 is formed by two nitrogen atoms, N11 and N12 (d(Cu6−N11) = 1.894(9) Å and d(Cu6−N12) = 1.973(8) Å), and two oxygen atoms, one from carbonyl O20 (d(Cu6−O20) = 1.987(7) Å) and one from O18 of the carbonate dianion (d(Cu6−O18) = 1.935(8) Å). Copper ion Cu6 lies almost in the plane of donor atoms N11N12O18O20, the deviation from this plane being only 0.012 Å. The carbonate dianion acts as a bridge between the mononuclear $[Cu(Fgg)]^-$ block and the hexanuclear metallacrown unit, with atom O18 linking the Cu^{II} and Gd^{III} ions (the angle Cu6−O18−Gd1 is 133.7(4)°). Selected bond lengths and angles for complexes 5 and 6 are presented in Tables S5 and S6 (Supporting Information).

Complex 6 is a 1D-chain polymer, containing Cu^{II} and glycinate, the latter being formed as a consequence of hydrolysis of glycinehydroxamate (more details in Figures S9 and S10 of the Supporting Information). Formation of this compound is additional evidence for hydrolysis of glycine hydroxamate in the reaction mixture, containing $[GdCu_5(Glyha)_5(NO_3)_2(H_2O)_6](NO_3)$ and 4,4′-diphenyldicarboxylate, because complexes 5 and 6 were obtained from the same reaction mixture.

Magnetic Properties of Compound 1. Only two compounds in this study (1 and 4) crystallized from the reaction mixture as sole products (in contrast to compounds 2 and 3, which formed as a mixture). One of the pure compounds, coordination polymer 1, was selected for a detailed analysis of the magnetic properties of this kind of material.

Magnetic susceptibility measurements in the temperature range 2–300 K were performed for a polycrystalline sample of 1. The ambient-temperature value of $\chi_M T$ for complex 1 is 10.00 cm^3 mol^{-1} K, which is close to the expected spin-only value (9.75 cm^3 mol^{-1} K for five Cu^{II} ($S = 1/2$) and one Gd^{III} ($S = 7/2$) ions with $g_{Cu} = g_{Gd} = 2.00$). With decreasing temperature, $\chi_M T$ falls to 8.65 cm^3 mol^{-1} K at 39.5 K, whereas further temperature reduction leads to a growth in $\chi_M T$, with it reaching a maximum of 9.02 cm^3 mol^{-1} K at 3.7 K. Below 3.7 K, $\chi_M T$ falls again to 8.91 cm^3 mol^{-1} K at 2.0 K (Figure 9).

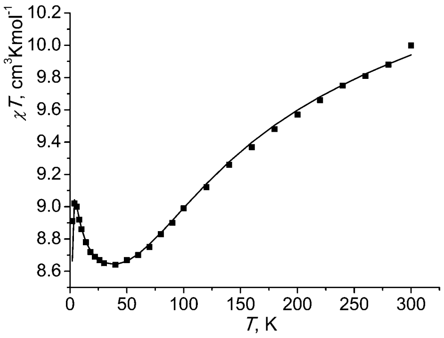


Figure 9. $\chi_M T$ vs T plot for complex 1: (■) experimental data, (solid line) the best fit with parameters obtained from the theoretical model (see text, eq 1).

Prior work[11,25,33] has also demonstrated that magnetic coupling in assemblies based on metallacrowns and polycarboxylates is dominated by the metallacrowns. Thus, for magnetic data fitting we used a model based on Hamiltonian (1), which includes exchange parameters only for within the metallacrown fragments.

$$\begin{aligned}\hat{\boldsymbol{H}}(\mathrm{GdCu}_5) = {} & -2J_1(S_1 \times S_{Gd} + S_2 \times S_{Gd} + S_3 \times S_{Gd} \\ & + S_4 \times S_{Gd} + S_5 \times S_{Gd}) \\ & - 2J_2(S_1 \times S_2 + S_2 \times S_3 + S_3 \times S_4 \\ & + S_4 \times S_1 + S_5 \times S_1) \end{aligned} \tag{1}$$

where J_1 is the exchange integral between the Cu^{II} ions and Gd^{III}, J_2 is the exchange integral between each pair of adjacent Cu^{II} ions, S_{Gd} is the spin operator for the Gd^{III} ion, and S_i are the spin operators for the Cu^{II} ions. Potential intermolecular interactions were taken into account through a molecular field model (eq 2)[14]

$$\chi_{MF} T = \frac{\chi_M T}{1 - \frac{zJ'\chi_M}{N_A g^2 \beta^2}} \tag{2}$$

The experimental data were simulated by a full-matrix diagonalization using the Mjöllnir software.[6c,22] The best correspondence between experimental and calculated curves was achieved with $J_1 = +0.60(2)$ cm^{-1}, $J_2 = -61.0(5)$ cm^{-1}, $zJ' = -0.035(4)$ cm^{-1}, TIP = 0.0011 cm^3 mol^{-1} (TIP is the temperature-independent paramagnetism, introduced in the usual way),[14] $g_{Gd} = 2.033(1)$ and $g_{Cu} = 2.10(2)$, $R^2 = 3.01 \times 10^{-5}$.[23] The value of J_1 for 1 is consistent with previously reported exchange coupling parameters for copper(II)–gadolinium(III) complexes.[24] In the case of both pentacopper(II) 12-MC-4 and copper(II)-lanthanide(III) 15-MC-5 complexes, the bridging group between two adjacent Cu^{II} ions is N–O, but Cu–Cu coupling in 1 is weaker than similar Cu–Cu interactions in pentacopper 12-MC-4 complexes, where J_{CuCu} was found to lie between −71 and −85 cm^{-1}.[25] The values obtained are consistent with previously made assumptions about the type and order of magnitude of exchange among paramagnetic centers in LnCu5 fragments.[8] A previously suggested[26] J vs d(Gd–Cu) correlation appears not to be applicable here.

A broad, slightly anisotropic X-band EPR was observed for a polycrystalline sample of complex 1 ($g \approx 2.2$) at 300 K. Decreasing the temperature to 100 K led to an increase in the anisotropy (Figure S11, Supporting Information). The EPR-derived g-value is adequately consistent with g_{Cu} obtained from the magnetic data.

The small value of the molecular field parameter ($zJ' = -0.035(4)$ cm^{-1}) for 1, which can correspond to intermolecular exchange coupling, evidence weak exchange interactions between the hexanuclear metallacrown units. Thus, the linking of LnCu$_5$ metallacrowns by phthalates, though allowing us to obtain a coordination polymer, have magnetic properties which are governed by exchange interactions within the hexanuclear units, similarly to other cases of coordination polymers assembled from polynuclear building blocks.[6c,27−29]

Notably, simulation of the $\chi_M T$ vs T data for compound 1, based on the additive model, which treats Gd^{III} and Cu^{II} interactions encompassed by the molecular field term (eq 2; Figure S12 (Supporting Information); a detailed description of this model is given in the Supporting Information), gave parameter values $J_{Cu\text{--}Cu} = -68(4)$ cm^{-1}, $zJ' = +0.030(2)$ cm^{-1}, TIP = 0.0013(1) cm^3·mol^{-1} and $g_{Gd} = 2.036(3)$ for fixed $g_{Cu} = 2.10$, $R^2 = 2.13 \times 10^{-5}$.

$$\chi_{total} = \chi_{Gd} + \chi_{Cu_5} \tag{3}$$

However, the additive model (eq 3) did not reproduce the experimental data in the range 2–7 K. Nonetheless, simulating the $\chi_M T$ vs T data for complex 1 by either of the two models gives values of J_{CuCu} and the g-factors, which are close to one another, emphasizing that the system is dominated by the antiferromagnetic interactions among the Cu^{II} ions in the crown. It also indicates that such an additive model can be used for estimation of J_{CuCu} parameters for LnCu$_5$ systems other than GdCu$_5$, where the contribution of spin–orbit coupling to the Ln^{III} magnetism makes direct calculation of J_{LnCu} extremely challenging, if not currently unfeasible.

Thermal analysis and sorption properties of compound 1. Thermogravimetric analysis (Figure 10) was performed to

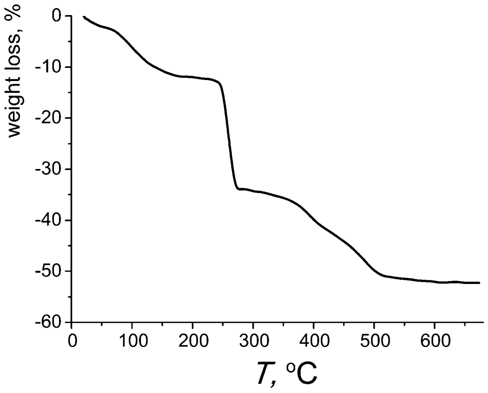


Figure 10. TG curve for compound 1.

determine the temperature at which decomposition of 1 occurs, which is important for selection of this compound's activation (desolvatation) temperature prior to sorption measurements. Weight loss is already apparent at room temperature and rises to 3% at 70 °C, corresponding to the elimination of 4.5 water molecules per $(Cu_5Gd)_2$ unit. Further heating leads to more pronounced weight loss, which plateaus from 180 to 230 °C (total weight loss 12%, corresponding to 18.5 H_2O). Heating above 230 °C leads to abrupt decomposition (34% loss by 270 °C).

The activation of the polycrystalline sample 1 was therefore performed at 130 °C (10^{-2} Torr). This temperature corresponds to an 11% weight loss (at 760 Torr) and probably not all the coordinated water molecules are removed.

The intense reflection at $2\theta = 7.4°$ in the calculated powder pattern, assigned to the (1,0,−1) plane in 1 may correspond to the intense one at $2\theta = 9°$ in the experimental pattern (Figure 11). The (1,0,−1) planes run through water-filled channels between 1D-chains of 1 (Figure S12, Supporting Information), and the diminution of this reflection seems entirely consistent with elimination of these water molecules during drying, leading to a decrease in the separation between neighboring (1,0,−1) planes from 11.98 to 9.82 Å. Drying of the compound 1 in vacuo (10^{-2} Torr) at 130 °C yields further intensity decreases in the powder pattern. The most intense reflections at $2\theta = 10.4$ and 26.6° are still present, although they are shifted to higher and lower angles, respectively, compared to the pattern of the air-dried sample ($2\theta = 9.1$ and 28.0°). The results are limited by compromise between preferred orientation of crystallites vs the desolvation and collapse that would be brought on by further desiccation.

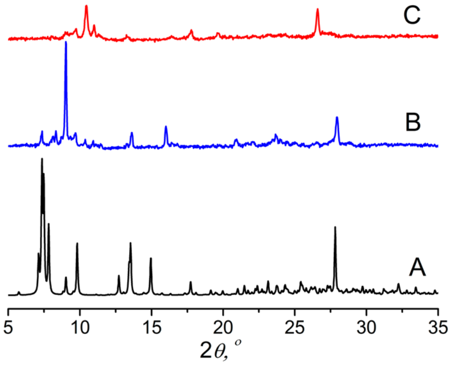


Figure 11. Powder X-ray diffraction patterns for 1: (A) calculated from the single-crystal X-ray structure, (B) sample taken from the mother liquor and dried in air at ambient temperature, (C) the same sample after drying at 130 °C in vacuo (10^{-2} Torr).

An activated sample of 1 absorbed a comparatively large quantity of methanol from the vapor phase at 293 K (Figure 12). The absorption isotherm is close to type I of the BDDT classification[30] and can be a result from filling of micropores. In contrast, the ethanol sorption capacity was negligibly small; the kinetic diameters of methanol and ethanol molecules are 3.6 and 4.5 Å, respectively.[31] The methanol sorption capacity was about 0.1 cm^3/g at $P/P_S \approx 0.9$ (where P is the current methanol pressure and P_S the saturation vapor pressure of this substrate at 293 K), which is in good agreement with the void volume estimated from the structural results (vide supra). There is virtually no absorption−desorption hysteresis in the methanol absorption/desorption isotherm, which is also typical for a type-I isotherm.

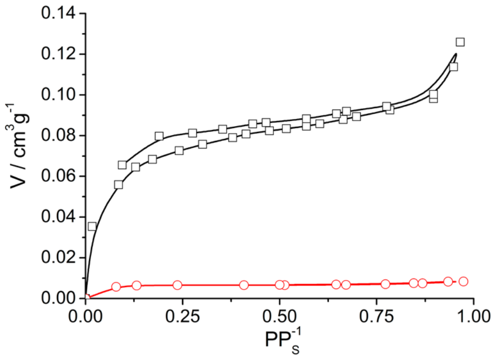


Figure 12. Isotherms for methanol (□) and ethanol (○) sorption−desorption by activated complex 1 at 293 K.

These results are very different from absorption of alcohols (methanol or ethanol), previously observed for other systems based on pentanuclear copper(II) metallacrowns.[25,32] In those cases, the absorption isotherms were characterized by wide absorption−desorption hystereses, which gave grounds to suspect significant structural rearrangements caused by interaction with the absorbate (such as the "gate-opening" phenomenon[13,33−36]). In contrast, in the case of 1, there is no reason to suppose any structural rearrangement on methanol absorption or any other behavior not typical for microporous sorbents.

The methanol sorption capacity of 1 at $P/P_S \approx 0.9$ corresponds to almost six CH_3OH per $\{Cu_5Gd\}_2$ unit (Figure S14, Supporting Information). Coordination of methanol to the metal ions cannot be excluded, but the absence of absorption−desorption hysteresis is an argument against such coordination.

■ CONCLUSIONS

We have shown that linking of hexanuclear metallacrown $[GdCu_5(Glyha)_5]^{3+}$ cations by isomeric 1,3- and 1,4-phthalates resulted in formation of coordination polymers containing the initial GdCu5 building block. The use of citrate instead of phthalates led to formation of a discrete adduct. Successful isolation of these compounds depends at least in some degree on their lower solubility in the reaction mixture, compared to the reagents, to drive the metathesis reactions to completion. In contrast, reaction of the same cation $[GdCu_5(Glyha)_5]^{3+}$ with 4,4-biphenyldicarboxylate produced a heptanuclear complex, which contained a derivative of the dipeptide GlyGly. This dipeptide formed as the result of a cascade of reactions that is likely to involve hydrolysis of glycinehydroxamate, possible due to long reaction time in solution. It can be concluded, that quite quick precipitation of the products in the case of hydroxamate-based metallacrowns is important to avoid undesired destruction of the initial building blocks. Analysis of the magnetic properties of the coordination polymer $\{[(GdCu_5(Glyha)_5(H_2O)_2)(GdCu_5(Glyha)_5(H_2O)_3)(1,3\text{-}bdc)_3]\cdot 16H_2O\}_n$ revealed that there were weak ferromagnetic interactions between Cu^{II} and Gd^{III} ions, whereas the Cu^{II} ions in the pentacopper metallacrown "ring" were antiferromagnetically coupled. The magnetic properties of this coordination polymer are thus dominated by exchange interactions within the hexanuclear building blocks. Desolvated compound 1 absorbs methanol, but not ethanol, the methanol sorption isotherm being typical for microporous sorbents, in contrast to previously reported systems based on pentanuclear copper(II) metallacrowns.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Selected bond lengths (Å) and angles (deg) for complexes 1−6 (Tables S1- S6), ESI mass spectra of reaction solution of complex 1 (Figure S1), additional figures of crystal structures of 1−6 (Figures S2−S10, S13), IR and EPR spectra for complex 1 (Figures S11 and S15), description of additive model used for interpretation of magnetic properties of 1 (Figure S14) and sorption isotherms in coordinates mole of alcohol per $GdCu_5$ unit vs P/P_S (Figure S14). This material is available free of charge via the Internet at http://pubs.acs.org. CCDC 950109, 950110, 950111, 950112, 950113, and 950114. contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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Notes

The authors declare no competing financial interest.

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