Structure of two novel binuclear complexes of Eu^{III} containing bridging DL- and L-α-alaninehydroxamic acids

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Two novel binuclear complexes of Eu^{III} with bridging DL- and L-α-alaninehydroxamic acids of the formulae $[Eu(DL\text{-}\alpha\text{-}Alaha)(H_2O)_6]_2(ClO_4)_6$ and $[Eu(L\text{-}\alpha\text{-}AlahaH)(H_2O)_6]_2(ClO_4)_8$ (further denoted as **1** and **2**) were synthesized from an aqueous solution at pH ≈ 4.5. Their crystal structures were determined by X-ray diffraction with the final $R = 0.036$ and 0.043 for compounds **1** and **2**, respectively. The structures were solved by direct methods and refined by full-matrix least-squares using SHELXTL-PC programs, on $4332F_0$ values for complex **1** and 5728 for complex **2**, with anisotropic temperature factors for the non-hydrogen atoms. Positions of hydrogen atoms were taken from the ΔF synthesis and refined with isotropic temperature factors. The title compounds crystallize in the $P2_1/n$ (**1**) and $C2$ (**2**) space groups, with the unit cell parameters as follows: **1** $a = 10.347(1)$, $b = 11.289(2)$, $c = 16.968(3)$ Å, $\beta = 95.37(1)°$; **2** $a = 19.912(3)$, $b = 8.620(2)$, $c = 15.881(3)$ Å, $\beta = 107.37(3)°$. The two structures consist of dimer units formed by two NO bridging groups of the aminohydroxamic acid molecules. In addition, the two metal ions are chelated by the CO and NO groups, forming five-membered rings. The bridging oxygen atoms in the complexes are not the carbonyl oxygens but rather the hydroxamic ones. Centrosymmetric dimers are formed in compound **1**, whereas in the case of the compound with the L-handed ligand the dimer possesses twofold axes. Additionally, two molecules of $HClO_4$ are present in the structure of **2**. Hydrogen bonds are created between N and O sites of the ligands (Alaha, H_2O molecules). A structural effect of the ligand chirality was found and the Eu—Eua distances were determined: these are equal to 4.114 and 4.079 Å for compounds **1** and **2**, respectively. These results are, to our knowledge, the first ones obtained for lanthanide complexes with aminohydroxamic acids from X-ray data.

In the past, great interest was expressed concerning metal ion interactions with hydroxamic acids and their amino derivatives. The main reason for this is their role in biological systems.[1–5] Hydroxamic and aminohydroxamic acids are ubiquitous and are intimately associated with ion-transport phenomena. It is also known that the hydroxamic acid moiety is a constituent of growth factors, tumor inhibitors and specific inhibitors of urease activity, the aminopeptidases.[1–8] The mechanism of inhibition appears to involve chelation of metals at their active sites. Coordination of aminohydroxamic acid can involve an amino group and hydroxamic acid groups and creates two types of five-membered chelate rings (two N atoms or two O atoms). Besides, both the two O and two N atoms can take part in a chelation leading to the formation of complex polynuclear systems.[9] Furthermore, its acid–base properties are complicated and lead to the formation of different species with metal ions in solution, depending on the pH.

Up to now the majority of reports have dealt with the complexes of transition metal ions (Cu, Ni, Fe) because of their importance,[10–14] a few only deal with lanthanide–hydroxamic acid compounds.[15–19] However, no data are available, neither in solution nor for the solid, on the interactions of lanthanides with amino derivatives of hydroxamic acids. In fact, only two papers contain the X-ray analysis of transition metal compounds with α-alaninehydroxamic acids[20] and with its β-amino derivatives.[21] This paper is the first one to present such data for lanthanides.

Since lanthanide ions are widely applied as spectroscopic probes in investigations of metal ion sites in biological systems, we have undertaken tests on the structural and spectral factors of lanthanide compounds with aminohydroxamic acids: bis(μ-DL-α-alaninehydroxamic acid-1:2κ^2*O*,1κ*O*′)bis(hexaeuropium)(6+) perchlorate, $[Eu(DL\text{-}\alpha\text{-}Alaha)(H_2O)_6]\cdot(ClO_4)_6$ (**1**), and bis(μ-L-α-alaninehydroxamoyloxonium-1:2κ^2*O*,1κ*O*′)bis(hexaeuropium)(8+) perchlorate, $[Eu(L\text{-}\alpha\text{-}AlahaH)(H_2O)_6]\cdot(ClO_4)_8$ (**2**).

Experimental

Yellow single crystals of the europium compound with DL- and L-α-alaninehydroxamic acid, hereafter denoted as **1** and **2**, were obtained from aqueous solutions of europium perchlorate ($c \approx 10^{-2}$ M) and Alaha (molar ratio Eu : Alaha was 1 : 1.5). The pH was kept constant (≈4.5).

The crystal density was determined by the flotation method in a mixture of bromoform and ethylene bromide. Concentrations of metal ions in the compounds and their compositions were determined using the ICP-AES (inductively coupled plasma-atomic emission spectroscopy) method and elemental analysis.

X-ray data were collected with MoKα radiation at 293 K on a Siemens P3 diffractometer for compound **1** and on a Kuma-Diffraction KM-4 diffractometer for compound **2**. The intensities were corrected for the Lorentz and polarization effects and the data reduction was performed with the learnt-profile method, using the DATPROC9 program.[22] The empirical absorption was applied based on Ψ scans for selected reflections. The structures were solved by direct methods and refined by full-matrix least-squares using SHELXTL-PC programs[23] and CSU program[31] on $4332F_0$ values for complex **1** and 5728 for complex **2**, with anisotropic temperature factors for non-hydrogen atoms. Positions of hydrogen atoms were taken from ΔF syntheses and refined with isotropic temperature factors for **1** but not refined for **2**. The crystal data and a summary of the data collection and the structure refinement are summarized in Table 1.

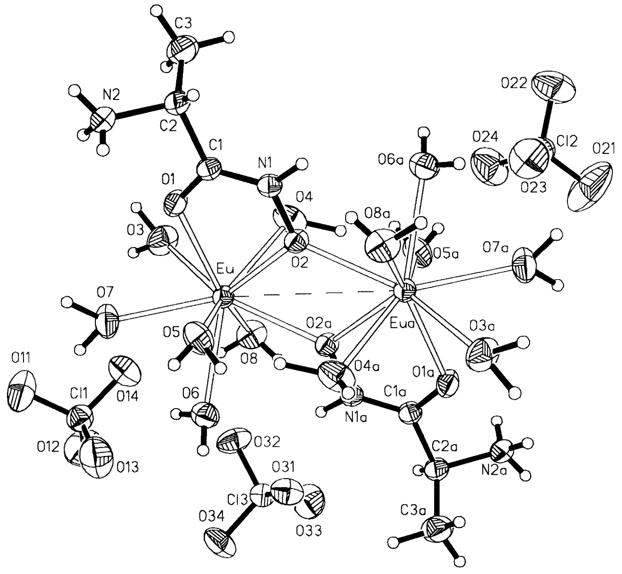

Fig. 1 Crystal structure of $[Eu(DL\text{-}\alpha\text{-}Alaha)(H_2O)_6]_2(ClO_4)_6$

Discussion

The final fractional coordinates and equivalent isotropic thermal parameters for the non-hydrogen atoms in **1** and **2** are listed in Tables 2 and 3; selected geometrical parameters are collected in Table 4. Views of the molecules of the title compounds, with the atom-labelling schemes, are shown in Fig. 1 and 2.

The NH_2 and hydroxamic groups of the α-alanine-hydroxamic acid molecule are in the α position with respect to each other, thus possessing the ability to form two types of five-membered chelating rings. In the case of our systems, two oxygen atoms from CO and NOH in the aminohydroxamic acid molecule create a chelate ring with two europium ions. Moreover, the NO groups play an additional bridging role, forming binuclear systems. The bridging oxygen in these complexes is not that of the carbonyl groups.

A centrosymmetric system exists in the complexes with the DL ligand, whereas in the compound with the L-handed ligand the dimer possesses twofold axes. In our earlier papers[24,25] we considered possibilities for the creation of non-centrosymmetric dimeric units with two non-equivalent lanthanide positions for compound **2**. This seems to be confirmed by the spectroscopic results. Consequently, the crystal structure was solved assuming the *P*1 space group. However, careful analysis of the X-ray data allows us to perform the structure refinement in the *C*2 space group as well, with an even better final *R* factor (0.043 instead of 0.084 for the *P*1 space group).

In the structure of the L-handed system, additionally two molecules of $HClO_4$ are present. A network of hydrogen bonds with the N and O sites of the ligands (Alaha, H_2O molecules) stabilize the structures. Table 5 compiles the

Table 1 Crystal data and summary of intensity data collection and structure refinement for compounds **1** and **2**

	1	**2**
Molecular formula	$C_6H_{40}N_4O_{40}Cl_6Eu_2$	$C_6H_{42}N_4O_{48}Cl_8Eu_2$
Formula weight	1325.03	1525.94
Space group	$P2_1/n$	$C2$
Temperature/°C	20	20
Unit cell parameters, from 25 reflections with 2θ in the range/°	14–28	12–30
a/Å	10.347(1)	19.912(3)
b/Å	11.289(2)	8.620(2)
c/Å	16.968(3)	15.881(3)
β/°	95.37(1)	107.37(3)
U/Å^3	1973.29	2661.53
Z	2	2
D_c/g cm^{-3}	2.225	1.903
D_m/g cm^{-3}	2.216	1.900
μ_{calc}(MoKα)/cm^{-1}	3.68	2.92
F(000)	1304	1504
Diffractometer/scan mode	P3/ω − 2θ	KM-4/ω − 2θ
Radiation (graphite monochromated)	MoKα (λ = 0.710 73 Å)	
Crystal size/mm	0.35 × 0.56 × 0.69	0.28 × 0.50 × 0.72
Scan width/°	0.9 below $K\alpha_1$ to 0.9 above $K\alpha_2$	0.8 + 0.345 tan θ
Scan speed (variable)/° min^{-1}	2.03–14.65	
Standard reflections	3, measured every 50 reflections	
Decay of standards	< 3%	
No. of reflections measured	4843	7386
No. of unique reflections	4510	6281
2θ range/°	0.2–55	0.2–60
Range of h, k, l	$0 < h < 13$ $0 < k < 14$ $-22 < l < 21$	$-27 < h < 27$ $-11 < k < 11$ $0 < l < 21$
Reflections observed $[F_0 > 4\sigma(F_0)]$	4332	5728
No. of parameters varied	270	308
Weights: $1/\sigma^2(F) + kF^2$, k =	0.000 978	0.014 451
GOF	0.965	0.913
Final R, R_w	0.036, 0.041	0.043, 0.049
Max. shift/error $(\Delta/\sigma)_{max}$	0.048	0.058
Largest features in the final ΔF map (ρ_{max}, ρ_{min}/e Å^{-3})	0.25, −0.38	2.25, −0.8

Table 2 Non-hydrogen fractional atomic coordinates and isotropic/equivalent displacement parameters (Å^2) with esd's in parentheses for complex **1**

Atom	x	y	z	U_{eq}[a]
Eu	0.0781(0)	0.0982(0)	0.0940(0)	0.037(0)
Cl1	0.2157(2)	0.1089(1)	0.3826(1)	0.061(0)
Cl2	−0.5771(1)	0.0772(1)	−0.1535(1)	0.061(0)
Cl3	−0.0761(1)	−0.1787(1)	0.3417(1)	0.046(0)
O1	0.1695(4)	0.2502(3)	0.0207(2)	0.054(1)
O2	0.0362(3)	0.0757(3)	−0.0476(2)	0.040(1)
O3	0.0500(5)	0.2906(4)	0.1637(3)	0.073(1)
O4	−0.1301(4)	0.1911(4)	0.0459(3)	0.069(1)
O5	0.2645(4)	−0.0035(4)	0.0426(2)	0.064(1)
O6	0.1557(4)	−0.0645(4)	0.1877(2)	0.057(1)
O7	0.2790(4)	0.1573(4)	0.1737(3)	0.071(1)
O8	−0.0790(4)	0.0717(4)	0.1930(3)	0.064(1)
O11	0.3113(6)	0.1994(6)	0.3892(4)	0.110(1)
O12	0.1646(10)	0.0857(6)	0.4543(4)	0.124(3)
O13	0.2647(6)	0.0027(6)	0.3501(5)	0.119(2)
O14	0.1112(7)	0.1475(6)	0.3280(4)	0.112(2)
O21	−0.6600(8)	−0.0175(7)	−0.1498(8)	0.187(5)
O22	−0.6319(7)	0.1680(6)	−0.2024(4)	0.119(2)
O23	−0.4613(5)	0.0418(6)	−0.1837(5)	0.105(2)
O24	−0.5559(8)	0.1248(8)	−0.0754(5)	0.119(2)
O31	−0.0426(5)	−0.2208(4)	0.2668(2)	0.066(1)
O32	−0.0803(5)	−0.0517(4)	0.3396(3)	0.081(1)
O33	−0.2023(5)	−0.2183(5)	0.3525(4)	0.092(2)
O34	0.0188(5)	−0.2167(5)	0.4028(3)	0.088(1)
N1	0.0901(3)	0.1604(3)	−0.0909(2)	0.039(1)
N2	0.3398(4)	0.3710(4)	−0.0598(3)	0.052(1)
C1	0.1532(4)	0.2455(4)	−0.0540(3)	0.042(1)
C2	0.2080(5)	0.3456(5)	−0.1004(3)	0.050(1)
C3	0.1242(6)	0.4512(6)	−0.1035(5)	0.072(2)

[a] $U_{eq} = \frac{1}{3} \sum_i \sum_j U_{ij} a_i^* a_j^* \mathbf{a}_i \cdot \mathbf{a}_j$.

hydrogen bonds created in the system under consideration. The most important seems to be the relatively short hydrogen bonds between the oxygens in the two perchlorate groups, namely Cl1 and Cl3 (cf. Fig. 1 and 2), and the water molecules (O5, O6 and O7). The lengths of these D—H···A hydrogen bonds vary from 2.698(6) to 2.977(9) Å for the D-to-A distances and from 1.856(4) to 2.647(4) Å for the H···A bonds.

Table 3 Non-hydrogen fractional atomic coordinates and isotropic/equivalent displacement parameters (Å^2) with esd's in parentheses for complex **2**

Atom	x	y	z	U_{eq}[a]
Eu	0.4070(0)	−0.0164(0)	0.9014(0)	0.019(0)
Cl1	0.7472(1)	−0.0107(6)	0.8396(2)	0.038(0)
Cl2	0.4051(2)	0.4516(4)	0.6538(3)	0.046(1)
Cl3	0.3580(1)	−0.1550(4)	0.4861(2)	0.038(1)
Cl4	0.1069(1)	−0.0202(6)	0.8765(2)	0.039(0)
O1	0.4552(4)	−0.0292(16)	0.7837(5)	0.034(2)
O2	0.5343(3)	−0.0353(13)	0.9449(4)	0.025(2)
O3	0.3117(4)	−0.1225(10)	0.7747(5)	0.032(2)
O4	0.4399(6)	−0.2913(14)	0.8950(10)	0.051(3)
O5	0.3389(11)	−0.1898(18)	0.9663(11)	0.083(5)
O6	0.3291(5)	0.1394(15)	0.9599(8)	0.043(3)
O7	0.3345(4)	0.1780(10)	0.7783(6)	0.036(2)
O8	0.4420(8)	0.2554(16)	0.9098(10)	0.063(3)
O11	0.8221(2)	−0.0092(14)	0.8772(6)	0.057(2)
O12	0.7192(5)	−0.1493(11)	0.8662(8)	0.071(5)
O13	0.7177(6)	0.1221(12)	0.8698(10)	0.252(18)
O14	0.7296(5)	−0.0067(19)	0.7453(3)	0.172(9)
O21	0.4543(5)	0.4654(13)	0.6043(7)	0.093(5)
O22	0.4043(6)	0.5929(9)	0.7011(9)	0.084(5)
O23	0.4255(6)	0.3257(12)	0.7151(8)	0.091(5)
O24	0.3362(4)	0.4225(16)	0.5949(7)	0.114(7)
O31	0.4187(4)	−0.2206(13)	0.4689(7)	0.086(5)
O32	0.3706(5)	−0.1413(17)	0.5795(3)	0.066(4)
O33	0.3443(7)	−0.0045(10)	0.4464(9)	0.156(10)
O34	0.2984(5)	−0.2536(15)	0.4499(8)	0.132(9)
O41	0.1817(2)	−0.0305(15)	0.9151(6)	0.089(4)
O42	0.0775(5)	0.0702(14)	0.9325(7)	0.086(5)
O43	0.0772(6)	−0.1729(9)	0.8667(9)	0.089(6)
O44	0.0915(6)	0.0524(16)	0.7917(5)	0.128(8)
N1	0.5628(5)	−0.0416(17)	0.8785(6)	0.038(3)
N2	0.5186(5)	−0.2096(13)	0.6743(6)	0.029(2)
C1	0.5208(5)	−0.0456(13)	0.7974(6)	0.026(3)
C2	0.5510(5)	−0.0642(17)	0.7210(8)	0.036(3)
C3	0.5330(10)	0.0563(24)	0.6571(13)	0.059(4)

[a] $U_{eq} = \frac{1}{3} \sum_i \sum_j U_{ij} a_i^* a_j^* \mathbf{a}_i \cdot \mathbf{a}_j$.

Formation of a bridge by an NO group in lanthanide systems has not yet been reported. The complexes are formed with the zwitterion form of the ligand, created by deprotonation of nitrogen in glycinehydroxamic acid,

Table 4 Selected geometrical parameters (in Å and deg) for complexes **1** and **2**

[Eu(DL-α-Alaha)(H$_2$O)$_6$]$_2$(ClO$_4$)$_6$, **1**

Eu—Eua	4.114(1)	Eu—O7	2.456(4)
Eu—O1	2.376(4)	Eu—O8	2.451(5)
Eu—O2	2.430(3)	O1—C1	1.264(6)
Eu—O2a	2.392(3)	O2—N1	1.357(5)
Eu—O3	2.496(5)	N1—C1	1.290(6)
Eu—O4	2.469(4)	N2—C2	1.497(7)
Eu—O5	2.479(4)	C1—C2	1.517(7)
Eu—O6	2.502(4)	C2—C3	1.472(9)
O1—Eu—O2	65.9(1)	O3—Eu—O8	71.0(2)
O1—Eu—O3	71.9(1)	O4—Eu—O5	139.4(1)
O1—Eu—O4	83.9(1)	O4—Eu—O6	137.9(1)
O1—Eu—O5	77.5(1)	O4—Eu—O7	137.3(2)
O1—Eu—O6	138.0(1)	O4—Eu—O8	70.6(2)
O1—Eu—O7	74.6(1)	O5—Eu—O6	70.8(1)
O1—Eu—O8	140.4(1)	O5—Eu—O7	71.0(1)
O2—Eu—O3	122.6(1)	O5—Eu—O8	140.7(1)
O2—Eu—O4	68.9(1)	O6—Eu—O7	69.6(1)
O2—Eu—O5	70.6(1)	O6—Eu—O8	71.2(1)
O2—Eu—O6	124.5(1)	O7—Eu—O8	104.2(2)
O2—Eu—O7	129.3(1)	O1—Cl—N1	122.1(4)
O2—Eu—O8	126.5(1)	O1—C1—C2	117.9(4)
O3—Eu—O4	69.6(2)	N1—C1—C2	120.0(4)
O3—Eu—O5	134.4(1)	N2—C2—C1	105.8(4)
O3—Eu—O6	112.9(1)	N2—C2—C3	111.7(5)
O3—Eu—O7	68.8(2)	C1—C2—C3	112.0(5)

[Eu(L-α-AlahaH)(H$_2$O)$_6$]$_2$(ClO$_4$)$_8$, **2**

Eu—Eua	4.074(1)	Eu—O7	2.651(8)
Eu—O1	2.345(9)	Eu—O8	2.437(14)
Eu—O2	2.426(6)	O1—C1	1.266(13)
Eu—O2a	2.376(6)	O2—N1	1.339(13)
Eu—O3	2.491(7)	N1—C1	1.310(12)
Eu—O4	2.469(12)	N2—C2	1.501(17)
Eu—O5	2.443(20)	C1—C2	1.515(17)
Eu—O6	2.436(13)	C2—C3	1.421(24)
O1—Eu—O2	65.3(3)	O3—Eu—O8	122.3(4)
O1—Eu—O3	74.5(3)	O4—Eu—O5	67.5(5)
O1—Eu—O4	75.2(4)	O4—Eu—O6	138.8(4)
O1—Eu—O5	135.9(5)	O4—Eu—O7	132.0(4)
O1—Eu—O6	142.1(4)	O4—Eu—O8	148.2(5)
O1—Eu—O7	72.8(3)	O5—Eu—O6	71.3(5)
O1—Eu—O8	84.9(4)	O5—Eu—O7	116.7(5)
O2—Eu—O3	133.2(3)	O5—Eu—O8	138.7(6)
O2—Eu—O4	71.3(4)	O6—Eu—O7	70.4(3)
O2—Eu—O5	120.2(5)	O6—Eu—O8	69.7(5)
O2—Eu—O6	131.2(3)	O7—Eu—O8	61.1(4)
O2—Eu—O7	123.0(3)	O1—C1—N1	119.3(10)
O2—Eu—O8	78.0(4)	O1—C1—C2	120.7(10)
O3—Eu—O4	76.2(4)	N1—C1—C2	130.0(10)
O3—Eu—O5	74.4(5)	N2—C2—C1	105.6(9)
O3—Eu—O6	95.3(3)	N2—C2—C3	106.1(12)
O3—Eu—O7	61.4(3)	C1—C2—C3	114.8(12)

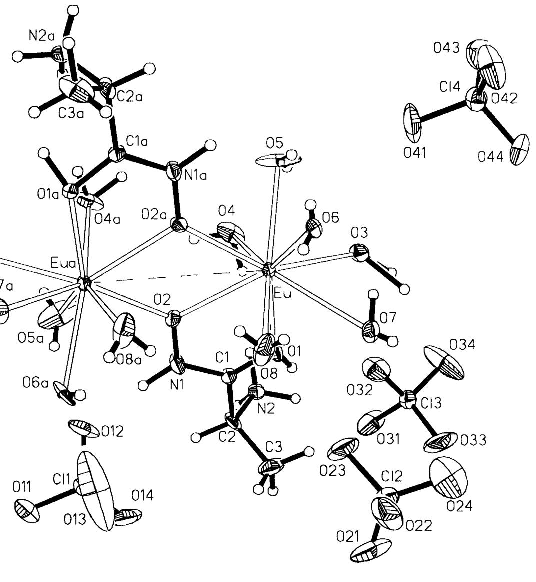

Fig. 2 Crystal structure of $[Eu(L\text{-}\alpha\text{-}AlahaH)(H_2O)_6]_2(ClO_4)_8$

$NH_3^+CH_2C(O)NOH$.[26] In our system the proton of the NOH group could create a zwitterion during complex formation with lanthanides.

Some maxima noticed by us in the electron density difference map might suggest the possibility of proton delocalization. Assuming formation of a simple $CH_3CHNH_3^+CONHO^-$ ion and partial delocalization of the protons on the N2 and O2 atoms does not change the *R* factor of the structure refinement. The electron density distribution in the region of the two O2 atoms of the dimer seems to confirm our assumption. In the presence of the heavy atom Eu^{III}, however, there is no possibility, without additional investigations of analogous deuterized compounds, to confirm or reject this hypothesis. Therefore, the structure models assumed are those shown in Fig. 1 and 2.

The lanthanide ions are coordinated by oxygen atoms: one from the CO group, two (bridging) from the NO groups and six from water molecules; thus, the coordination number is nine. This type of coordination, as well as the formation of dimers in both structures under consideration, are in contrast with the structures reported before for lanthanide complexes with simple hydroxamic acid, where monomeric compounds of different composition are formed.[19]

The bond lengths for **1** and **2** are collected in Table 4. For **1** the shortest Eu—O bond length [2.376(4) Å] was found in the Eu—O—C moiety; a little longer one is the Eu—O2 bond involving the NO goup [2.430(5) Å]. The lengths of the $Eu—OH_2$ bonds vary from 2.451(5) to 2.502(4) Å for compound **1** (the racemic system). The Eu—Eu distance in the centrosymmetric dimer is equal to 4.114 Å.

Comparison of these data for the two title compounds indicates that the bridging lengths Eu—O2 are comparable: 2.426(6) and 2.430(3) for **2** and **1**, respectively; Eu—O1 (CO group) in **2** is equal to 2.345(9) Å and is a little shorter than in **1**. The $M—OH_2$ lengths vary from 2.436 (13) to 2.651 (8) Å and are longer in **2**. However, the Eu—Eu distance in **2** is shorter (4.074 Å).

A comparison of the X-ray data of the systems under consideration with that for other compounds studied before (dimers created with DL- and L-alanine)[27,28] proves the formation of less bonded Eu^{III} ions in both the centro- and non-centrosymmetric dimers (the Eu—Eu distance is ≈4.41 Å), whereas the $M—OH_2$ distances are shorter: 2.44–2.54 Å. The lengths of the M—O bonds with the carboxyl group oxygens are also shorter (2.31 and 2.36 Å).[27] The strongest coupling of metal ions in the dimer was found in the centrosymmetric dimer formed in the diglycine complexes, in which the Nd—Nd distance (3.99 Å) is the shortest, when compared with all the known dimeric and polymeric compounds with amino acids.[28]

Let us return to the data of the d electron systems. As mentioned before, two types of coordination modes were found in complexes with transition metal ions (Cu): *via* two N and two O atoms. Most probably, polynuclear systems exist in solutions of Cu^{2+} and α-alaninehydroxamic acid.[21] Very complex polynuclear systems are also formed with β-alaninehydroxamic acid in the solid state of the copper complex.[21]

According to the available X-ray data, unexpected coordinations of the metal were also found for Ni^{2+} complexes.[20]

X-ray crystallographic parameters are available for the complexes of transition metals with α-[20] and β-alaninehydroxamic acid[21] derivatives. Two structures were solved: square planar for *trans*-bis(α-alaninehydroxamato) nickel(II)[Ni(α-Alaha)$_2$] and *trans*-bis(α-alaninehydroxamato)

Table 5 Hydrogen bonds in complexes **1** and **2**

D—H···A/Å		D—H···A/°	Symmetry code for acceptor
$[Eu(DL\text{-}\alpha\text{-}Alaha)(H_2O)_6]_2(ClO_4)_6$, **1**			
N2—H2b···O1	0.908(5) 2.416(4) 2.698(6)	98.1(3)	*x*, *y*, *z*
N2—H2c···O32	0.779(5) 2.160(5) 2.832(7)	144.8(4)	1/2 + *x*, 1/2 − *y*, 1/2 + *z*
O4—H41···O33	0.806(5) 2.022(6) 2.754(8)	151.0(4)	−1/2 + *x*, 1/2 + *y*, 1/2 − *z*
O4—H42···O5	1.111(4) 1.856(4) 2.878(6)	151.0(3)	−*x*, −*y*, −*y*
O6—H61···O7	0.856(4) 2.570(5) 2.830(6)	98.8(3)	*x*, *y*, *z*
O6—H61···O13	0.856(4) 2.208(8) 2.977(9)	149.4(3)	*x*, *y*, *z*
O7—H72···O34	1.060(4) 1.912(5) 2.931(7)	160.0(3)	1/2 − *x*, 1/2 + *y*, 1/2 − *z*
O8—H81···O32	0.876(5) 2.303(5) 2.852(7)	120.8(3)	*x*, *y*, *z*
O8—H82···O6	0.841(5) 2.647(4) 2.883(6)	97.7(3)	*x*, *y*, *z*
$[Eu(L\text{-}\alpha\text{-}AlahaH)(H_2O)_6]_2(ClO_4)_8$, **2**			
N1—H1···O5	0.961(10) 2.542(22) 2.942(19)	106.2(12)	1 − *x*, *y*, 2 − *z*

copper(II)[Cu(α-Alaha)$_2$]. In these complexes coordination *via* the nitrogens of the amino, as well as of the hydroxamate groups, was clearly shown. Besides, in the Cu^{II} compound, an oxygen of the carbonyl group of a neighboring molecule is bonded in the axial position (Cu—O ≈ 2.878 Å), forming a penta-coordinated polyhedron. In the two crystals the M—N distances are comparable to those found earlier in complexes with glycinehydroxamic acid.[29,30] Note that the ligand is here deprotonated at the nitrogen atom of the hydroxamate group.

In contrast to the mononuclear complexes with α-alaninehydroxamic acid, Cu^{2+} ions could also form a pentanuclear compound with β-alaninehydroxamic acid having the formula $[Cu_5(\beta\text{-AlahaH})_4](ClO_4)_2 \cdot 5H_2O$.

Although the nature of the chemical bonds in the two types of compounds (the title and copper ones) is different, in both systems the oxygen atoms of ligand molecules are involved in the coordination so we compare the results of their X-ray analysis. All the donor goups of the four ligand molecules are involved in copper ion coordination and, as in our title system, the N—O groups play the bridging role. These parameters of the structure can be compared with those found for the complexes investigated by us. The unusual structure of the Cu^{II} compound consists of twelve five- and six-membered rings; it seems reasonable to compare the bond lengths in the five-membered rings where, similarly to our structure, two oxygen atoms are involved in the metal ion coordination. The Eu—O bonding lengths are significantly longer, as could be expected because of the larger ionic radii and the type of bonding, than in the Cu^{II} polynuclear complex; however, the two bridging lengths Eu—O2 and Eua—O2 are almost equal, as in the copper systems:[21] Cu1—O12 = 1.936(6) Å and O12—Cu5 = 1.898(4) Å; Cu5—O42 = 1.932(4) Å and Cu4—O42 = 1.937(4) Å. Note that these bond lengths are significantly shorter than in the title crystals. In addition, the C11—O11 bond (1.287 Å) is similar to C1—O1 [1.264(6) Å] in **1**; similarly C11—N11 [1.305(8) Å] can be related to C1—N1 [1.290(6) Å]. On the other hand, N11—O12 = 1.441 Å differs meaningfully from the N1—O2 = 1.357(5) Å found in our crystals.

The bond length N11—O12 in the copper-containing system is almost equal to the N1—O1 one (1.434 Å) in a simple zwitterion structure of glycinehydroxamic acid, having a deprotonated nitrogen in the hydroxamic moiety $NH_3{}^+CH_2C(O)NOH$ and a protonated NOH group. A comparison of C1—O1 (1.264 Å) and C1—N1 (1.290 Å) in compound **1** with the amide C=O (1.235 Å) and C—N (1.333 Å) suggests a delocalization of the pure double bond of the carbonyl group of the amide over the hydroxamate group, as a result of bonding with metal ions.

It seems also important to analyse the structure of the dimers created in racemic **1** and L-handed **2** crystals. In the centrosymmetric dimer the EuO2EuaO2a group (see Fig. 1) is planar. The Eu—O2—N1—C1—O1 five-membered rings in compound **1** are also planar (as concluded from the calculation of the atom deviations from the plane) and are oriented to the dimer plane with a 3.52° angle. Consequently, the dimer unit is built of two five-membered rings and a Eu—O—Eu—O square in an almost planar form. This planarity of the rings in the europium structure differs significantly from the conformation of the rings in the pentanuclear copper compound reported in ref. 21.

In the structure of **2** the planarity of the rings is not so pronounced as in **1**. The EuO2EuaO2a group becomes less planar too, with the following atomic e.s.d.s: Eu 0.077; O2 0.075; Eu 0.086; O2 −0.088 Å. Thus, in the L-handed crystal the dimer possesses two-fold axes and the locations of the rings *versus* the dimer plane deviate by 4.50°.

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