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Tetra-μ-α-alanine-bis[tetraaqua-gadolinium(III)] hexaperchlorate

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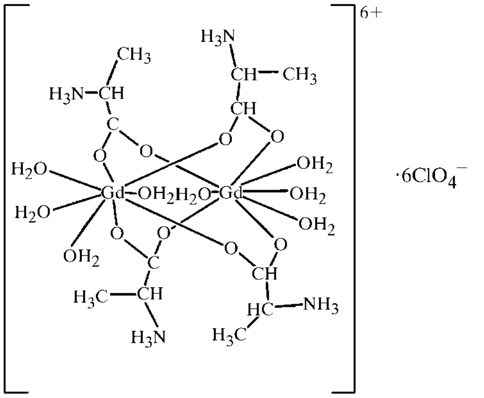
The title complex, $[Gd_2(C_3H_7NO_2)_4(H_2O)_8](ClO_4)_6$, contains centrosymmetric dimeric $[Gd_2(Ala)_4(H_2O)_8]^{6+}$ cations (Ala is α-alanine) and perchlorate anions. The four alanine molecules act as bridging ligands linking two Gd^{3+} ions through their carboxylate O atoms. Each Gd^{3+} ion is also coordinated by four water molecules, which complete an eightfold coordination in a square-antiprism fashion. The perchlorate anions and the methyl groups of the alanine ligands are disordered.

Comment

In recent years, rare earth elements have become widely used. Increasingly, they are entering the environment and thus the human body *via* the food chain. Therefore, it is important to study the biological effects of these elements. The structural investigation of rare earth ion–amino acid complexes is of interest with respect to both the understanding of the biological effects of rare earth elements and the enrichment of rare-earth coordination chemistry. Some structures of such complexes have been reported; see, for example, Legendziewicz *et al.* (1984), Csoregh *et al.* (1989), Glowiak *et al.* (1991), Hu *et al.* (1995), Ma *et al.* (1995) and Wang *et al.* (1994). However, reports of the crystal structures of gadolinium–amino acid complexes are rare (Zheng *et al.*, 1993; Gao *et al.*, 2001) and there are no reports of the crystal structures of gadolinium–alanine complexes. In this paper, the crystal structure of a rare-earth complex with an amino acid, (I), has been studied in order to predict the structural parameters of unknown complexes of rare earth elements with amino acids by artificial neural networks.

The title compound crystallized in the triclinic system and the structure consists of centrosymmetric dimeric $[Gd_2(Ala)_4(H_2O)_8]^{6+}$ complex cations (Ala is α-alanine) and ClO_4^- anions. The configuration of the ions is illustrated in Fig. 1 and selected geometric parameters are listed in Table 1. The alanine molecules exist in the zwitterionic form, with the amine groups protonated and the carboxyl groups deprotonated. The two gadolinium ions in the dimeric $[Gd_2(Ala)_4(H_2O)_8]^{6+}$ complex cation are connected by four bridging carboxylate groups; the Gd···Gd distance is 4.410 (2) Å, indicating that there is no metal–metal bond in the complex.



(I)

The average $Gd-O_{carboxylate}$ bond length is 2.333 Å. Each pair of carboxylate groups is coplanar with the two Gd^{3+} ions and the dihedral angle between the two planes is 89 (1)°, showing the two planes to be almost perpendicular. The coordination polyhedron around the Gd^{3+} ion is a square antiprism, with

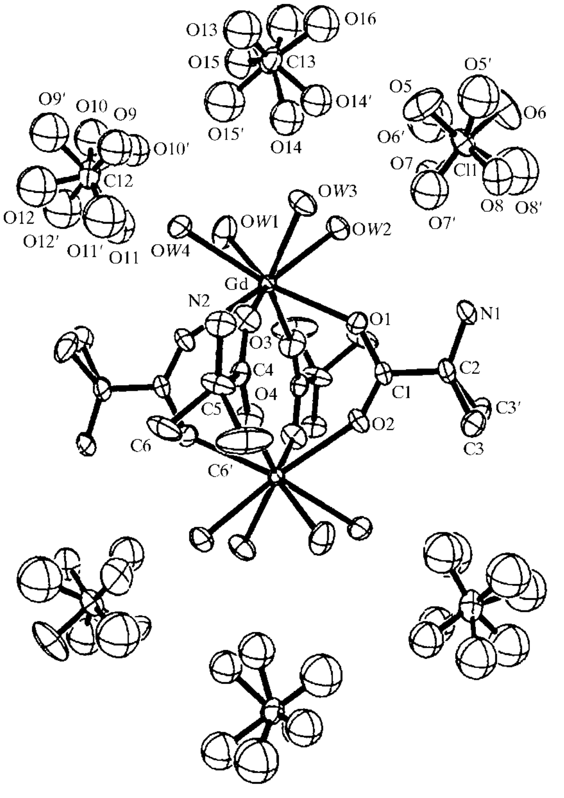


Figure 1
The structure of $[Gd_2(Ala)_4(H_2O)_8](ClO_4)_6$. Displacement ellipsoids are shown at the 50% probability level and H atoms have been omitted.

four of the sites occupied by the carboxylate O atoms and the other four sites occupied by the O atoms of the four coordinated water molecules (mean Gd—O$_{water}$ = 2.453 Å), completing an eightfold coordination. The arrangement of ions in the unit cell is shown in Fig. 2. The perchlorate anions are disordered and reside in the cavities of the crystal. Two perchlorate O atoms form hydrogen bonds with the $-NH_3^+$ group and coordinated water molecules from two $[Gd_2(Ala)_4(H_2O)_8]^{6+}$ cations. This hydrogen-bonded structure stabilizes the crystal packing.

The optic purity of L-alanine is 68.9%. Though the content of L-alanine is higher than that of D-alanine, in the complex, the methyl groups are disordered over two positions corresponding to the D and L configurations of alanine. According to statistical results, the probability of methyl groups occupying two positions is equal. In addition, the two different orientations of the methyl groups can decrease their potential energy and enhance the symmetry of the crystal structure. Therefore, equal numbers of L- and D-alanine molecules were selected to form the dimeric cations with Gd^{III} ions.

The structures of $[Gd_2(Pro)_6(H_2O)_6](ClO_4)_6$ (Pro is proline; Zheng *et al.*, 1993) and $[Gd(Gly)_3(H_2O)_2]Cl_3\cdot H_2O$ (Gly is glycine; Gao *et al.*, 2001) have been reported. They both consist of one-dimensional chains in which two neighboring Gd^{3+} ions are connected by bridging carboxylate groups; the Gd···Gd distances are 4.722 and 4.765 Å, respectively, and the mean Gd—O$_{carboxylate}$ bond lengths are 2.357 and 2.489 Å, respectively. By comparing the dimeric form with the chain structures, it is found that the Gd—O$_{carboxylate}$ bond lengths influence the distances between neighboring Gd^{III} ions. The shorter mean Gd—O$_{carboxylate}$ length (2.333 Å) found in the dimeric structure leads to a Gd···Gd distance (4.410 Å) which is considerably shorter than the corresponding distances found in the chain structures. In addition, this can make the dimeric complex more stable.

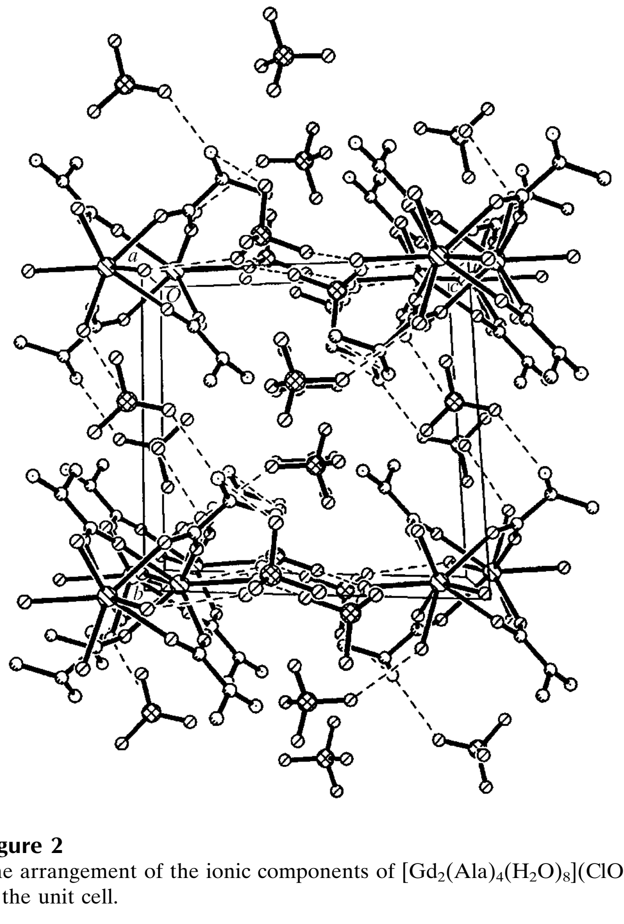


Figure 2
The arrangement of the ionic components of $[Gd_2(Ala)_4(H_2O)_8](ClO_4)_6$ in the unit cell.

Experimental

For the preparation of the title compound, gadolinium perchlorate and alanine were mixed in a 1:1 molar ratio in water. The mixed solution was neutralized with NaOH to a pH of 7.0 with stirring. The gadolinium ions were partially hydrolyzed to form a precipitate which was filtered off. The remaining filtrate was evaporated slowly at room temperature, yielding colorless prismatic crystals.

Crystal data

$[Gd_2(C_3H_7NO_2)_4(H_2O)_8](ClO_4)_6$
$M_r = 1411.71$
Triclinic, $P\overline{1}$
$a = 11.057$ (2) Å
$b = 11.0584$ (18) Å
$c = 11.339$ (3) Å
$\alpha = 78.420$ (18)°
$\beta = 64.689$ (16)°
$\gamma = 65.696$ (16)°
$V = 1141.7$ (4) Å^3
$Z = 1$
$D_x = 2.053$ Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 23 reflections
$\theta = 4.7$–8.2°
$\mu = 3.35$ mm^{-1}
$T = 293$ (2) K
Prismatic, colorless
0.52 × 0.40 × 0.32 mm

Data collection

Siemens *P*4 diffractometer
ω scans
Absorption correction: ψ scan (*SHELXTL*; Siemens, 1994)
$T_{min} = 0.640$, $T_{max} = 0.947$
5251 measured reflections
4367 independent reflections
3879 reflections with $I > 2\sigma(I)$
$R_{int} = 0.025$
$\theta_{max} = 26.0°$
$h = -12 \rightarrow 11$
$k = -13 \rightarrow 1$
$l = -13 \rightarrow 13$
3 standard reflections every 97 reflections intensity decay: none

Table 1
Selected geometric parameters (Å, °).

Gd—O4^i	2.304 (6)	Gd—O*W*1	2.408 (6)
Gd—O2^i	2.328 (5)	Gd—O*W*2	2.463 (5)
Gd—O3	2.347 (5)	Gd—O*W*3	2.429 (6)
Gd—O1	2.356 (5)	Gd—O*W*4	2.511 (6)
O4^i—Gd—O2^i	77.2 (2)	O*W*1—Gd—O*W*3	102.2 (3)
O4^i—Gd—O3	122.4 (2)	O4^i—Gd—O*W*2	76.8 (2)
O2^i—Gd—O3	77.8 (2)	O2^i—Gd—O*W*2	142.1 (2)
O4^i—Gd—O1	75.4 (2)	O3—Gd—O*W*2	139.9 (2)
O2^i—Gd—O1	123.6 (2)	O1—Gd—O*W*2	74.9 (2)
O3—Gd—O1	77.1 (2)	O*W*1—Gd—O*W*2	69.6 (2)
O4^i—Gd—O*W*1	82.4 (3)	O*W*3—Gd—O*W*2	70.8 (2)
O2^i—Gd—O*W*1	80.1 (3)	O4^i—Gd—O*W*4	141.3 (2)
O3—Gd—O*W*1	141.2 (2)	O2^i—Gd—O*W*4	71.5 (2)
O1—Gd—O*W*1	141.5 (2)	O3—Gd—O*W*4	72.4 (2)
O4^i—Gd—O*W*3	142.9 (2)	O1—Gd—O*W*4	141.7 (2)
O2^i—Gd—O*W*3	139.9 (2)	O*W*1—Gd—O*W*4	70.5 (2)
O3—Gd—O*W*3	76.3 (2)	O*W*3—Gd—O*W*4	71.8 (2)
O1—Gd—O*W*3	79.2 (2)	O*W*2—Gd—O*W*4	116.4 (2)

Symmetry code: (i) $-x, -y, -z$.

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Refinement

Refinement on F^2	$w = 1/[\sigma^2(F_o^2) + (0.0750P)^2 + 3.0801P]$ where $P = (F_o^2 + 2F_c^2)/3$
$R[F^2 > 2\sigma(F^2)] = 0.044$	$(\Delta/\sigma)_{\max} = 0.042$
$wR(F^2) = 0.119$	$\Delta\rho_{\max} = 1.32$ e Å^{-3}
$S = 1.01$	$\Delta\rho_{\min} = -1.06$ e Å^{-3}
4367 reflections	Extinction correction: *SHELXL*97
312 parameters	Extinction coefficient: 0.0187 (13)
H-atom parameters not refined	

The perchlorate groups and the methyl groups of the alanine ligands were found to be disordered. The occupancy factors for the disordered atoms, each in two positions, were estimated on the basis of electron densities. All non-H atoms were refined anisotropically, except for those with occupancy factors less than 0.5, which were refined isotropically. H-atom parameters were not refined.

Data collection: *P*4 *Software* (Siemens, 1995); cell refinement: *P*4 *Software*; data reduction: *P*4 *Software*; program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1997); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *SHELXTL* (Siemens, 1994); software used to prepare material for publication: *SHELXL*97.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: VJ1183). Services for accessing these data are described at the back of the journal.

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