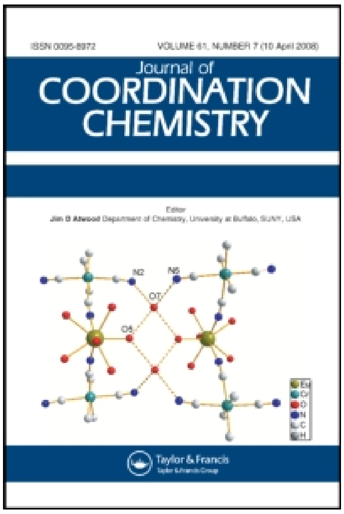

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CRYSTAL STRUCTURE AND INFRARED SPECTRA OF A LANTHANUM COORDINATION COMPOUND WITH GLYCINE, $\{[La(Gly)s\cdot 2H_2O]\cdot(ClO_4)_3\}_n$

Ma Aizeng[a]; Li Laiming[a]; Lin Yonghua[a]; Xi Shiquan[a]
[a] Changchun Institute of Applied Chemistry, Academia Sinica, Jilin, China

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CRYSTAL STRUCTURE AND INFRARED SPECTRA OF A LANTHANUM COORDINATION COMPOUND WITH GLYCINE, $\{[La(Gly)s \cdot 2H_2O] \cdot (ClO_4)_3\}_n$

MA AIZENG, LI LAIMING, LIN YONGHUA and XI SHIQUAN*

Changchun Institute of Applied Chemistry, Academia Sinica, Changchun, Jilin 130022, China

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A lanthanum coordination compound with glycine $\{[La(Gly)_3 \cdot 2H_2O] \cdot (ClO_4)_3\}_n$ (Gly = $NH^+{}_3$-CH_2-COO^-) was synthesized and obtained in the form of single crystals. Its X-ray crystal structure has been determined and the IR spectrum has been studied. Crystallographic data for the compound are $Mr = 698.6$, triclinic, space group $P\bar{1}$, with $a = 10.730(4)$, $b = 12.958(4)$, $c = 8.806(3)$ Å, $\alpha = 97.10(2)$, $\beta = 113.05(3)$, $\gamma = 71.52(3)°$, $V = 1068.55\ (0.67)$ $Å^3$, $Z = 2$; $D_{calc} = 2.17$ cm^{-3}, $\mu = 25.1$ cm^{-1}; T = 298K; $\lambda(MoK\alpha) = 0.71069$ Å, $2\theta_{max} = 60.0°$. Final $R = 0.044$ for 5554 observed reflections with $I > 3\sigma$ (I). Glycine molecules coordinate with lanthanum atoms through alternate "two-four carboxylate bridges" to form a one-dimensional chain compound of infinite length. Some of the glycine molecules coordinate to lanthanum atoms as bridging bidentates ligands and the others as bridging-chelating terdentate ligands. The IR spectrum of the compound is compared with that of $\{[Sm_2(Gly)_6 \cdot 4H_2O] \cdot (ClO_4)_6 \cdot 5H_2O\}_n$. Differences in their IR spectra indicate differences of structures.

KEYWORDS: lanthanum, X-ray structure, glycine, IR spectra, synthesis

INTRODUCTION

Rare earth elements now are used extensively in agriculture, medicine and biochemical research.[1,2] It is necessary to know the rare earths' biological effects. Since biomacromolecules such as peptides and proteins, are composed of amino acids, it is important to explain the bonding of Ln(III) in coordination compounds with amino acids. Such investigations are also important for the general chemistry of lanthanides.

Some authors have paid attention to structures and properties of rare earth coordination compounds with amino acids.[3–7] Since the structure of $Nd_2(Gly)_6 \cdot (ClO_4)_6 \cdot 9H_2O$ was reported by Legendziwicz,[6] several structures of glycine with rare earths have been published.[3,7,8–12]

We have synthesized a series of different rare earth coordination compounds with different kinds of amino acids, studied their IR spectra and obtained eighteen crystal structures[12,13] which include nine different types of amino acids. In this

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*Author for correspondence.

paper, the crystal structure and IR spectrum of $\{[La(Gly)_3 \cdot 2H_2O] \cdot (ClO_4)_3\}_n$ are reported and discussed.

EXPERIMENTAL

Synthesis

Equimolar amounts of lanthanum perchlorate and glycine were added to distilled water. While stirred, the solution was heated at 50°C. After the solids dissolved completely, the solution was adjusted to pH~4 by adding hydrochloric acid. Heating was continued for 7h, then the solution was concentrated on a bath until most of the water was evaporated. The concentrated solution was finally dried in a vacuum desiccator over phosphorus pentoxide for two months when colorless crystals were obtained. *Anal.*; calc. for $La(Gly)_3(ClO_4)_3 \cdot 2H_2O$; La, 19.88; C, 10.31; H, 2.72; N, 6.01%. Found: La, 19.90; C, 10.23; H, 2.91; N. 5.89%.

IR spectra

IR spectra were recorded at room temperature in the region 4000–400cm $^{-1}$ with a resolution of 4cm^{-1} on a Digilab FTS-20E IR spectrometer with KBr pellets.

Crystal data and structure determination

The crystal chosen for analysis with dimensions 0.28 x 0.42 x 0.54 mm was mounted on a glass fibre. Experimental conditions are reported in Table 1. Intensity data were collected on a Nicolet R3/M diffractometer with graphite-monochromatized MoKα radiation at *ca* 298K. Cell parameters were obtained by least-squares methods using 25 reflections for which $12.04° < 2\theta < 28.37°$. A total of 6691 (including 6484 unique) reflections was collected. Two standard reflections were measured for every 100 others. Intensity variations of the standard reflections were ±2% about the mean value.

The measured intensity data were collected for Lorentz, polarization factors and absorption using empirical scan data. Linear decay corrections were applied. A total of 5554 reflections with $I > 3\sigma(I)$ was considered observed, and all were used in the refinement.

The structure was solved by direct methods. The La atom was located in the E map. The all non-hydrogen atoms were located in succeeding Fourier syntheses. The structure was refined by full-matrix least-squares techniques with anisotropic thermal parameters for all non-hydrogen atoms. In the course of the conventional full-matrix least-squares refinement of the positional and anisotropic vibrational parameters of non-hydrogen atoms, one N atom of a glycine ligand was found to exhibit partial positional disorder; N(33) was located in two distinct positions with an occupancy factor of 0.5, respectively. This phenomenon did not permit the location of the H atoms in difference Fourier syntheses. Consequently, the H atoms were placed in calculated positions and were assigned isotropic thermal parameters ($U = 0.08Å^2$). Final $R = \Sigma||Fo| - |Fc||/\Sigma|Fo| = 0.044$, $R_w = [\Sigma(|Fo| - |Fc)|^2/\Sigma\, w\, Fo^2]^{1/2} = 0.047$ and $S = [\Sigma\, w(|Fo| - |Fc|)^2/(No\text{-}N)^{1/2} = 1.26$, $w = 1/\sigma^2(Fo)$, $(\Delta/\sigma)_{max} = 0.013$; in the final difference electron density synthesis the largest

Table 1 Crystallographic data for $\{[La(Gly)_3 \cdot 2H_2O] \cdot (ClO_4)_3\}_n$.

Chemical formula	$C_6H_{19}O_{20}N_3Cl_3La$
Formula weight	698.6
Crystal system	triclinic
Space group	$P\bar{1}$
a (Å)	10.730(4)
b (Å)	12.958(4)
c (Å)	8.806(3)
α (°)	97.10(2)
β (°)	113.05(3)
γ (°)	71.51(3)
V (Å^3)	1068.55(0.67)
Z	2
μ (cm^{-1})	25.1
F(000)	688
2θ max(°)	60.0
D_{calc}(gcm^{-3})	2.17
Radiation	MoKα ($\lambda = 0.71069$Å)
Correction	Lp, ψ
Residuals: R, R_w	0.044, 0.047
Goodness of fit:s	1.26
No. Unique data	6484
No. observation with $I > 3\sigma(I)$	5554
Max. shift $(\Delta/\sigma)_{max}$ in final cycle	0.013
Largest/smallest peaks in final difference map (eÅ^{-3})	1.43/-0.89
Scan type	ω

and smallest heights were 1.43 and -0.89 eA^{-3} in the vicinity of the La and Cl atoms. The main computer program used was SHELXTL.[14] Scattering factors are from international Tables for X-ray Crystallography (1974).[15]

RESULTS AND DISCUSSION

Atomic coordinates and thermal parameters are listed in Table 2 and the important bond lengths and angles are given in Tables 3 and 4, respectively.

Description of the structure

In the compound, glycine molecules coordinate with lanthanum atoms *via* alternate "two-four carboxylate bridges" to form an one-dimensional chain of infinite length. A part of the chain is shown in Figure 1. There are two types of La-Gly contacts (Fig. 2). The first type has each oxygen of a glycine connected to two different La atoms. The second type has both oxygens of a glycine bonded to one La atom and one of the oxygens bridges to another symmetry-independent La atom. These two types of glycines are also regarded as bridging bidentate ligands and chelating-bridging terdentate ligands, respectively. In the infinite chain, the glycine molecules of two bridges and two glycine molecules of four bridges are chelating-bridging terdentate ligands; the other two glycine molecules of the four bridges are bridging bidentate ligands. However, in the structure of $\{Sm_2(Gly)_5(ClO_4)_6 \cdot 9H_2O\}_n$[12] (Fig. 4), only two glycines of four bridges are chelating-bridging terdentate ligands; one of the two glycines is a weak chelating-bridging terdentate ligand (Sm_2-O_4 3.083Å

Table 2 Final atomic parameters (× 10^4) with equivalent isotropic temperature factors ($Å^2$ × 10^3).

Atom	*x/a*	*y/b*	*z/c*	*U*
La	143(1)	4944(1)	2615(1)	23(1)
Cl(1)	3609(1)	212(1)	6750(2)	51(1)
Cl(2)	1363(1)	8837(1)	1847(2)	47(1)
Cl(3)	4484(1)	6421(1)	7540(2)	61(1)
N(13)	2711(5)	1104(3)	619(6)	50(2)
N(23)	4780(4)	2479(3)	5703(5)	43(2)
N(33)	617(10)	8700(6)	5685(11)	48(4)
N(33')	868(13)	8009(8)	7538(11)	60(5)
O(1)	854(3)	3975(2)	61(3)	29(1)
O(2)	1481(4)	2841(2)	2070(4)	39(1)
O(3)	2426(3)	4122(3)	4963(4)	38(1)
O(4)	2248(3)	4027(3)	7408(4)	35(1)
O(5)	338(4)	6098(3)	5633(4)	43(1)
O(6)	154(4)	6966(3)	3568(4)	41(1)
O(7)	-1838(3)	4112(3)	661(4)	40(1)
O(8)	2260(3)	5596(3)	2623(4)	43(1)
O(11)	3128(6)	980(5)	5474(7)	88(3)
O(12)	4478(6)	-785(4)	6394(7)	86(3)
O(13)	4430(5)	631(4)	8285(6)	77(2)
O(14)	2395(6)	80(5)	6938(8)	89(3)
O(21)	368(10)	9528(6)	2458(9)	144(5)
O(22)	2222(5)	7978(5)	2990(8)	96(3)
O(23)	2201(8)	9309(7)	1544(11)	158(5)
O(24)	518(8)	8420(7)	429(9)	123(4)
O(31)	4062(11)	7375(8)	8613(12)	171(6)
O(32)	5726(5)	6528(5)	7518(7)	82(3)
O(33)	3352(6)	6685(7)	6079(8)	119(4)
O(34)	4647(10)	5563(6)	8382(10)	131(5)
C(11)	1467(4)	3042(3)	724(4)	25(1)
C(12)	2212(5)	2167(3)	-184(5)	33(1)
C(21)	2873(4)	3805(3)	6417(5)	28(1)
C(22)	4394(4)	3080(4)	7082(5)	36(1)
C(31)	280(4)	6934(3)	5005(5)	28(1)
C(32)	368(7)	7939(5)	6043(10)	93(3)

is longer than 2.822Å of Sm_1-O_5). The others are bridging bidentate ligands. There is a centre of inversion between each pair of metal atoms linked by carboxylate bridges in $\{[La(Gly)_3 \cdot 2H_2O]. (ClO_4)_3\}_n$, but not in $\{Sm_2\ (Gly)_s(ClO_4)_s \cdot 9H_2O\}_n$.

Each La atom is coordinated to ten oxygen atoms; eight of them are from glycine molecules and two from water molecules. The mean distance for La-O is 2.621Å.

The bond distances and angles for the three glycine molecules given in Table 3 and Table 4 show similar configurations for all glycine molecules (except for the disorder of N(33)) in accord with data found in the literature.[16] All glycine molecules may be regarded as zwitterions, so N atoms of the glycine molecules do not take part in La coordination. The amino groups form intermolecular hydrogen bonds with carboxylate groups (N(13)-O(2) 2.678Å, N(23)-O(3) 2.643Å, N(33)-O(6) 2.788Å, N(33)-O(5) 2.896Å.

The ClO_4^- groups do not take part in La coordination, but are held between the chains by weak hydrogen bonds and electrostatic forces, thus increasing the stability of the crystals. The separation of La atoms is larger than 4.312 Å, so there is no metal to metal bond.

Table 3 Bond lengths (Å)

Atoms	Distance	Atoms	Distance
La-O(1)	2.694(3)	La-O(2)	2.730(3)
La-O(3)	2.517(2)	La-O(5)	2.851(3)
La-O(6)	2.653(4)	La-O(7)	2.602(3)
La-O(8)	2.660(4)	La-O(1a)	2.560(3)
La-O(4a)	2.482(3)	La-O(5a)	2.460(4)
Cl(1)-O(11)	1.420(6)	Cl(1)-O(12)	1.415(5)
Cl(1)-O(13)	1.444(5)	Cl(1)-O(14)	1.438(8)
Cl(2)-O(21)	1.399(9)	Cl(2)-O(22)	1.415(6)
Cl(2)-O(23)	1.352(11)	Cl(2)-O(24)	1.389(7)
Cl(3)-O(31)	1.522(10)	Cl(3)-O(32)	1.391(7)
Cl(3)-O(33)	1.367(6)	Cl(3)-O(34)	1.340(9)
N(13)-C(12)	1.470(6)	N(23)-C(22)	1.487(7)
N(33)-C(32)	1.204(14)	N(33')-C(32)	1.216(12)
O(1)-C(11)	1.267(4)	O(1)-Laa	2.560(3)
O(2)-C(11)	1.238(6)	O(3)-C(21)	1.250(5)
O(4)-C(21)	1.252(6)	O(4)-Lab	2.482(3)
O(5)-C(31)	1.249(6)	O(5)-Lab	2.460(4)
O(6)-C(31)	1.223(5)	C(11)-C(12)	1.505(6)
C(21)-C(22)	1.518(5)	C(31)-C(32)	1.502(8)

Symmetry codes: (a) -*X*, 1-*Y*, -*Z*; (b) -*X*, 1-*Y*, 1-*Z*.

Table 4 Selected bond angles(°).

Atoms	Angle	Atoms	Angle
O(1)-La-O(2)	47.8(1)	O(1)-La-O(3)	99.4(1)
O(2)-La-O(3)	66.3(1)	O(1)-La-O(5)	159.7(1)
O(2)-La-O(5)	130.2(1)	O(3)-La-O(5)	67.4(1)
O(1)-La-O(6)	123. 3(1)	O(2)-La-O(6)	151.7(1)
O(3)-La-O(6)	93.2(1)	O(5)-La-O(6)	46.2(1)
O(1)-La-O(7)	71.2(1)	O(2)-La-O(7)	73.8(1)
O(3)-La-O(7)	131.2(1)	O(5)-La-O(7)	129.2(1)
O(6)-La-O(7)	132.8(1)	O(1)-La-O(8)	72.2(1)
O(2)-La-O(8)	91.1(1)	O(3)-La-O(8)	68.0(1)
O(5)-La-O(8)	88.1(1)	O(6)-La-O(8)	62.1(1)
O(7)-La-O(8)	141.0(1)	O(11)-Cl(1)-O(12)	110.5(4)
O(11)-Cl(1)-O(13)	109.2(3)	O(12)-Cl(1)-O(13)	108.6(3)
O(11)-Cl(1)-O(14)	108.6(4)	O(12)-Cl(1)-O(14)	112.1(4)
O(13)-Cl(1)-O(14)	107.9(4)	O(21)-Cl(2)-O(22)	108.0(4)
O(21)-Cl(2)-O(23)	115.6(6)	O(22)-Cl(2)-O(23)	109.2(4)
O(21)-Cl(2)-O(24)	102.5(5)	O(22)-Cl(2)-O(24)	108.6(4)
O(23)-Cl(2)-O(24)	112.6(6)	O(31)-Cl(3)-O(32)	102.5(6)
O(31)-Cl(3)-O(33)	100.8(4)	O(32)-Cl(3)-O(33)	113.9(5)
O(31)-Cl(3)-O(34)	102.5(6)	O(32)-Cl(3)-O(34)	115.3(5)
O(33)-Cl(3)-O(34)	118.3(5)	O(1)-C(11)-O(2)	122.5(3)
O(1)-C(11)-C(12)	117.2(4)	O(2)-C(11)-C(12)	120.3(3)
N(13)-C(12)-C(11)	111.0(4)	O(3)-C(21)-O(4)	128.7(3)
O(3)-C(21)-C(22)	115.4(4)	O(4)-C(21)-C(22)	115.8(3)
N(23)-C(22)-C(21)	109.9(3)	O(5)-C(31)-O(6)	122.3(4)
O(5)-C(31)-C(32)	119.2(5)	O(6)-C(31)-C(32)	118.5(5)
N'(33)-C(32)-C(31)	128.3(7)	N(33)-C(32)-C(31)	124.2(9)

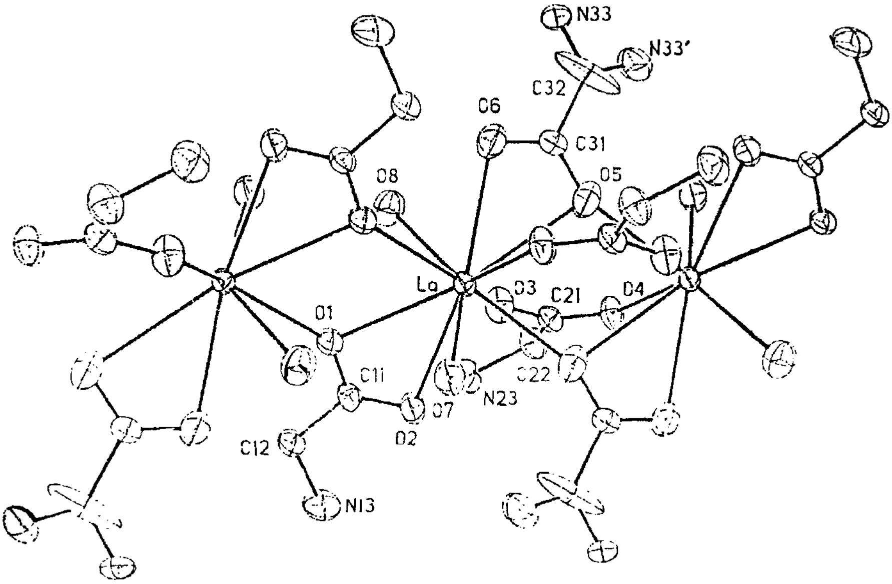

Figure 1 A part of the polymeric chain of the compound.

IR studies

IR spectra of the compound and glycine are shown in Figure 3. In the spectrum of glycine, the characteristic IR bands of the -COO$^-$ group at 1611cm^{-1} (υ as), 1412cm, 697cm^{-1} (δ), 607cm^{-1}(w), 503cm^{-1} (ρ) and of the -NH$^+{}_3$ group such as 3168cm^{-1} (υ as), 2824cm^{-1} (υ s), 1598cm^{-1} (δ as), 1521 and 1506cm^{-1} (δ s) appear.[17] This result also indicates that glycine molecules may be regarded as zwitterions NH$^+{}_3$-CH$_2$-COO$^-$. In the spectrum of the compound, characteristic

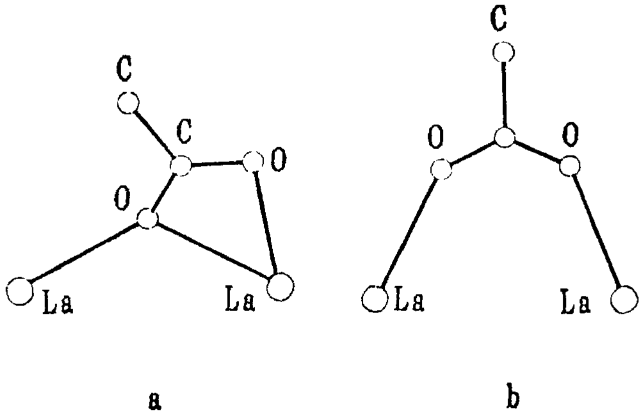

Figure 2 The two types of La-glycine contacts: (a) chelating-bridging terdentate; (b) briding bidentate; N atoms and H atoms are omitted.

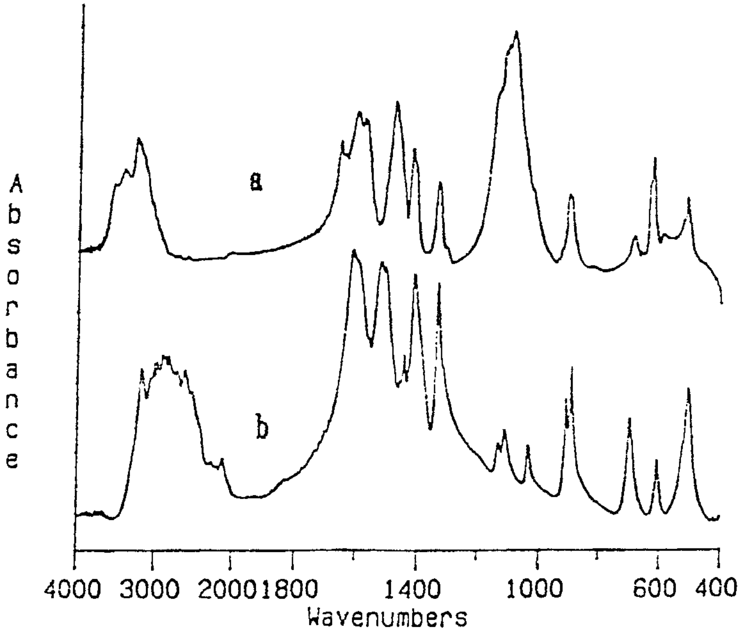

Figure 3 IR spectra of the compound (a) and glycine (b).

bands for -COO$^-$ and -NH$^+_3$ group also occur, and the characteristic bands of the -COOH group do not, again pointing to glycine retaining the zwitterion structure in the compound. The IR spectrum reveals υ as-COO$^-$ and υ s -COO$^-$ at 1657 cm^{-1} and 1422cm^{-1}, respectively, reflecting coordination of glycine molecules to La atoms *via* -COO$^-$ groups. The stretching bands of the -NH^+_s groups in the spectrum of the compound shift toward higher values, appearing at 3249 cm^{-1} and 2887 cm^{-1}, and bending bands toward lower values, appearing at 1580cm^{-1} and 1481cm^{-1} (compared with those of free glycine). This is due to strong intermolecular hydrogen bonds of -NH$^+_3$ with -COO$^-$ groups in free glycine[16] being destroyed

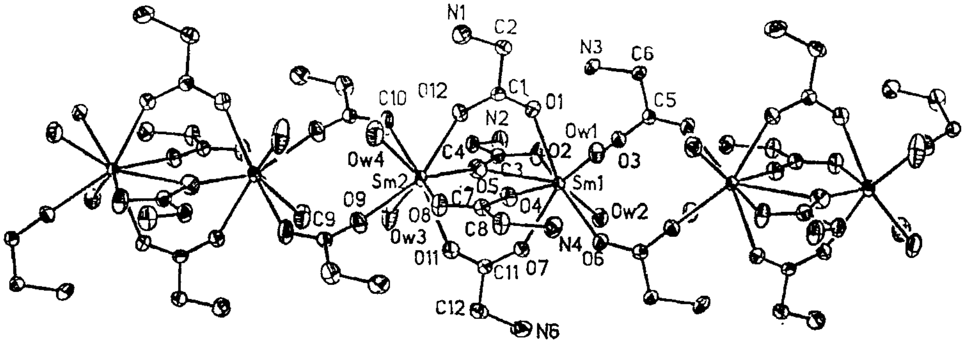

Figure 4 A part of the polymeric chain of $\{Sm_2(Gly)_6(ClO_4)_6 \cdot 9H_2O\}_n$.

when the compound is formed. A strong absorption band at 3549cm^{-1} in the compound is assigned to O-H stretching of coordinated water molecules.

In the IR spectrum of the compound, a weak band at 940cm^{-1}, three strong and broad bands from 1140–1070cm^{-1}, and a strong band at 630cm^{-1} are υ_1, υ_3 and υ_4 of the $ClO^-{}_4$ group, respectively; they are characteristic of ionic perchlorate. The appearance of υ_1 also indicates that the $ClO^-{}_4$ groups exist are distorted tetrahedra in the compound.[18]

In this compound, υ_{as}-COO^{-1} appears at 1657cm^{-1}, which is much higher than in free glycine and other compounds such as $\{Sm_2(Gly)_6(ClO_4)_6 \cdot 9H_2O\}_n$.[12] We also found that this case is in all related dimeric or polynuclear compounds[16] that have a centre of inversion between the two metal atoms linked by carboxylate bridges. The shift toward high values of υ as -COO$^-$ is a result of υ as -COO$^-$ coupling with Ln-O stretching vibrations in this special symmetric structure. In this case, the separation (Δ) between υ as -COO and υ s -COO$^-$ in this compound is 235cm^{-1}, greater than 214cm^{-1} in $\{Sm_2(Gly)_6 \cdot (ClO_4) \cdot 9H_2O\}_n$. Therefore, we can take Δ as a criterion for distinguishing the complexes.

Supplementary Material

Further information concerning details of the structure analysis is available from the authors on request, as are lists of observed and calculated structure factors, H atom positions and thermal parameters.

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