Inorganica Chimica Acta, 92 (1984) 151–157

Spectroscopy and Crystal Structure of Neodymium Coordination Compound with Glycine: $Nd_2(Gly)_6 \cdot (ClO_4)_6 \cdot 9H_2O$

J. LEGENDZIEWICZ, E. HUSKOWSKA

Institute of Chemistry, University of Wrocław, 50-380 Wrocław, Joliot-Curie 14, Poland

A. WAŚKOWSKA

Institute for Low Temperature and Structure Research, Polish Academy of Sciences, 50-950 Wrocław, Pl. Katedralny 1, Poland

Gy. ARGAY

Central Research Institute for Chemistry, Hungarian Academy of Sciences, Budapest-114, POB. 17, H-1525 Hungary

Received October 7, 1983

Neodymium complex compound with glycine: $Nd_2(Gly)_6 \cdot (ClO_4)_6 \cdot 9H_2O$ was synthesized and obtained in the form of monocrystals. Absorption spectra recorded in the region of 8000–35 000 cm^{-1} were measured along the crystallographic axes. Intensities of the f–f transitions were analysed on the basis of the Judd theory. The X-ray crystal structure determination of the complex is reported. Crystals are triclinic, space group $P\bar{1}$, with $a = 11.554(4)$ Å, $b = 14.108(1)$ Å, $c = 15.660(3)$ Å, $\alpha = 97.14(1)°$, $\beta = 102.82(2)°$, $\gamma = 105.28(1)°$, $V = 2355.25$ Å^3, $Z = 2$, $M.W. = 1495.4$, $D_c = 2.129(3)$ g cm^{-3}, $D_m = 2.103(1)$ g cm^{-3}. *The structure was solved by Patterson's method and successive Fourier syntheses giving the locations of all nonhydrogen atoms. The final R factor was 0.062 and* $R_w = 0.073$ *for 12869 reflections with* $|F_o| > 5\sigma|(F_o)|$. *The asymmetric unit consists of a dimeric formula unit. The coordination polyhedron of Nd atoms comprises seven oxygen atoms from glycine and two from water molecules. The neodymium–glycine bonding mode is compared with that of the calcium–glycine complex.*

Introduction

Lanthanide ions are widely applied as metal probes in systems of biological importance [1, 2]. Substitution of spectroscopically inert Ca(II) by Ln(III) allows the absorption, luminescence and NMR spectra to be studied [3–9]. Since in peptide and protein complexes Ca(II) is attached to aspartate and glutamate residues, it is important to explain the bonding of La(III) in the coordination compounds with amino acids. Such investigations are also important in the chemistry of lanthanides.

Studies in solution have shown that amino acids connect the lanthanide ions through the oxygen atoms of carboxyl groups, and the bonding *via* the nitrogen of the amino group in the pH range of 1.5 to 5.6 seems dubious [7–9, 11, 12]. When the pH is higher than 5.6, dimeric or polynuclear forms can be encountered [7, 11, 12]. Brittain's work (CPL method) yielded essential information on the conformation of amino acids in mixed-ligand complexes with Ln ions [10]. Up to the present, with the exception of the preliminary data on $NdCl_3 \cdot 3HGly \cdot 3H_2O$ by Poray-Koshits [13, 14], no X-ray diffraction studies on the structures of these compounds have been completed, however.

We have undertaken spectroscopic and X-ray studies on the crystal structure of $Nd_2(Gly)_6 \cdot (ClO_4)_6 \cdot 9H_2O$ which can be treated as a model for investigations of binding of the functional groups in amino acids.

Experimental

Spectroscopic Studies

The neodymium complex $Nd_2(Gly)_6 \cdot (ClO_4)_6 \cdot 9H_2O$ (hereinafter NGCH) was crystallized from an aqueous solution containing an excess of Nd^{3+} ions over the amino acid. The pH of the solution was kept in the range 1.4–3.3. The concentration of Nd^{3+} ions in the crystal was determined by EDTA titration using xylenol orange as the end-point indicator. The Nd^{3+} concentration was determined to be 2.7998 *M*. The density measured by the flotation method in a mixture of chloroform and ethylene bromide indicates the presence of approximately 4 water molecules per one $Nd(Gly)_3 \cdot (ClO_4)_3$ molecule. Chemical analysis indicates the presence of 5 water molecules. The crystal structure

0020-1693/84/$3.00

TABLE I. Atomic Positional Parameters and B_{eq} with e.s.d.s in Parentheses. The temperature factor is of the form: B_{eq} = 4/3* TRACE (B*G) (see ref. 15, p. 316).

	x/*a*	y/*b*	z/*c*	B_{eq}
Nd1	0.14822(4)	0.13091(3)	0.13745(3)	1.89(2)
Nd2	0.34691(4)	0.36430(2)	0.36216(2)	1.54(2)
Cl1	0.5596(2)	0.1480(2)	0.8404(2)	2.8(1)
Cl2	0.2908(2)	0.0356(2)	0.5232(2)	3.1(1)
Cl3	0.7605(3)	0.2428(2)	0.2564(2)	4.1(2)
Cl4	0.8270(2)	0.3230(1)	0.6263(1)	2.2(1)
Cl5	0.7675(2)	0.4628(2)	0.9723(1)	3.4(1)
Cl6	0.2252(2)	0.3967(2)	0.7246(2)	3.3(1)
O1A	0.6181(7)	0.1616(6)	0.7696(5)	3.7(4)
O1B	0.4624(7)	0.0539(5)	0.8169(6)	4.3(5)
O1C	0.5063(7)	0.2283(5)	0.8550(5)	3.6(4)
O1D	0.6474(10)	0.1475(7)	0.9224(6)	6.4(7)
O2A	0.4245(7)	0.0780(6)	0.5491(6)	4.7(5)
O2B	0.2597(8)	−0.0608(6)	0.5465(7)	4.9(6)
O2C	0.2353(8)	0.0976(7)	0.5688(8)	5.5(5)
O2D	0.2486(10)	0.0296(9)	0.4278(7)	6.7(7)
O3A	0.6447(19)	0.2633(15)	0.2515(14)	4.8(4)
O3B	0.8703(19)	0.3273(15)	0.2890(14)	4.8(4)
O3C	0.7597(18)	0.2088(15)	0.1635(13)	4.7(4)
O3D	0.7660(29)	0.1695(23)	0.3113(21)	5.0(8)
O3C′	0.7695(28)	0.1445(23)	0.2285(20)	5.0(8)
O3D′	0.7689(23)	0.2295(19)	0.3471(17)	5.0(6)
O4A	0.9154(7)	0.4144(5)	0.6199(5)	3.5(4)
O4B	0.7095(7)	0.3168(8)	0.5677(6)	5.8(5)
O4C	0.8673(8)	0.2398(5)	0.6026(6)	4.3(5)
O4D	0.8164(6)	0.3295(5)	0.7167(4)	2.9(4)
O5A	0.8017(8)	0.4248(7)	0.8954(5)	5.6(6)
O5B	0.7650(8)	0.3952(7)	1.0326(5)	5.4(5)
O5C	0.6430(8)	0.4708(7)	0.9437(7)	5.8(5)
O5D	0.8589(10)	0.5573(7)	1.0184(6)	8.0(8)
O6A	0.3434(7)	0.3983(7)	0.7820(6)	5.5(4)
O6B	0.1333(8)	0.3680(8)	0.7709(6)	5.3(5)
O6C	0.1946(9)	0.3244(8)	0.6461(7)	7.8(7)
O6D	0.2275(11)	0.4939(7)	0.7092(9)	8.4(9)
O11	0.0416(6)	−0.0456(4)	0.0975(4)	2.9(4)
O21	−0.0663(7)	−0.1849(5)	−0.0004(4)	4.3(5)
C11	0.0092(7)	−0.1374(5)	0.0728(5)	1.9(4)
C21	0.0664(9)	−0.1990(6)	0.1325(6)	3.1(5)
N11	0.1390(7)	−0.1385(6)	0.2222(5)	3.3(5)
O12	0.3641(5)	0.2046(4)	0.3048(4)	2.2(3)
O22	0.3023(5)	0.0561(4)	0.2161(4)	2.8(3)
C12	0.3739(7)	0.1193(5)	0.2843(5)	1.9(4)
C22	0.4767(7)	0.0881(5)	0.3398(5)	2.4(4)
N12	0.5478(7)	0.1662(5)	0.4212(5)	2.8(4)
O13	0.1674(5)	0.2446(4)	0.3840(4)	2.5(3)
O23	0.0894(6)	0.1081(4)	0.2746(4)	2.7(3)
C13	0.0961(7)	0.1578(5)	0.3480(5)	2.1(4)
C23	0.0049(8)	0.1089(6)	0.3967(6)	2.7(4)
N13	0.0260(8)	0.1706(6)	0.4862(5)	3.0(4)
O14	0.4621(5)	0.5376(4)	0.4012(4)	2.5(3)
O24	0.5773(6)	0.6787(4)	0.4957(3)	2.6(3)
C14	0.5161(6)	0.6294(5)	0.4187(4)	1.6(3)
C24	0.5101(7)	0.6870(5)	0.3446(5)	2.1(4)
N14	0.4272(7)	0.6210(5)	0.2584(4)	2.5(4)
O15	0.1968(5)	0.4467(4)	0.2775(4)	2.6(3)
O25	0.1520(5)	0.2915(4)	0.2083(4)	2.4(3)

(continued on facing page)

TABLE I. *(continued)*

	x/*a*	y/*b*	z/*c*	B_{eq}
C15	0.1309(7)	0.3743(5)	0.2168(5)	1.8(4)
C25	0.0201(7)	0.3852(5)	0.1509(5)	2.1(4)
N15	−0.0089(7)	0.4784(5)	0.1840(5)	2.8(4)
O16	0.3360(5)	0.2517(4)	0.1247(4)	2.7(3)
O26	0.4158(5)	0.3933(4)	0.2282(3)	2.4(3)
C16	0.4125(7)	0.3359(5)	0.1592(4)	2.0(4)
C26	0.5151(8)	0.3735(6)	0.1147(5)	2.4(4)
N16	0.5127(7)	0.2934(6)	0.0417(5)	3.1(4)
OW1	−0.0907(7)	0.1048(7)	0.1145(6)	5.8(4)
OW2	0.2380(6)	0.0539(5)	0.0229(5)	3.9(4)
OW3	0.5856(5)	0.3810(4)	0.3918(4)	2.9(3)
OW4	0.2537(5)	0.4600(4)	0.4665(4)	2.6(3)
OW5	0.0160(7)	0.3726(6)	0.4742(5)	3.7(4)
OW6	0.4959(9)	0.0870(7)	0.0624(7)	5.3(6)
OW7	0.0465(8)	0.1293(6)	0.6925(6)	5.1(6)
OW8	0.2800(9)	0.2761(8)	0.9204(6)	5.6(6)
OW9	0.2194(9)	0.0767(8)	0.8212(8)	6.6(6)
H21A	−0.001(1)	−0.256(1)	0.139(1)	4.3
H21B	0.124(1)	−0.226(1)	0.104(1)	4.3
H22A	0.442(1)	0.023(1)	0.358(1)	3.4
H22B	0.536(1)	0.077(1)	0.302(1)	3.4
H23A	−0.082(1)	0.102(1)	0.360(1)	3.6
H23B	0.011(1)	0.041(1)	0.403(1)	3.6
H24A	0.476(1)	0.743(1)	0.359(1)	3.0
H24B	0.596(1)	0.716(1)	0.338(1)	3.0
H25A	0.037(1)	0.388(1)	0.092(1)	3.0
H25B	−0.055(1)	0.326(1)	0.144(1)	3.0
H26A	0.502(1)	0.432(1)	0.088(1)	3.5
H26B	0.598(1)	0.395(1)	0.160(1)	3.5

determination revealed, however, only 4.5 water molecules.

Absorption spectra of the monocrystals, polished along the crystallographic axes, were recorded at room temperature in the region of 8000–35 000 cm^{-1} on a CARY 14 spectrophotometer. The oscillator strengths of f–f transitions were estimated by means of the standard integrating program ICH30.

X-ray Analysis

A NGCH crystal of dimensions 0.28 X 0.14 X 0.70 was mounted in a Lindemann-glass capillary to protect it from moisture. Intensity data were collected on an Enraf-Nonius CAD-4 diffractometer with graphite monochromated MoK_α radiation (λ = 0.71069 Å) using $2\theta-\omega$ scan technique in the θ range 1.5 to 30°. Cell constants were determined by the least-squares fit of the setting angles of 25 reflections. After data reduction of 17841 independent observations 12869 reflections with $|F_o| > 5\sigma(|F_o|)$ were taken as observed. No absorption correction (μMoK_α = 26.6 cm^{-1}) was applied. The positions of Nd^{3+} ions were derived from a Patterson map. Subsequent structure factor and Fourier calculations revealed the positions of 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 of the ClO_4^- groups was found to exhibit partial positional disorder. Two of its oxygen atoms, O(3C) and O(3D), were located in two distinct positions with an occupancy factor of 0.5, respectively. The Cl–O distances in this distorted tetrahedron were constrained to the average of the other five ClO_4^- tetrahedrons (1.43 Å). This phenomenon did not permit the location of the H atoms in difference Fourier synthesis. Consequently, the H atoms belonging to CH_2 groups could only be generated from assumed geometries with C–H distances constrained to 1.00 Å. The other H atoms could not be located, however. The refinement was terminated at R = 0.062, R_w = 0.073 ($w = [\sigma^2(F_o) + 0.25(pF_o)^2]^{-1}$ with p = 0.01) and R_{tot} = 0.078.

Scattering factors for neutral atoms were taken from International Tables for X-ray Crystallography [15]. Atomic positional parameters with B_{eq} are given in Table I (anisotropic thermal parameters and list of F_o and F_c have been deposited). Crystallographic calculations were performed on a PDP 11/34 computer using the Enraf-Nonius SDP-34 program package.

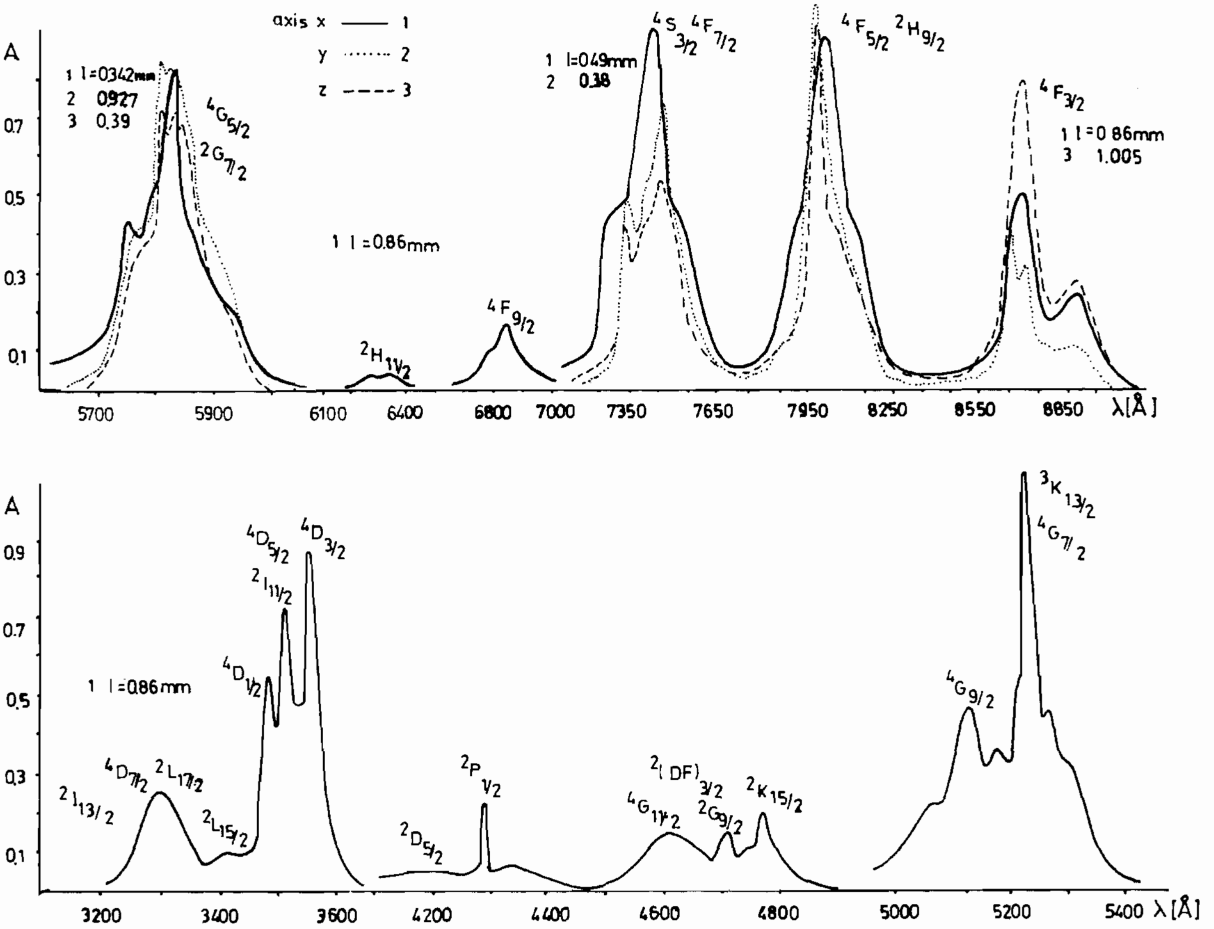

Fig. 1. Absorption spectra of NGCH measured along the three crystallographic axes.

TABLE II. Oscillator Strengths of f–f Transitions for the $Nd_2(Gly)_6(ClO_4)_6 \cdot 9H_2O$ Crystal.

Spectral Region	S'L'J'	P × 10^8		P × 10^8		P × 10^8	
		Expt-a	Calc.	Expt-b	Calc.	Expt-c	Calc.
9090–9300	$^4F_{3/2}$	203.01	214.86	314.06	216.92	294.86	227.79
8330–7700	$^4F_{5/2}$ $^2H_{9/2}$	862.90	900.11	863.70	862.40	905.97	855.80
7700–7200	$^4S_{3/2}$ $^4F_{7/2}$	1004.00	1048.99	926.32	981.79	848.17	958.35
7040–6580	$^4F_{9/2}$	75.77	77.78	62.02	73.37	77.20	71.92
6410–6170	$^2H_{11/2}$	18.00	21.30	8.78	20.14	14.53	19.92
6024–5500	$^4G_{5/2}$ $^2G_{7/2}$	1282.20	1303.50	1228.78	1242.94	1035.10	1054.50
5376–4950	$^2K_{13/2}$ $^4G_{7/2}$ $^4G_{9/2}$	832.23	555.38	729.25	538.87	799.21	534.51
4950–4460	$^2K_{15/2}$ $^2G_{9/2}$	257.50	140.70	238.50	136.50	274.60	138.40

(continued on facing page)

TABLE II. *(continued)*

Spectral Region	S'L'J'	$P \times 10^8$		$P \times 10^8$		$P \times 10^8$	
		Expt-a	Calc.	Expt-b	Calc.	Expt-c	Calc.
	$(^2D^2F)_{9/2}$						
	$^2G_{11/2}$						
4330–4250	$^2P_{1/2}$	47.00	52.60	52.02	53.80	74.80	57.91
4250–4130	$^2D_{5/2}$						
3620–3360	$^4D_{3/2}$	919.30	977.20	934.41	998.40	975.80	1063.61
	$^2I_{11/2}$						
	$^4D_{1/2}$						
	$^2L_{15/2}$						
3360–3190	$^2I_{13/2}$	304.50		291.80		292.81	
	$^4D_{7/2}$						
	$^2L_{17/2}$						
	RMS Deviation	1.15×10^{-7}		0.94×10^{-7}		1.28×10^{-7}	

The τ_λ parameters values

	$\tau_2 \times 10^9$	$\tau_4 \times 10^9$	$\tau_6 \times 10^9$
a	3.65 ± 0.85	5.48 ± 0.78	11.49 ± 1.10
b	3.25 ± 0.68	5.67 ± 0.53	10.70 ± 0.88
c	1.83 ± 0.93	6.17 ± 0.86	10.40 ± 1.20
Mean	2.83 ± 0.76	5.92 ± 0.71	10.80 ± 0.99

Results and Discussion

Spectroscopic Studies

The absorption spectra of NGCH measured along the three crystallographic axes are shown in Fig. 1. The oscillator strength of an electric dipole transition within the $4f^N$ ground configuration of a rare-earth ion is given by

$$P = 4.32 \times 10^{-9} \int_{\sigma_1}^{\sigma_2} \epsilon_\sigma d\sigma \qquad (1)$$

where ϵ_σ is the molar extinction coefficient for the particular value of the transition energy σ expressed in cm^{-1}.

The absorption spectrum is complex and different along the three crystallographic axes. The oscillator strength for all measured bands was calculated; the results are shown in Table II. A relation was set up between the intensities of f–f transitions and the position of crystallographic axes. Based on the Judd theory, the intensities of f–f transitions were analysed taking into account the anisotropy of intensities along the axis directions in the crystal. From the oscillator strengths the values of parameters τ_λ were calculated from the Judd–Ofelt equation:

$$P = \sum_{\lambda=2,4,6} \tau_\lambda \sigma |\langle f^N SLJ \| U^\lambda \| f^N S'L'J' \rangle|^2 (2J+1)^{-1} \qquad (2)$$

where $\langle f^N SLJ \| U^\lambda \| f^N S'L'J' \rangle$ is the reduced matrix element of the unit tensor operator, U^λ, τ_λ are phenomenological parameters estimated from experimental data and σ is the wavenumber in cm^{-1}.

Since eqn. 2 comprises no polarization or angular terms, the total integrated absorbances (over direction and polarization) are required in order to fit the theory. The best procedure is to average the oscillator strengths of each band over the three directions.

It should be noted that the intensity of the so called hypersensitive transition $^4J_{9/2} \rightarrow {}^4G_{5/2}, {}^2G_{7/2}$ is not as high as would be expected for such a low symmetry.

The values of τ_λ shown in Table II for defined orientations of the crystal were calculated from averaged oscillator strengths over all the bands. For three distinct orientations of the crystal, considerable differences were observed in the τ_λ parameters. The values of τ_λ exceeded those of aquo ion and of tetra phosphates. It seems that the intensities of hypersensitive transitions are influenced not only by the symmetry of the Ln ion but probably also by the metal–oxygen distances.

TABLE III. Nd–O Distances (Å) [* and ** means atoms with symmetry operations (–x, –y, –z) and (1 – x, 1 – y, 1 – z) respectively] and Bond Distances (Å) and Angles (°) in Glycine Molecules (numbered as i = 1, ..., 6). (E.s.d.s in bond distances Nd–O vary from 0.005–0.008; in glycine molecules from 0.005–0.010 in bonds and from 0.8–1.0 in angles.

Nd1–O11	2.401	Nd2–O12	2.395
Nd1–O12	3.037	Nd2–O13	2.425
Nd1–O22	2.478	Nd2–O14	2.382
Nd1–O23	2.425	Nd2–O15	2.558
Nd1–O25	2.381	Nd2–O25	2.773
Nd1–O16	2.445	Nd2–O26	2.446
Nd1–OW1	2.622	Nd2–OW3	2.634
Nd1–OW2	2.532	Nd2–OW4	2.579
Nd1–O21*	2.443	Nd2–O24**	2.417

i	O_{1i}–C_{1i}	O_{2i}–C_{1i}	C_{1i}–C_{2i}	C_{2i}–N_{1i}
1	1.234	1.257	1.515	1.486
2	1.247	1.266	1.507	1.491
3	1.260	1.245	1.507	1.488
4	1.246	1.262	1.497	1.500
5	1.247	1.252	1.511	1.500
6	1.249	1.254	1.516	1.494

i	$<O_{1i}C_{1i}O_{2i}$	$<O_{1i}C_{1i}C_{2i}$	$<O_{2i}C_{1i}C_{2i}$	$<C_{1i}C_{2i}N_{1i}$
1	124.9	118.7	116.3	112.0
2	123.0	120.4	116.7	111.0
3	127.2	117.2	115.5	111.5
4	124.4	119.0	116.5	110.8
5	122.5	119.5	118.0	110.2
6	127.3	117.3	115.4	110.5

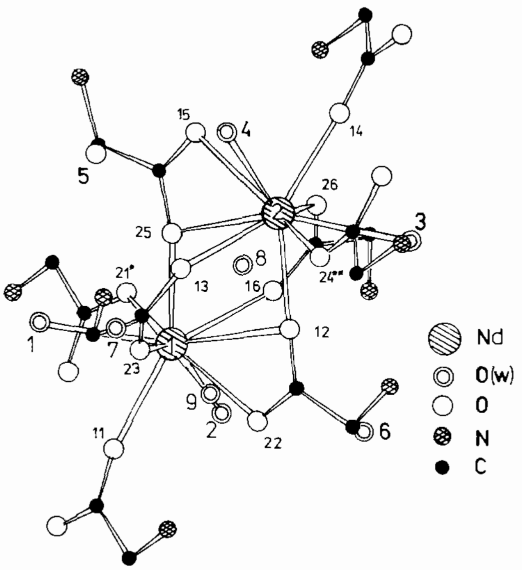

Fig. 2. Coordination of the Nd^{3+} cations.

Description of the Structure

The structure of NGCH consists of binuclear $[Nd(Gly)_3 \cdot 2H_2O]^{3+}$ cations, perchlorate ions and water molecules. The stereochemistry of the cation is shown in Fig. 2. Both Nd ions located in two symmetrically distinct positions are coordinated to nine O atoms: seven of them are from glycine and two from water molecules. The Nd–O distances are listed in Table III. The mean distances for Nd(1)–O and Nd(2)–O are 2.529(7) and 2.512(7) Å. There are two types of Nd–Gly contacts (Fig. 3). Gly(2) and Gly(5) contribute both of their oxygens to the coordination sphere of the one Nd atom and, in addition, one of the oxygens from each glycine forms the oxygen bridge with another Nd atom (Fig. 3a). Each oxygen of Gly(1), (3), (4) and (6) is in contact with two symmetry independent Nd atoms (Fig. 3b). The presence of oxygen bridges explains the considerable differences in the Nd–Nd distances:

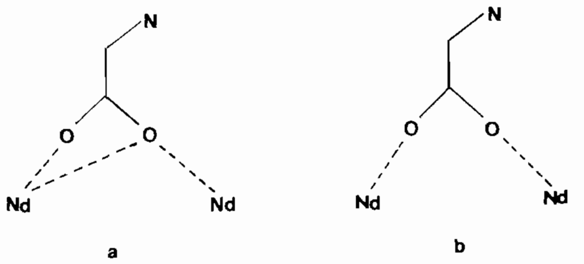

Fig. 3. Nd–glycine contacts: (a) both oxygens of glycine bonded to one Nd atom and oxygen bridge to the symmetry independent Nd (glycines 2 and 5); (b) each oxygen of glycine connected to two different Nd atoms.

$Nd(1)^{I}$–$Nd(2)^{I}$ = 4.248(1) Å
$Nd(1)^{I}$–$Nd(1)^{II}$ = 5.171(1) Å
$Nd(2)^{I}$–$Nd(2)^{II}$ = 5.271(1) Å
I: x, y, z II: $\bar{x}, \bar{y}, \bar{z}$

The bond distances and angles for the six glycine molecules given in Table III show similar configurations for all Gly molecules in accord with data found in the literature [16, 17]. All Gly molecules may be regarded as zwitterions, $NH_3^+CH_2COO^-$. The

TABLE IV. Bond Distances and Angles for Non Distorted ClO_4 Tetrahedra with their E.S.D.s.

	Cl–O (A)			O–Cl–O (°)		
	min	max	ave	min	max	ave
1	1.428(6)	1.451(8)	1.440	107.7(7)	111.6(7)	109.4
2	1.425(8)	1.449(8)	1.436	107.4(8)	110.4(8)	109.4
4	1.410(5)	1.449(6)	1.434	106.7(7)	111.9(7)	109.4
5	1.423(6)	1.447(9)	1.438	107.5(7)	113.0(8)	109.5
6	1.408(8)	1.452(8)	1.423	106.5(9)	114.0(9)	109.4

C and O atoms form planar groups. The ClO_4 groups do not take part in the Nd coordination. Their geometries (except that of Cl(3)) are given in Table IV.

Conclusions

1. It was found that the f–f transition intensities depend strongly on the direction of measurements with respect to the crystallographic axis.

2. Due to the presence of the oxygen bridge the Nd(1)–Nd(2) distance is much shorter than the $Nd(1)^I$–$Nd(1)^{II}$ and $Nd(2)^I$–$Nd(2)^{II}$ distances. This fact explains the considerable increase of energy transfer in the Tb–Eu systems containing amino acids [9]. The presented structure confirms our earlier suggestion on the existence of dimers in systems of Ln ions with amino acids in aqueous solution [8, 9].

A comparison of the structures of NGCH and $(NH_2CH_2COOH)_3CaI_2 \cdot H_2O$ [16] shows considerable differences in the bonding of glycine molecules with Nd^{3+} and Ca^{3+} ions. In NGCH, all oxygen atoms of Gly molecules are involved in bonding with the metal ion. Two of six glycine molecules form a bidentate bond with one Nd atom, and simultaneously connect to the next symmetry independent Nd atom through an oxygen bridge (mode 1). The other glycine units are bonded to two different Nd atoms (mode 2). In the complex compound with calcium, only one of the Gly molecules is bidentate, connected to two Ca atoms; the other glycine molecules are monodentate. Although the Nd^{3+} and Ca^{2+} ions combine the same functional groups in both complex compounds, the bonding modes are different.

Acknowledgement

The authors thank Professor A. Kálmán (Budapest) for his approval for and interest in the joint work.

References

1 R. B. Martin and F. S. Richardson, *Quart. Rev. Biophys., 12,* 181 (1979).

2 E. Niober, 'Structure and Bonding' (1975).

3 W. De W. Horrocks, Jr. and D. R. Sudnick, *J. Am. Chem. Soc., 101,* 334 (1979).

4 W. De W. Horrocks, Jr. and W. E. Collier, *J. Am. Chem. Soc., 103,* 2856 (1981).

5 H. G. Brittain, F. S. Richardson and R. B. Martin, *J. Am. Chem. Soc., 98,* 8255 (1976).

6 H. G. Brittain, *Coord. Chem. Rev.* (in press).

7 H. G. Brittain, *J. Inorg. Nucl. Chem., 43,* 1719 (1981).

8 J. Legendziewicz, E. Huskowska, H. Kozłowski and B. J. Trżebiatowska, *Inorg. Nucl. Chem. Letters, 15,* 349 (1959); *ibid., 17,* 57 (1981); *ibid., 14,* 400 (1978).

9 J. Legendziewicz and E. Huskowska, *J. of Luminescence, 24/25,* 819 (1981).

10 H. G. Brittain, *Inorg. Chim. Acta, 70,* 91 (1983).

11 R. Prados, L. G. Stadtherr, H. Donato Jr. and R. B. Martin, *J. Inorg. Nucl. Chem., 36,* 689 (1974).

12 H. G. Brittain, *Inorg. Chem., 18,* 1740 (1979).

13 K. F. Belayeva, M. A. Poray-Koshits, T. J. Malinowski, L. A. Aslanov, L. S. Sukhanova and L. T. Matynenko, *Z. Struct. Khimii, 10 (3),* 557 (1969).

14 K. F. Belayeva, M. A. Poray-Koshits, T. J. Malinowski and N. D. Mitrofanowa, *Tezisy Dokl. 12-th Vses. Chugaevskoe Soveshch. Khim. Kompleks. Sojedin, 2,* 246 (1975).

15 International Tables for X-ray Crystallography, Vol. IV, Kynoch Press, Birmingham (1974).

16 S. Natarajan and J. K. Mohana Rao, *J. Inorg. Nucl. Chem., 43,* 1693 (1981).

17 K. Itoh and T. Mitsui, *Ferroelectrics, 5,* 241 (1975).