Synthesis, properties and structure of δ-valerolactam lanthanide perchlorate complexes

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Abstract

Complexes with formula $[LnL_8](ClO_4)_3$ (Ln = La–Ho) and $[LnL_7](ClO_4)_3$ (Ln = Er–Lu, Y; L = δ-valerolactam) were synthesized and characterized by conductance measurements, IR spectra, X-ray powder diffraction patterns, electronic absorption spectra of the neodymium and emission spectrum of the europium compounds. X-ray single crystal structural analysis of the neodymium compound showed that it forms monoclinic crystals, space group $P2_1/n$ with $a = 25.491(4)$, $b = 16.074(3)$, $c = 13.051(3)$ Å and $\beta = 90.15(3)°$. Neodymium ions are coordinated in a square-antiprismatic arrangement to eight oxygen atoms of the δ-valerolactam ligands. The average Nd–O bond length is 2.45(1) Å. The non-coordinated ClO_4^- ions are partially disordered.

Introduction

Lanthanide complexes containing eight equal unidentate ligands are known from the literature [1–3] to prefer a square-antiprismatic geometry in the metal coordination sphere. But with some ligands such as pyridine-*N*-oxide two different crystalline forms for the $M(PyO)_8(ClO_4)_3$ [1] (M = La, Nd) complexes have been found: one of square-antiprismatic geometry around the metal ion and the second where the coordination geometry is intermediate between a cube and a square-antiprism (SAP). With a similar ligand, 4-picoline-*N*-oxide, we have recently synthesized the complexes $Ln(4\text{-}pic\text{-}NO)_n(CF_3SO_3)_3$ ($n = 8$ for La–Gd; 7 for Tb–Lu, Y) [3] which have been characterized also by X-ray powder diffractions and X-ray single crystal analysis on the Nd derivative. Only one crystalline modification of SAP geometry has been ascertained. We have already reported the synthesis, characterization [4] and a thermogravimetric study [5] on the δ-valerolactam lanthanide trifluoromethane sulfonate complexes of composition $LnL_8(CF_3SO_3)_3$ (Ln = La–Lu, Y). In order to compare the behaviour of the δ-valerolactam ligand in salts containing the perchlorate as counter ion, complexes of the whole lanthanide series were synthesized. The resulting compounds are of composition $[LnL_8](ClO_4)_3$ (Ln = La–Ho) and $[LnL_7](ClO_4)_3$ (Ln = Er–Lu, Y). The physicochemical characterization of these compounds together with the crystal and molecular structure of the Nd derivative are the subject of the present paper.

Experimental

The complexes were prepared by reaction of the hydrated lanthanide perchlorate with δ-valerolactam (Aldrich) using triethyl-orthoformate (teof) as reaction medium. After standing for about 2 h the compounds were filtered, washed with teof and dried *in vacuo* over anhydrous calcium chloride.

Analysis and measurements

Lanthanides were determined by complexometric titration with EDTA [6] and carbon, hydrogen and nitrogen by the usual microanalytical procedures. Electrolytic conductance data in acetonitrile and nitromethane were determined at 25.00 ± 0.02 °C using a bridge composed of a pointer galvanometer, a resistance box and a cell ($K_c = 0.10708$ cm^{-1}) from Leeds and Northrup. IR

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spectra were recorded in a Perkin-Elmer model 180 spectrophotometer, using Nujol mulls, between KBr plates. Absorption spectra of neodymium compound Kel-F mulls were recorded at room temperature and at 77 K, and also in acetonitrile and nitromethane solutions at room temperature in a Cary 17 spectrophotometer. The emission spectrum of the europium complex was determined in a Perkin-Elmer MPF-4 spectrofluorimeter, with 391 nm excitation radiation. The refractive indexes of the solutions were determined at 25 °C with an Abbé type, Bausch and Lomb refractometer.

X-ray diffraction studies

Single crystal data

A large number of crystals were examined for crystallographic suitability. A white prismatic crystal was selected for data collection. Data were obtained on a PW1100 Philips four-circle computer-controlled diffractometer. Mo Kα ($\lambda = 0.71069$ Å) radiation with graphite crystal monochromator in the incident beam, was utilized in the data collection. The unit cell dimensions were obtained by a least-squares fit of 25 centered reflections in the range $10 \leqslant \theta \leqslant 13°$. Intensity data were collected using the ω–2θ technique to a maximum 2θ of 46°. The scan width, for each reflection was 1.20° with a scan speed 1.8°/min. Background measurements were made for a total of 20 s at both limits of each scan. Three standard reflections were monitored every 60 min. No systematic variations in intensities were found. Reflections with $I \leqslant 3\sigma I$ were considered unobserved and were rejected from the refinement process.

Intensities were corrected for Lorentz, polarization and absorption effects (based on the Ψ scans of three reflections). The structure was solved using three-dimensional Patterson and Fourier techniques and refined by block-matrix least-squares (two blocks) with ani-

TABLE 1. Crystal and refinement data for $[NdL_8](ClO_4)_3$

Formula	$C_{40}H_{72}N_8O_{20}Cl_3Nd$
Formula weight	1235.65
Space group	$P2_1/n$
a (Å)	25.491(4)
b (Å)	16.074(3)
c (Å)	13.051(3)
β (°)	90.15(3)
D_c (g cm^{-3})	1.54
No. unique reflections	8309
No. reflections with ($I \geqslant 3\sigma I$)	4371
R[a]	0.058
R_w[a]	0.065
GOF	1.57
w	$[\sigma^2(F_o) + 0.003708(F_o)^2]^{-1}$

[a] $R = \Sigma(|F_o| - |F_c|)/\Sigma|F_o|$; $R_w = [\Sigma w(|F_o| - |F_c|)^2/\Sigma w|F_o|^2]^{1/2}$.

TABLE 2. Fractional coordinates with equivalent isotropic thermal parameters with e.s.d.s in parentheses

Atom	x/a	y/b	z/c	$U_{iso*/eq}$[a]	pp[b]
Nd	0.44086(2)	0.25339(4)	0.38373(4)	0.0313(2)	
Cl(1)	0.6881(2)	0.2306(4)	0.4016(4)	0.089(2)	
O(12)	0.7048(9)	0.257(1)	0.313(2)	0.171(8)*	
O(11)	0.6976(7)	0.136(1)	0.396(1)	0.157(7)*	
O(13)	0.6334(5)	0.2331(8)	0.404(1)	0.093(4)*	
O(14)	0.706(1)	0.242(1)	0.491(2)	0.190(9)*	
Cl(2)	0.4551(3)	0.2740(4)	0.8527(4)	0.106(3)	
O(21)	0.449(6)	0.366(1)	0.874(1)	0.063(5)*	0.6
O(22)	0.4528(5)	0.2626(7)	0.746(1)	0.097(4)*	
O(210)	0.893(2)	0.246(2)	0.388(3)	0.12(1)*	0.4
O(230)	0.958(1)	0.246(2)	0.460(3)	0.094(9)*	0.4
O(240)	0.941(2)	0.359(4)	0.370(4)	0.23(3)*	0.4
O(231)	0.5116(8)	0.257(1)	0.880(2)	0.090(6)*	0.6
O(241)	0.429(1)	0.224(2)	0.896(2)	0.089(7)*	0.6
Cl(3)	0.8155(2)	0.7373(5)	0.6164(4)	0.115(3)	
O(31)	0.7591(5)	0.7399(7)	0.624(1)	0.093(4)*	
O(341)	0.835(2)	0.761(3)	0.722(3)	0.16(2)*	0.5
O(330)	0.825(1)	0.721(2)	0.508(2)	0.084(8)*	0.5
O(331)	0.838(1)	0.765(2)	0.527(3)	0.12(1)*	0.5
O(340)	0.825(1)	0.837(2)	0.629(2)	0.13(1)*	0.5
O(320)	0.841(1)	0.701(2)	0.690(3)	0.13(1)*	0.5
O(321)	0.826(1)	0.634(2)	0.641(2)	0.112(9)*	0.5
O(1)	0.3655(3)	0.1719(5)	0.3209(6)	0.043(3)	
C(11)	0.3444(6)	0.1456(7)	0.239(1)	0.044(5)	
N(1)	0.3658(4)	0.1531(7)	0.1490(8)	0.054(4)	
C(13)	0.3448(6)	0.135(1)	0.054(1)	0.071(7)	
C(14)	0.2935(6)	0.081(1)	0.064(1)	0.098(9)	
C(15)	0.2603(6)	0.096(1)	0.152(1)	0.096(9)	
C(16)	0.2960(5)	0.102(1)	0.249(1)	0.056(5)	
O(2)	0.5158(3)	0.3318(5)	0.3212(7)	0.047(3)	
N(2)	0.5165(6)	0.363(1)	0.152(1)	0.092(6)	
C(21)	0.5394(4)	0.3540(7)	0.241(1)	0.039(4)	
C(26)	0.5905(5)	0.384(1)	0.249(1)	0.095(9)	
C(25)	0.6214(6)	0.392(1)	0.147(1)	0.102(9)	
C(24)	0.584(1)	0.414(2)	0.056(1)	0.14(1)	
C(23)	0.5390(9)	0.390(2)	0.066(2)	0.15(1)	
O(3)	0.4068(3)	0.3309(5)	0.2373(6)	0.042(3)	
C(31)	0.3675(6)	0.3563(8)	0.1903(9)	0.040(5)	
N(3)	0.3218(4)	0.3560(7)	0.2354(8)	0.048(4)	
C(35)	0.3192(5)	0.405(1)	0.027(1)	0.064(6)	
C(34)	0.2794(6)	0.437(1)	0.096(1)	0.068(6)	
C(33)	0.2705(6)	0.377(1)	0.184(1)	0.071(6)	
C(36)	0.3704(5)	0.391(1)	0.086(1)	0.058(5)	
O(4)	0.4747(3)	0.3351(6)	0.5249(7)	0.057(4)	
C(41)	0.5145(6)	0.3672(8)	0.565(1)	0.053(5)	
N(4)	0.5638(5)	0.3448(7)	0.543(1)	0.062(5)	
C(43)	0.6118(6)	0.371(1)	0.595(1)	0.085(7)	
C(44)	0.6033(8)	0.441(1)	0.659(2)	0.12(1)	
C(45)	0.5543(8)	0.449(2)	0.709(2)	0.15(1)	
C(46)	0.5067(6)	0.4346(9)	0.648(1)	0.068(6)	
O(5)	0.4739(3)	0.1762(5)	0.2339(6)	0.046(3)	
C(51)	0.5134(4)	0.1477(7)	0.1894(9)	0.034(4)	
N(5)	0.5604(4)	0.1505(7)	0.2325(9)	0.050(4)	
C(53)	0.6082(5)	0.123(1)	0.186(1)	0.061(6)	
C(54)	0.5981(6)	0.064(1)	0.096(1)	0.080(7)	
C(55)	0.5588(6)	0.099(1)	0.030(1)	0.65(6)	
C(56)	0.5083(5)	0.109(1)	0.088(1)	0.064(6)	
O(6)	0.5123(3)	0.1649(6)	0.4472(7)	0.054(3)	
C(61)	0.5349(5)	0.1313(8)	0.5209(9)	0.039(4)	

(*continued*)

TABLE 2. (*continued*)

Atom	x/a	y/b	z/c	$U_{iso*/eq}$[a]	pp[b]
N(6)	0.5191(4)	0.1474(7)	0.6134(8)	0.053(4)	
C(63)	0.5449(7)	0.111(1)	0.709(1)	0.084(8)	
C(64)	0.5751(8)	0.043(1)	0.690(1)	0.095(8)	
C(65)	0.6071(6)	0.050(1)	0.601(1)	0.101(9)	
C(66)	0.5771(6)	0.065(1)	0.501(1)	0.078(7)	
O(7)	0.4073(3)	0.1739(6)	0.5306(6)	0.053(3)	
C(71)	0.3656(5)	0.1497(7)	0.575(1)	0.043(4)	
N(7)	0.3196(4)	0.1557(8)	0.5285(9)	0.057(4)	
C(73)	0.2682(6)	0.139(1)	0.581(1)	0.078(6)	
C(74)	0.2750(6)	0.096(2)	0.678(2)	0.13(1)	
C(75)	0.3211(7)	0.096(2)	0.733(1)	0.12(1)	
C(76)	0.3732(5)	0.110(1)	0.675(1)	0.059(6)	
O(8)	0.3658(3)	0.3366(6)	0.4476(6)	0.052(3)	
C(81)	0.3426(5)	0.3638(8)	0.525(1)	0.041(5)	
N(8)	0.3673(5)	0.3518(7)	0.6174(9)	0.059(5)	
C(86)	0.2923(6)	0.401(1)	0.519(1)	0.078(7)	
C(85)	0.271(1)	0.420(2)	0.623(1)	0.15(1)	
C(84)	0.2940(7)	0.420(2)	0.702(2)	0.13(1)	
C(83)	0.3413(7)	0.372(1)	0.717(1)	0.082(7)	

[a] U_{eq} is defined as one third of the trace of the orthogonalized U_{ij} tensor. [b] Indicated when different from 1.

sotropic thermal parameters assigned to the non-hydrogens atoms of the NdL_8 units. The perchlorate anions were disordered and two main statistic distributions for two of them were considered in the isotropic refinement. Hydrogen atoms were introduced at the idealized positions, C–H fixed at 0.98 Å with a unique thermal factor ($U = 0.08$ Å^2). Atomic scattering factors were taken from ref. 7. Pertinent crystallographic data are reported in Table 1.

Data processing and computation were carried out using the SHELX 76 program package [8], and drawings were performed by ORTEP [9].

Final fractional coordinates for non-hydrogen atoms with equivalent thermal parameters are reported in Table 2, while main bond lengths and angles are reported in Table 3.

Powder spectra

The products were aggregates of microcrystalline particles and were powdered in an agate mortar. Some of the compounds were deliquescent and the powder spectra collection was possible only for Ce, Pr, Nd and Lu. Thin layers of the samples were deposited from acetone solutions on an oriented quartz-plate. The tube-generated, X-ray data were collected using Cu Kα radiation on a Philips PW1700 automated powder diffractometer using Cu Kα 1,2 radiations ($\lambda_1 = 1.54051$, λ_2 1.54430 Å) with diffracted-beam curved graphite monochromators. The experimental conditions were: focusing geometry with θ–2θ scanning mode, stationary flat specimen, divergence slit (1°), peak angle range 5–60°, range in d spacing 1.54–17.63 Å, peak position criterion top of smoothed data, crystal peak width range 0–2°, generator settings 40 kV, 40 mA.

TABLE 3. Selected bond distances (Å) and angles (°) with e.s.d.s in parentheses

Nd–O(1)	2.464(8)	Nd–O(2)	2.432(8)
Nd–O(3)	2.439(8)	Nd–O(4)	2.419(9)
Nd–O(5)	2.466(8)	Nd–O(6)	2.453(9)
Nd–O(7)	2.460(9)	Nd–O(8)	2.480(9)
O(1)–C(11)	1.27(2)	C(11)–N(1)	1.30(2)
C(11)–C(16)	1.42(2)	N(1)–C(13)	1.38(2)
C(13)–C(14)	1.57(2)	C(14)–C(15)	1.44(2)
C(15)–C(16)	1.57(2)	O(2)–C(21)	1.25(2)
N(2)–C(21)	1.31(2)	N(2)–C(23)	1.33(3)
C(21)–C(26)	1.39(2)	C(26)–C(25)	1.55(2)
C(25)–C(24)	1.57(3)	C(24)–C(23)	1.21(3)
O(3)–C(31)	1.24(2)	C(31)–N(3)	1.31(2)
C(31)–C(36)	1.47(2)	N(3)–C(33)	1.51(2)
C(35)–C(34)	1.44(2)	C(35)–C(36)	1.53(2)
C(34)–C(33)	1.52(2)	O(4)–C(41)	1.25(2)
C(41)–N(4)	1.34(2)	C(41)–C(46)	1.55(2)
N(4)–C(43)	1.46(2)	C(43)–C(44)	1.42(3)
C(44)–C(45)	1.41(3)	C(45)–C(46)	1.47(3)
O(5)–C(51)	1.25(1)	C(51)–N(5)	1.32(1)
C(51)–C(56)	1.47(2)	N(5)–C(53)	1.43(2)
C(53)–C(54)	1.53(2)	C(54)–C(55)	1.44(2)
C(55)–C(56)	1.50(2)	O(6)–C(61)	1.24(1)
C(61)–N(6)	1.30(2)	C(61)–C(66)	1.54(2)
N(6)–C(63)	1.52(2)	C(63)–C(64)	1.36(3)
C(64)–C(65)	1.42(3)	C(65)–C(66)	1.54(2)
O(7)–C(71)	1.27(2)	C(71)–N(7)	1.32(2)
C(71)–C(76)	1.47(2)	N(7)–C(73)	1.50(2)
C(73)–C(74)	1.46(3)	C(74)–C(75)	1.37(3)
C(75)–C(76)	1.54(2)	O(8)–C(81)	1.25(2)
C(81)–N(8)	1.37(2)	C(81)–C(86)	1.42(2)
N(8)–C(83)	1.49(2)	C(86)–C(85)	1.49(3)
C(85)–C(84)	1.20(3)	C(84)–C(83)	1.45(3)
O(5)–Nd–O(7)	118.5(3)	O(3)–Nd–O(4)	116.4(3)
O(2)–Nd–O(8)	116.2(3)	O(1)–Nd–O(6)	112.4(3)
Nd–O(1)–C(11)	141.8(8)	Nd–O(2)–C(21)	143.5(8)
Nd–O(3)–C(31)	147.1(8)	Nd–O(4)–C(41)	146.0(9)
Nd–O(5)–C(51)	146.0(8)	Nd–O(6)–C(61)	148.8(8)
Nd–O(7)–C(71)	143.5(8)	Nd–O(8)–C(81)	145.6(8)

Results and discussion

The analytical data in Table 4 are in agreement with the proposed stoichiometries. The conductance data (Table 5) of millimolar solutions show a behaviour of 1:3 electrolytes in acetonitrile and 1:2 in nitromethane (in this case attributed to the existence of ion-pairs) [10].

Table 6 contains the most pertinent IR frequencies. The carbonyl streching mode is shifted towards lower frequencies as compared to the free ligand. νCN was not significantly shifted. These facts are indicative of a ligand coordination through the carbonyl oxygen. The assumption that the perchlorate is ionic is supported

TABLE 4. Summary of analytical results for the compounds of formula $[LnL_x](ClO_4)_3$ ($x=8$ for Ln=La–Ho; $x=7$ for Ln=Er–Lu, Y)

Ln	Lanthanide		Carbon		Hydrogen		Nitrogen	
	Theor.	Exp.	Theor.	Exp.	Theor.	Exp.	Theor.	Exp.
La	11.37	11.49	39.05	38.53	5.90	6.07	9.12	9.19
Ce	11.39	11.80	39.02	38.67	5.90	6.00	9.11	9.15
Pr	11.44	11.79	38.99	38.35	5.89	5.74	9.10	9.31
Nd	11.68	11.75	38.89	38.44	5.88	5.58	9.08	9.38
Sm	12.12	12.59	38.69	38.86	5.85	5.67	9.03	9.12
Eu	12.23	13.01	38.64	38.48	5.84	5.78	9.02	9.08
Gd	12.60	13.05	38.48	38.25	5.82	5.71	8.98	8.88
Tb	12.72	12.57	38.43	38.12	5.81	5.75	8.97	8.90
Dy	12.98	13.13	38.32	37.86	5.79	5.89	8.94	8.64
Ho	13.14	13.45	38.24	37.66	5.78	5.80	8.93	8.78
Er	14.43	14.12	36.29	35.88	5.48	5.36	8.46	8.40
Tm	14.56	14.34	36.24	35.95	5.47	5.50	8.45	8.34
Yb	14.85	15.41	36.07	35.57	5.45	5.39	8.41	8.38
Lu	14.98	15.36	36.02	35.62	5.44	5.48	8.40	8.42
Y	8.23	8.00	38.92	38.45	5.88	5.81	9.08	9.16

TABLE 5. Electrolytic conductance data in acetonitrile and nitromethane

Ln	Acetonitrile		Nitromethane	
	Conc. (mM)	Λ_m[a]	Conc. (mM)	Λ_m[a]
La	0.99	333	1.01	173
Ce	1.09	335	1.05	171
Pr	0.98	331	0.97	169
Nd	0.98	330	0.99	173
Sm	0.98	345	1.04	176
Eu	0.99	354	0.97	177
Gd	0.97	333	0.99	174
Tb	0.97	338	1.04	179
Dy	0.95	335	1.03	177
Ho	0.97	327	1.01	176
Er	0.99	325	1.00	177
Tm	1.04	313	1.06	170
Yb	1.00	313	1.03	168
Lu	1.03	310	0.99	170
Y	0.99	311	0.98	174

[a] $\Lambda_m = \Omega^{-1}$ cm^2 mol^{-1}.

TABLE 6. IR data (cm^{-1})

	ν(C–O)	ν(C–N)	(ClO_4)	
			ν_3	ν_4
δ-Valerolactam	1650	1498		
La	1618	1496	1088	626
Ce	1620	1498	1090	620
Pr	1620	1498	1076	622
Nd	1622	1498	1080	628
Sm	1618	1496	1076	624
Eu	1620	1498	1088	620
Gd	1618	1496	1086	622
Tb	1618	1496	1086	624
Dy	1614	1494	1090	624
Ho	1618	1498	1096	622
Er	1620	1498	1094	626
Tm	1620	1498	1096	628
Yb	1622	1498	1098	628
Lu	1620	1498	1098	626
Y	1618	1496	1090	620

by the presence of one strong and characteristic broad band ν_3 in the 1100 cm^{-1} region and ν_4 in the 620 cm^{-1} region.

The neodymium absorption spectra at room temperature, at 77 K and in acetonitrile and nitromethane solutions are very similar to the corresponding trifluoromethanesulfonate complex [4]. The nephelauxetic parameter ($\beta=0.984$), the covalent factor [11] ($b^{1/2}=0.088$) and Sinha's parameter [12] ($\delta=1.57$) were determined from the spectrum at room temperature, using the $^4I_{9/2}\rightarrow{}^4G_{5/2}$, $^2G_{7/2}$ transitions. The gravity center of the absorption bands was calculated by applying Simpson's rule [13]. The nephelauxetic parameter was calculated by comparison with the values of a Nd^{3+}:LaF_3 standard. The parameters indicate the electrostatic nature of the bonds between Nd^{3+} and the ligands, with a small covalent contribution. The oscillator strengths [14] in nitromethane ($P\times10^6=18.7$) and acetonitrile ($P\times10^6=19.7$) and the similar spectral shapes are indicative of the existence of the same species in solution.

The emission spectrum at 77 K (Fig. 1) does not present a $^5D_0\rightarrow{}^7F_0$ transition. Three peaks were observed for the $^5D_0\rightarrow{}^7F_1$ transition: one at 588 nm attributed to an A_2 species and two at 593 and 594 nm due to an E_1 species. One peak and a shoulder

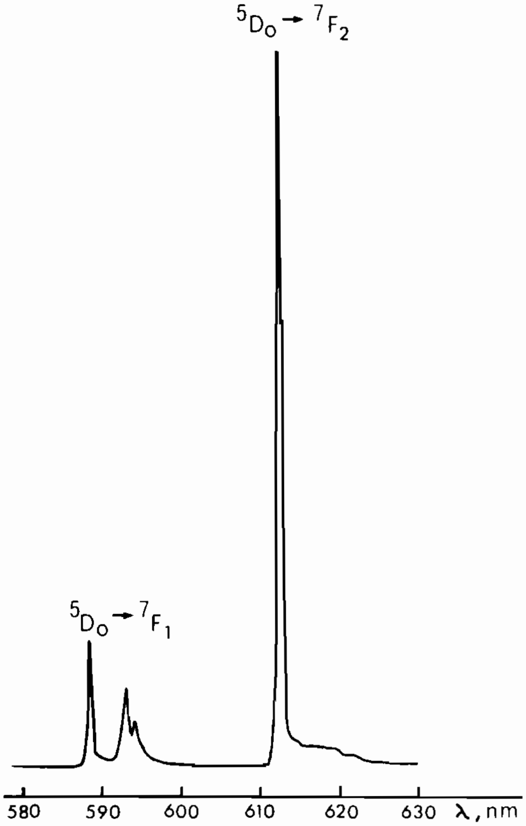

Fig. 1. Emission spectrum of the europium compound at 77 K.

at 612.5, 613 nm due to an E_1 species of a $^5D_0 \rightarrow {}^5F_2$ transition was also observed. The spectrum was interpreted in terms of a D_{4d} symmetry [15]. The same was concluded for the trifluoromethanesulfonate complex [4].

These results were confirmed by the X-ray single crystal structure carried out on the neodymium derivative. Its structure consists of well separated NdL_8 complex cations and disordered ClO_4 anions. An ORTEP view of the cation is given in Fig. 2. The Nd is octa-coordinated, being bonded to eight oxygens of the δ-valerolactam ligand. The coordination sphere geometry is very close to that of an ideal square-antiprism. The two square faces of the antiprism are rather parallel (the dihedral angle between the two planes is 2.7 (2)°) and the rotation of one square face of the polyhedron (defined by O(2), O(3), O(4), O(8)) with respect to the second one (defined by O(1), O(5), O(6), O(7)) is 47.7° very close to the ideal value of 45°. The polyhedron has an approximately D_{4d} symmetry with an $1/s$ (average ratio) of 1.037 and a θ value (averaged) of 57.9° which match very well with the shape parameters for the idealized square-antiprism $1/s = 1.057$ and $\theta = 57.3°$ [16] (θ is the angle between the Nd–O bonds and 8 axis characteristic for SAP geometry). There are at the present time three structures of Nd with octakis monodentate ligands which can be compared, where L = δ-valerolactam (present determination), pyridine oxide in $Nd(PyO)_8(ClO_4)_3$ [1] and 4-picoline-*N*-oxide in $Nd(4picNO)_8(CF_3SO_3)_3$ [3]. In these compounds the Nd coordination geometry is SAP. The significant characteristics of the three polyhedrons are reported in Table 7. It is worth noting that in the present study the SAP polyhedron is rather regular, and the range of Nd–O bond distances is also rather narrow when compared to the values found in similar compounds: the higher flexibility of the δ-valerolactam ligand probably allows a better packing on the crowded metal coordination sphere.

The δ-valerolactam ligands present conformations varying from a rather pure half chair to a rather twisted half chair showing an easy interchange of conformation according to the steric requirements of the metal coordination. The half chair conformation has been found also in α-chloro δ-valerolactam [17].

The carbon–carbon bond distances have the value expected for normal sp^3–sp^3 bonds (1.53_{av} Å); the corresponding bond angles (mean value 111°) are normal as well [18]. With regard to the $N-\overset{|}{C}=O$ fragment we notice an increase of the C–O bond distance from 1.23 Å found in the δ-valerolactam adduct with tungsten(II) *cis*-amino halides [19] and 1.200 Å in the uncomplexed lactam (Hvall) in $[Rh_2(vall)_4(Hvall)_2]$-2Hvall [20] to 1.26(1) Å in the present determination, due to the oxygen metal coordination. (This value is also in agreement with the value of 1.250(5) Å reported for the axial bonded δ-valerolactam ligand in the rhodium complex previously mentioned [20].) The N–C

TABLE 7. Polyhedron shapes for Nd–O_8 units

	$1/s$	θ (°)	M–O (Å)	Square faces twisting (°)
Nd(δ-valerolactam)$_8$	1.037	57.9	2.417(9)–2.475(9)	47.7_{av}
Nd(PyO)$_8$ [1]	1.093	55.5	2.36(2)–2.45(2)	42.1–47.8
Nd(4picNO)$_8$ [3]	1.062	54.4	2.38(1)–2.47(1)	37.6_{av}
Ideal value MFP [16] (most favourable polyhedron)	1.057	57.3		45.0

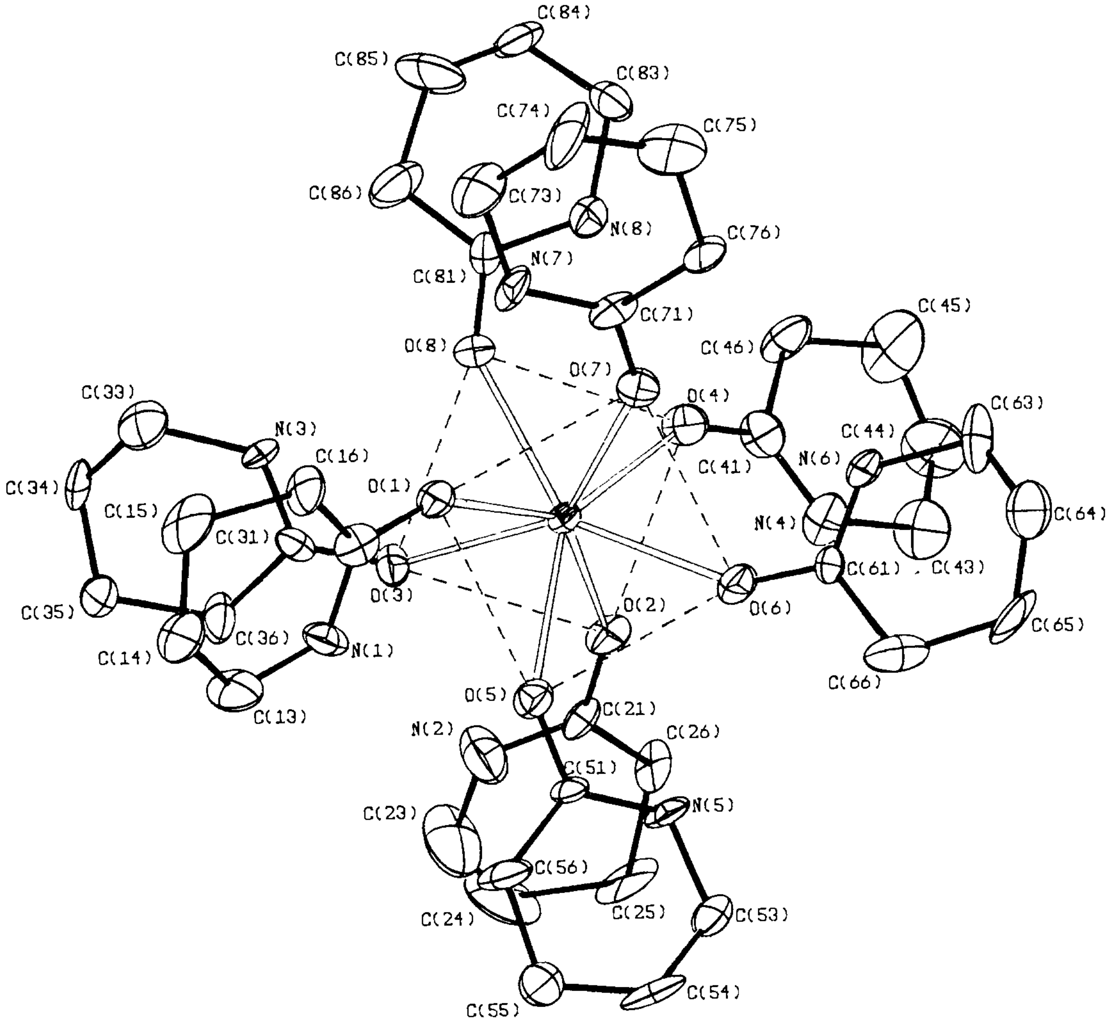

Fig. 2. ORTEP view of the NdL_8 complex cation.

TABLE 8. Crystallographic data from single crystal (Nd only) and powder X-ray diffraction studies (isomorphous Ce, Pr, Nd)

	Volume (Å^3)	a (Å)	b (Å)	c (Å)	β (°)
(a) Crystallographic data					
Nd: monoclinic $P2_1/n$					
crystal	5347.5	25.491(4)	16.074(3)	13.051(3)	90.15(3)
powder	5240.5	25.39(4)	16.05(2)	13.01(2)	90.32(9)

(b) Selected powder X-ray diffraction data

Ce		Pr		Nd	
d	I/I_o	d	I/I_o	d	I/I_o
4.10	34	4.09	25	4.09	80
4.13	41	4.13	29	4.13	100
4.57	6	4.57	7	4.54	54
7.99	100	7.98	100	7.98	89
9.40	8	9.35	5	9.34	22
11.66	5	11.60	3	11.51	21

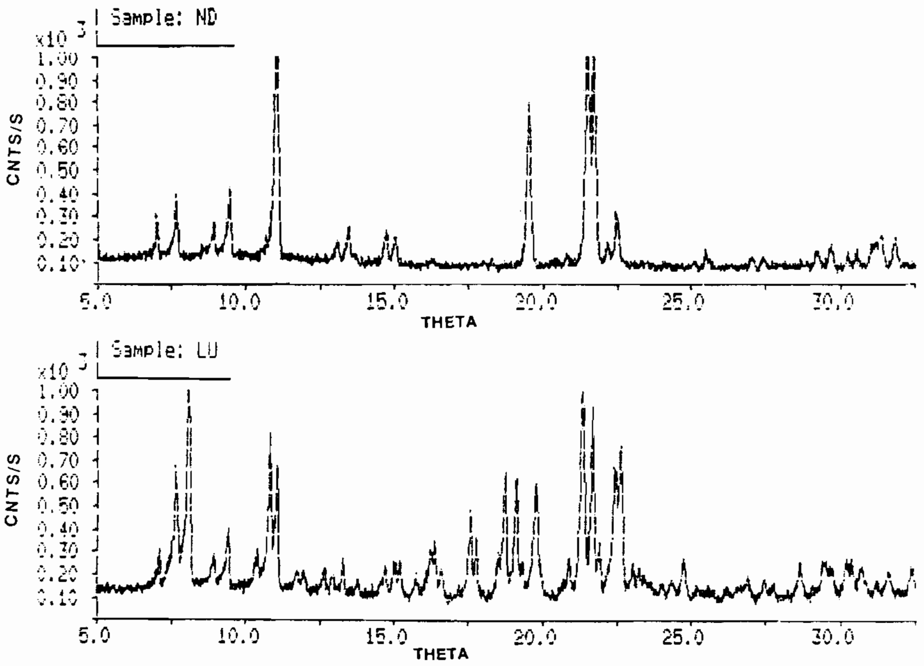

Fig. 3. X-ray diffraction powder patterns for Nd(top) and Lu(bottom) δ-valerolactam derivatives.

bond distance (average 1.32(1) Å) does not seem to be influenced by the adjacent oxygen metal coordination having a value comparable to that reported for uncomplexed and complexed δ-valerolactam ligands: 1.32 Å in the tungsten adduct [19] and 1.315(3) Å in the Rh complex [20].

The X-ray powder patterns were recorded for Ce, Pr, Nd and Lu derivatives only; the samples of the remaining compounds were rather deliquescent and not suitable. From the Nd powder spectrum analysed with the program TREOR [21] the cell parameters reported in Table 8 were obtained. They match with those obtained by single-crystal X-ray diffraction, indicating that we are dealing with the same crystal phase. Comparison of Nd powder spectra with those of Ce and Pr shows (Table 8) that the compounds are isomorphous, while as expected those of the Lu derivative are different, as shown in Fig. 3. We have tried also with a computer program [22] to calculate the peak positions and intensities from the Nd single-crystal data and to simulate a diffractogram for comparison with experimental data. However, particularly for the low angle peaks, they do not match the experimental intensities. This is a common problem in powder X-ray studies due to the preferential orientation of the particles when packed in the holder. In any case this technique has been useful in assessing the isomorphism of some derivatives and indicating the presence of the same phase in the crystal and powder forms.

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