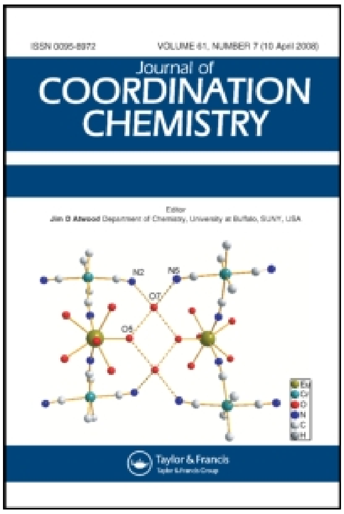

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STUDIES ON LANTHANOID COMPLEXES OF OPEN CHAIN MULTIDENTATE LIGANDS. VIII. PREPARATION AND STRUCTURAL CHARACTERIZATION OF THE UNDECACOORDINATE COMPLEX OF NEODYMIUM NITRATE WITH *N,N'*-BIS(4-METHOXYPHENYL) TETRAGLYCOLLIC DIAMIDE

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STUDIES ON LANTHANOID COMPLEXES OF OPEN CHAIN MULTIDENTATE LIGANDS. VIII. PREPARATION AND STRUCTURAL CHARACTERIZATION OF THE UNDECACOORDINATE COMPLEX OF NEODYMIUM NITRATE WITH *N,N′*-BIS(4-METHOXYPHENYL) TETRAGLYCOLLIC DIAMIDE

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The title compound $[Nd(L)(NO_3)_3].2CH_3CN$ was formed by reaction of neodymium nitrate with *N,N′*-bis(4-methoxyphenyl)tetraglycollic diamide (L). The complex crystallizes in the monoclinic system, space group *Cc* with $Z = 4$, $a = 21.305(6)$, $b = 11.470(4)$, $c = 14.436(3)$Å, $\beta = 97.41(2)°$, $V = 3498(2)$ Å^3. The pentadentate organic ligand wraps around the neodymium ion which is also bonded to three bidentate nitrate groups, achieving uncommon undecacoordination with the following mean bond lengths: Nd—O(etheric), 2.703; Nd—O(carbonyl), 2.518; Nd—O(nitrate), 2.546Å

KEYWORDS: Neodymium nitrate, *N,N′*-bis (4-methoxyphenyl) tetraglycollic diamide, complex, crystal structure

INTRODUCTION

Many lanthanoid complexes with multidentate ligands have been investigated in recent years.[1–3] The previous work was mainly devoted to coordination compounds with macrocyclic ligands such as crown ethers and cryptands,[1] while less attention

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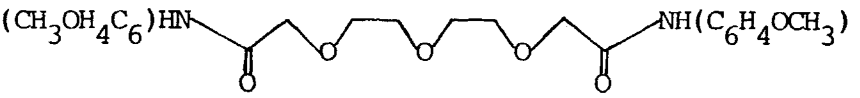
was paid to the behaviour of lanthanoid ions towards noncyclic multidentate ligands.[4,5] Some polyethylene glycols and their derivatives exhibit a "crown-like" behaviour in the lanthanoid complexes,[5] and some can be used for lanthanoid separation,[6,7] and for stabilizing the Ln(II) oxidation state.[8] As part of a systematic investigation of lanthanoid complexes with open chain multidentate ligands,[9] this paper reports the preparation and structure of a complex of neodymium nitrate with *N,N'*-bis(4-methoxyphenyl)tetraglycollic diamide.



N,N'-Bis(4-methoxyphenyl)tetraglycollic diamide (L)

EXPERIMENTAL

Chemicals

Hydrated neodymium nitrate was prepared by dissolving Nd_2O_3 (AnalaR) in 1:1 nitric acid. The ligand was provided by the Lanzhou Institute of Chemical Physics. All other chemicals were AnalaR grade.

Preparation

Neodymium nitrate hexahydrate (0.438 g, 1 mmol) in ethyl acetate (25 cm^3) was added to a solution of the ligand (0.432 g, 1 mmol) in ethyl acetate (25 cm^3) with stirring. The complex precipitated gradually. After being 10 h the complex was isolated by filtration, washed with ethyl acetate and recrystallized from a solution of acetonitrile by slow evaporation. Purple crystals of the complex, $[Nd(L)(NO_3)_3].2CH_3CN$, were formed from the solution. Yield 60%. Calcd. for $C_{26}H_{34}N_7NdO_{16}$: C, 36.97; H, 4.06; N, 11.61; Nd, 17.07%. Found: C, 36.68; H, 3.98; N, 11.25; Nd, 17.32%. The crystals are stable in air at room temperature for many months.

Crystal structure determination

Crystal data:

$C_{26}H_{34}N_7NdO_{16}$, M = 844.81, monoclinc, space group Cc, a = 21.305(6), b = 11.470(4), c = 14.436(3) Å, β = 97.41(2)°, V = 3498(2) Å^3, Z = 4, D_c = 1.60 g cm^{-3}, λ(MoKα) = 0.71073 Å, μ = 15.4 cm^{-1}, F(000) = 1708.

A single crystal of dimensions 0.2 × 0.4 × 0.5 mm was selected for data collection on an R3M/E diffractometer with graphite-monochromated Moka radiation, using the $\theta/2\theta$ scan technique. Some 25 reflections were used for measuring lattice parameters and 2569 independent reflections were collected in the range $1° < 2\theta < 45°$. Of these, 2150 reflections with $I \geq 3\sigma(I)$ were used in the structure determination and refinement. Data were corrected for Lorentz-polarization effects. No absorption correction was applied. The structure was solved

Table 1 Final Atomic Coordinates ($\times 10^4$) and Thermal Parameters ($A^2 \times 10^3$)[a].

Atom	*x/a*	*y/b*	*z/c*	u^b
Nd	0	8102(1)	0	40(1)
O(1)	1040(3)	7160(5)	395(6)	50(2)
O(2)	1101(4)	9340(6)	403(6)	60(3)
O(3)	47(7)	10387(5)	116(16)	82(4)
O(4)	- 1102(3)	9337(6)	- 393(5)	47(2)
O(5)	- 1064(4)	7044(6)	- 430(5)	49(2)
O(6)	- 608(10)	8295(16)	1395(13)	69(4)
O(7)	391(8)	8302(14)	1797(13)	67(5)
O(8)	- 212(5)	8162(11)	2815(5)	91(4)
O(9)	- 390(10	8334(17)	- 1705(13)	81(5)
O(10)	578(10)	8556(17)	- 1360(16)	73(5)
O(11)	204(8)	8696(14)	- 2821(8)	124(5)
O(12)	- 47(6)	6025(11)	758(9)	60(4)
O(13)	112(8)	6134(12)	- 689(7)	54(4)
O(14)	13(13)	4448(6)	- 86(21)	93(4)
O(15)	2431(4)	2079(6)	1067(7)	66(3)
O(16)	- 2448(6)	2096(8)	- 1264(9)	97(3)
N(1)	- 148(4)	8288(8)	2000(5)	50(3)
N(2)	119(6)	8526(11)	- 2016(8)	78(4)
N(3)	2(10)	5515(7)	20(10)	60(2)
N(4)	2093(4)	6915(6)	1012(6)	48(3)
N(5)	- 2081(9)	6822(15)	- 989(17)	65(5)
N(6)	- 3270(8)	8025(13)	- 1740(21)	87(5)
N(7)	- 1787(7)	6687(16)	- 3253(23)	93(5)
C(1)	3052(10)	1538(15)	1410(12)	103(5)
C(2)	2404(6)	3320(11)	1184(11)	76(4)
C(3)	2909(6)	4076(11)	1447(10)	66(4)
C(4)	2771(5)	5318(8)	1399(8)	48(3)
C(5)	2163(4)	5626(7)	952(7)	41(3)
C(6)	1663(5)	4904(10)	839(9)	57(4)
C(7)	1850(5)	3725(10)	628(9)	57(4)
C(8)	1538(4)	7514(8)	756(7)	43(3)
C(9)	1632(5)	8798(10)	957(12)	74(4)
C(10)	1123(13)	10596(16)	525(16)	71(5)
C(11)	585(6)	10977(8)	- 192(13)	96(5)
C(12)	- 543(5)	11111(12)	- 23(12)	75(4)
C(13)	- 1043(5)	10532(9)	- 681(12)	80(4)
C(14)	- 1661(10)	8818(13)	- 889(10)	54(5)
C(15)	- 1596(4)	7527(10)	- 730(6)	38(3)
C(16)	- 2162(5)	5686(12)	- 1063(8)	60(4)
C(17)	- 2737(5)	5115(11)	- 1297(9)	57(4)
C(18)	- 2831(5)	3981(10)	- 1350(8)	52(3)
C(19)	- 2363(5)	3243(8)	- 1059(7)	41(3)
C(20)	- 1753(5)	3716(11)	- 925(10)	64(4)
C(21)	- 1705(6)	4860(11)	- 571(9)	64(4)
C(22)	- 3035(5)	1627(10)	- 1643(10)	60(4)
C(23)	- 3655(10)	8750(17)	- 1983(19)	69(5)
C(24)	- 4253(17)	9258(25)	- 2103(22)	95(6)
C(25)	- 1249(7)	6452(16)	- 3122(16)	51(4)
C(26)	- 692(15)	5664(23)	- 2771(24)	99(6)

[a] Estimated standard deviations in parentheses.

[b] Equivalent isotropic U defined as one third of the orthogonalized U_{ij} tensor.

by the Patterson method and Fourier techniques, and refined by full-matrix least-squares methods with anisotropic thermal factors for all non-hydrogen atoms and isotropic thermal parameters for hydrogen atoms. The weighting scheme $w = [1\text{-}\exp(-5)(\sin\theta/\lambda)^{2,}]/[\sigma^2(F) + 0.0002F^2]$; final $R = 0.041$, $R_w = 0.038$ values were obtained. The maximum and minimum residual electron densities in the final difference map were 1.43 and − 1.04 e Å^{-3}. Lists of anisotropic thermal parameters, H-atom parameters, and observed and calculated structure factors are available from the authors on request.

Table 2 Selected bond lengths (Å)[a].

Nd-O(1)	2.456(6)	Nd-O(7)	2.608(8)
Nd-O(2)	2.750(8)	Nd-O(9)	2.527(9)
Nd-O(3)	2.629(6)	Nd-O(10)	2.519(10)
Nd-O(4)	2.731(6)	Nd-O(12)	2.611(14)
Nd-O(5)	2.579(7)	Nd-O(13)	2.489(15)
Nd-O(6)	2.524(9)		

[a] Estimated standard deviations in parentheses.

Table 3 Selected bond angles (°)[a].

O(1)-Nd-O(2)	57.2(2)	O(4)-Nd-O(6)	66.9(5)
O(1)-Nd-O(3)	113.4(4)	O(4)-Nd-O(7)	108.3(4)
O(1)-Nd-O(4)	174.7(2)	O(4)-Nd-O(9)	64.8(5)
O(1)-Nd-O(5)	125.9(2)	O(4)-Nd-O(10)	103.0(5)
O(1)-Nd-O(6)	113.0(5)	O(4)-Nd-O(12)	118.5(3)
O(1)-Nd-O(7)	69.5(4)	O(4)-Nd-O(13)	120.7(4)
O(1)-Nd-O(9)	116.6(5)	O(5)-Nd-O(6)	73.1(5)
O(1)-Nd-O(10)	75.8(5)	O(5)-Nd-O(7)	115.8(4)
O(1)-Nd-O(12)	65.7(3)	O(5)-Nd-O(9)	69.1(5)
O(1)-Nd-O(13)	64.2(4)	O(5)-Nd-O(10)	114.6(5)
O(2)-Nd-O(3)	56.3(4)	O(5)-Nd-O(12)	66.0(3)
O(2)-Nd-O(4)	117.6(2)	O(5)-Nd-O(13)	66.7(4)
O(2)-Nd-O(5)	176.6(2)	O(6)-Nd-O(7)	48.7(6)
O(2)-Nd-O(6)	107.2(5)	O(6)-Nd-O(9)	129.1(7)
O(2)-Nd-O(7)	65.9(4)	O(6)-Nd-O(10)	162.9(6)
O(2)-Nd-O(9)	108.6(5)	O(6)-Nd-O(12)	72.5(5)
O(2)-Nd-O(10)	64.2(5)	O(6)-Nd-O(13)	118.7(5)
O(2)-Nd-O(12)	117.3(3)	O(7)-Nd-O(9)	168.9(6)
O(2)-Nd-O(13)	115.5(4)	O(7)-Nd-O(10)	129.0(6)
O(3)-Nd-O(4)	61.4(4)	O(7)-Nd-O(12)	72.1(4)
O(3)-Nd-(5)	120.7(4)	O(7)-Nd-O(13)	116.0(4)
O(3)-Nd-O(6)	83.2(6)	O(9)-Nd-O(10)	48.9(7)
O(3)-Nd-O(7)	81.1(6)	O(9)-Nd-O(12)	118.7(5)
O(3)-Nd-O(9)	87.8(7)	O(9)-Nd-O(13)	75.0(5)
O(3)-Nd-O(10)	79.8(7)	O(10)-Nd-O(12)	124.4(5)
O(3)-Nd-O(12)	151.7(6)	O(10)-Nd-O(13)	78.1(6)
O(3)-Nd-O(13)	157.6(6)	O(12)-Nd-O(13)	49.9(4)
O(4)-Nd-O(5)	59.3(2)		

[a] Estimated standard deviations in parentheses.

RESULTS AND DISCUSSION

Final atomic coordinates and equivalent isotropic thermal parameters are given in Table 1 and selected bond lengths and bond angles in Tables 2 and 3. Figure 1 shows the structure and the numbering scheme for the complex molecule. Figure 2 shows the molecular packing arrangement in the unit cell.

The unit cell consists of the complex molecules and separate, uncoordinated acetonitrile molecules. The ligand wraps around the metal ion with its oxygen atoms and assumes a ring-like structure similar to that of the crown ethers.[1] The neodymium ion in the complex is eleven-coordinated by three bidentate nitrate groups and one pentadentate ligand. Six Nd-O (nitrate) distances vary between 2.489 Å and 2.611 Å (mean 2.546 Å). The Nd—O(L) distances are of two types: as expected, the two terminal Nd—O (carbonyl) distances (mean 2.518 Å) are significantly shorter than the three Nd—O (etheric) distances (mean 2.703 Å). This is probably due to the higher electron density on the carbonyl oxygen.

A noteworthy feature of the molecular structure is the eleven-coordinate polyhedron around the metal ion. Undecacoordination is not common in inorganic chemistry.[10,11] Other reported undecacoordinated lanthanoid complexes with organic ligands are [La(15-crown-5)$(NO_3)_3$],[12] [La(monoaza-15-crown-5)$(NO_3)_3$][13] [La(naphtho-16-crown-5)$(NO_3)_3$],[14] [La(TEG)$(NO_3)_3$] (Where TEG = tetraethylenglycol),[15] La(DAPBAH)$(NO_3)_3$] (where DAPBAH = 2,6-diacetyl-

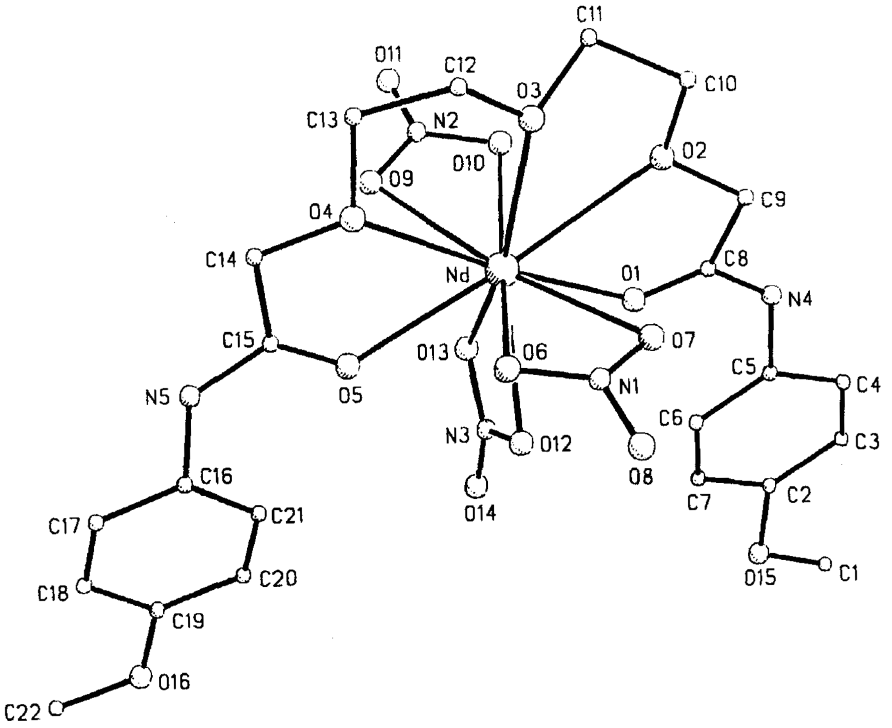


Figure 1 Structure and numbering scheme for the complex.

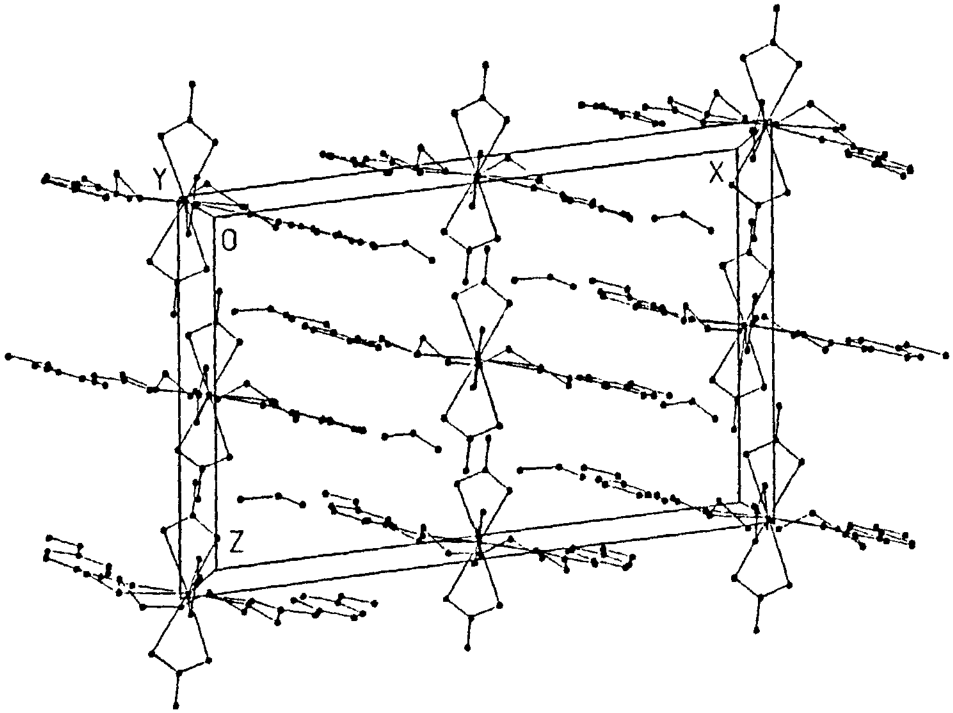


Figure 2 Molecular packing in the unit cell.

pyridinebis(benzoic acid hydrazone),[16] [Ce(15-crown-5)$(NO_3)_3$],[17] [Ce(4,4'-bipy)$(NO_3)_4(H_2O)_2]^-$ anion (where 4,4'-bipy = 4,4' -bipyridyl),[18] and [Eu(15-crown-5)$(NO_3)_3$].[11] In general, the coordination polyhedra in these complexes are not easily definable nor comparable, and seem to be more determined by the shapes and characteristics of the bonded ligands than by the common coordination number.[10,15]

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