Pergamon

PII: S0277-5387(97)00088-0

Polyhedron Vol. 16, No. 19, pp. 3247–3251, 1997

0277-5387/97 $17.00+0.00

Crystal structure and properties of neodymium complex with hexaazacyclooctadecane ligand

Xian-He Bu,[a] Shou-Liang Lu,[a] Ruo-Hua Zhang,[a]* Hong-Gen Wang[b] and Xin-Kan Yao[b]

[a] Department of Chemistry, Nankai University, Tianjin 300071, P.R. China

[b] Central Laboratory, Nankai University, Tianjin 300071, P.R. China

(Received 21 January 1997; accepted 25 February 1997)

Abstract—The neodymium complex with hexaazacyclooctadecane ([18]aneN_6) has been obtained as a single crystal by the reaction of neodymium nitrate and macrocycle ligand in methanol solution. The crystal structure of the complex [Nd([18]aneN_6)(NO_3)$_3$] was determined by X-ray diffraction. The neodymium centre is 10-coordinate with the coordination polyhedron being an irregular capped square-antiprism. The absorption spectrum of the complex was measured and the intensities of *f–f* transitions were analyzed according to the Judd–Ofelt theory. © 1997 Elsevier Science Ltd

Keywords: crystal structure; neodymium complex; hexaazacyclooctadecane; properties.

The lanthanide complexes of polyazamacrocyclic ligands are currently attracting much attention, not only for their well-established biological and chemical importance, but also for their specific applications in nuclear magnetic resonance imaging (MRI) and light-conversion molecular devices, etc [1, 2].

Although lanthanide complexes of hexaazacyclooctadecane ligand functionalized with pendant side arms have been reported [3, 4], until now, little is known about these lanthanide complexes of saturated 18-membered hexaazamacrocycles, particularly their crystal structures [5].

Herein, we report a novel neodymium complex of 18-membered hexaazamacrocycle ([18]aneN_6) and its crystal structure. The spectroscopic properties of the complex and the intensities of *f–f* transitions are also described and discussed.

EXPERIMENTAL

Materials and general method

All the chemical reagents were of analytical grade. Hexaazacyclooctadecane ligand was prepared according to literature method [6]. Hydrated neodymium nitrate was prepared from Nd_2O_3(99.95%).

Preparation of the complex

A solution of $Nd(NO_3)_3 \cdot nH_2O$ (0.5 mmol) and [18]aneN_6 ligand (0.5 mmol) in methanol (20 cm^3) was stirred at 60–70°C for 10 h. The pink crystals were deposited from the solution by the method of ether diffusion at room temperature. Found: C, 24.50; H, 4.99; N, 21.84%. Calc. for $C_{12}H_{30}N_9O_9Nd$: C, 24.73; H, 5.10; N, 21.42%.

Chemical and physical measurement

Elemental analyses (C,H,N) were performed on a Perkin–Elmer 240C elemental analyser. The Infrared spectrum was recorded on a WFH-30 spectrometer in the region of 400–4000 cm^{-1} using potassium bromide pellet. DTA/TG data were measured on a PCT-1 mode thermal analyzer. The electronic spectra of the complex in methanol and aqueous solution were recorded on a Shimadzu UV-240 spectrophotometer. The reflection spectrum was also measured and the samples of the complex were diluted by $BaSO_4$ which was also used as a standard. Experimental oscillator strength values of solution absorption bands were

---

* Author to whom correspondence should be addressed.

obtained by the graphical integration of the area under the absorption curves after appropriate correction of the base line. The values of Ω_λ parameters were calculated from the following Judd–Ofelt [7–9] relation:

$$P = (8\pi^2 mc/3h)(2J+1)^{-1} \times \chi\delta\Sigma_{\lambda=2,4,6}\Omega_\lambda(f^n\Psi J//U^\lambda//f^n\Psi' J')^2 \quad (1)$$

Where P is the oscillator strength, $\chi = (n^2+2)^2/9n$ where n is the reflective index, J is the total quantum number of the ground state, $(f^n\Psi J//U^\lambda//f^n\Psi' J')$ is the reduced matrix element of the unit tensor operator U^λ calculated by Carnall *et al.* [10] and Ω_λ are empirical least-squares fitted parameters.

X-ray data collection, structure, solution and refinement

A pink crystal with the size of 0.3 × 0.3 × 0.25 mm was used for the measurement. The X-ray data were collected on an Enraf–Nonius CAD4 diffractometer with graphite-monochromized Mo-Kα radiation using the $\omega/2\theta$ scan mode. A total of 1887 reflections were collected, of which 1790 reflections were considered to be observed [$I \geqslant 3\sigma(I)$]. An empirical absorption correction was applied. The structure was solved by direct methods. The final refinement was carried out by the full-matrix least-squares method with anisotropic thermal parameters for non-hydrogen atoms and converged with unweighted and weighted agreement factors 0.030 and 0.039, respectively. All the calculations were carried on a PDP11/44 computer using a SDP-PLUS computer program package.

Crystallographic data for [Nd([18]aneN$_6$)(NO$_3$)$_3$]. $C_{12}H_{30}N_9O_9Nd$. Formula weight: 588.67, monoclinic, space group Cc, $a = 10.668(3)$Å, $b = 15.026(3)$ Å, $c = 13.817(3)$ Å, $\beta = 96.74(2)°$, $V = 2199(2)$ Å^3, $Z = 4$, $D_x = 1.778$ Mgm^{-3}.

RESULTS AND DISCUSSION

Description of the structure

The complex [Nd([18]aneN$_6$)(NO$_3$)$_3$] crystallises from methanol solution to form air-stable, pink, monoclinic crystals of space group Cc.

Bond distances (Å) and angles (°) for the complex are given in Table 1. The Tables of atomic coordinates and thermal parameters, refined displacement parameter expressions-Beta's and observed and calculated structure factors are included as supplementary material. An ORTEP plot showing atom-labelling for the title complex is shown in Fig. 1.

The crystal structure consists of discrete monomeric molecular unit [Nd([18]aneN6)](NO$_3$)$_3$] and reveal a

Table 1. Selected bond distances (Å) and angles (°) for the title complex

Nd(1)—O(11)	2.555(9)	Nd(1)—N(2)	2.69(2)
Nd(1)—O(12)	2.62(1)	Nd(1)—N(3)	2.75(2)
Nd(1)—O(21)	2.40(1)	Nd(1)—N(4)	2.72(1)
Nd(1)—O(31)	2.51(1)	Nd(1)—N(5)	2.73(1)
Nd(1)—N(1)	2.65(2)	Nd(1)—N(6)	2.66(1)
O(11)—Nd(1)—O(12)	49.7(1)	O(21)—Nd(1)—N(6)	136.9(5)
O(11)—Nd(1)—O(21)	145.2(4)	O(31)—Nd(1)—N(1)	73.7(4)
O(11)—Nd(1)—O(31)	132.1(4)	O(31)—Nd(1)—N(2)	118.7(4)
O(11)—Nd(1)—N(1)	125.0(3)	O(31)—Nd(1)—N(3)	142.4(5)
O(11)—Nd(1)—N(2)	108.2(4)	O(31)—Nd(1)—N(4)	83.4(4)
O(11)—Nd(1)—N(3)	67.6(5)	O(31)—Nd(1)—N(5)	64.7(4)
O(11)—Nd(1)—N(4)	85.1(4)	O(31)—Nd(1)—N(6)	72.7(4)
O(11)—Nd(1)—N(5)	68.3(3)	N(1)—Nd(1)—N(2)	62.1(5)
O(11)—Nd(1)—N(6)	77.9(3)	N(1)—Nd(1)—N(3)	125.7(5)
O(12)—Nd(1)—O(21)	130.7(4)	N(1)—Nd(1)—N(4)	149.8(2)
O(12)—Nd(1)—O(31)	142.3(4)	N(1)—Nd(1)—N(5)	119.0(4)
O(12)—Nd(1)—N(1)	80.0(3)	N(1)—Nd(1)—N(6)	64.7(4)
O(12)—Nd(1)—N(2)	68.7(4)	N(2)—Nd(1)—N(3)	63.9(4)
O(12)—Nd(1)—N(3)	75.3(5)	N(2)—Nd(1)—N(4)	115.8(4)
O(12)—Nd(1)—N(4)	128.9(4)	N(2)—Nd(1)—N(5)	176.4(2)
O(12)—Nd(1)—N(5)	107.9(4)	N(2)—Nd(1)—N(6)	117.4(5)
O(12)—Nd(1)—N(6)	71.9(4)	N(3)—Nd(1)—N(4)	65.0(4)
O(21)—Nd(1)—O(31)	72.0(2)	N(3)—Nd(1)—N(5)	114.5(4)
O(21)—Nd(1)—N(1)	82.2(4)	N(3)—Nd(1)—N(6)	142.8(2)
O(21)—Nd(1)—N(2)	62.2(4)	N(4)—Nd(1)—N(5)	65.2(4)
O(21)—Nd(1)—N(3)	78.8(5)	N(4)—Nd(1)—N(6)	126.9(4)
O(21)—Nd(1)—N(4)	72.0(5)	N(5)—Nd(1)—N(6)	61.7(4)
O(21)—Nd(1)—N(5)	121.0(4)		

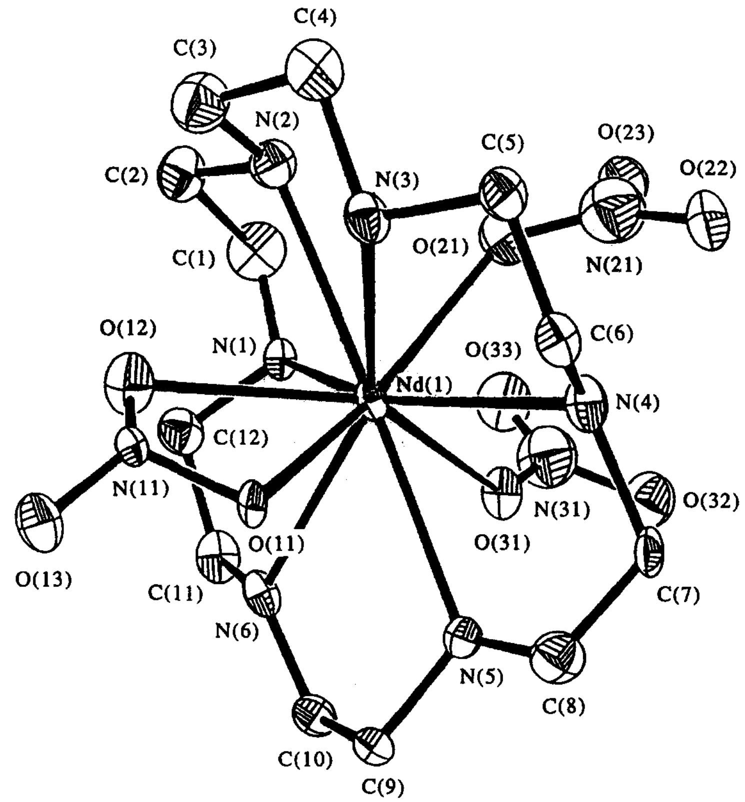

Fig. 1. The ORTEP plot of the title complex with hydrogen atoms omitted.

10-coordination polyhedron for the neodymium ion, being bonded to the six nitrogen donors of macrocycle and to one bidentate chelating nitrate ion on one side of the macrocycle and the two monodentate nitrate ions on the other side. The coordinated polyhedron can be described as an irregular antiprism capped on its square faces by the macrocyclic nitrogen donors [O(2) and O(5)]. The dihedral angle between the two square planes [N(1)–O(21)–N(3)–O(12)] and [N(6)–O(31)–N(4)–O(11)] is 7.20 ± 1.18° (Fig. 2). The average Nd–N distances (2.65–2.75 Å) are a little longer than the Nd–O distances (2.40–2.62 Å). The Nd–N average bond length is 2.70(1)Å which is slightly longer than the sum of ionic radi 2.593–2.70Å (Nd^{3+} 1.27Å (C.N. = 12) 1.163Å (C.N. = 9) and N^{3-} 1.43Å) [11]. Neodymium ion is present in the cavity of the macrocycle. This result also indicates that the bonds between the neodymium ion and the macrocycle ligand are mainly ion-dipole and non-directional, since the 4f electrons are effectively shielded.

Thermal stability and infrared spectrum

The thermal analysis (TG and DTA) data of the complex show that the starting point of decomposition is 300°C. The DTA curve shows one sharply exothermic peak at 307°C and one broadly exothermic peak at 461°C. Thus this complex is more stable in an air atmosphere. The TG curve exhibits two decomposition steps. The final weight loss indicates the formation of Nd_2O_3 (weight percentage loss: Calc. for Nd_2O_3, 71.39%, found, 70.41%).

The IR spectrum of the complex exhibits the band of NH groups (3250 cm^{-1}) and the bands (1503, 1470, 1440, 1326, 1281, cm^{-1}) of coordinate nitrate groups [12].

Electronic spectroscopy

The electronic spectra of the complex contain strong absorptions (for methanol solution λ_{max}: 210.5nm ε: 1.82×10^4 cm^{-1} mol^{-1} l and for aqueous solution λ_{max}: 201 nm ε: 2.97×10^4 cm^{-1} mol^{-1}l) which may be attributed to intraligand transitions. In addition to these strong absorptions, weak Laporte forbidden metal *4f–4f* transitions are found in the visible region.

The data of the electronic spectrum in the solid state show a shift of most spectral bands toward lower energy as compared to those of respective aquoion which is known as nephelauxetic effect. The nephelauxetic parameter [13] ($\beta = 0.996$), the bonding parameter [14] ($b^{1/2} = 0.0435$) and covalency parameter [15] ($\delta = 0.3814$) show very weak covalent properties between the metal and ligand.

The results of oscillator strengths and a set of three parameters (Ω_2, Ω_4 and Ω_6) are given in Table 2. The most differences are observed for both oscillator

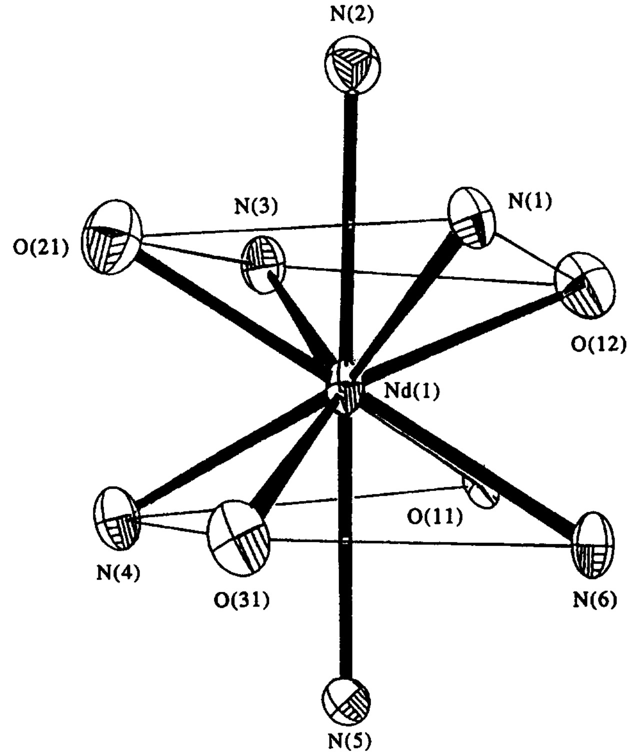

Fig. 2. The coordination geometry around the neodymium ion.

Table 2. Oscillator strength values P_{exp} ($P_{calc.}$) and Ω_λ parameter values for title complex in methanol solution and aqueous solution

Transition $^4I_{9/2} \rightarrow$	Methanol solution P_{exp} ($P_{calc.}$) $\times 10^6$	Aqueous solution P_{exp} ($P_{calc.}$) $\times 10^6$
$^4F_{3/2}$	1.856 (2.235)	1.413 (2.588)
$^4F_{5/2}$ $^4H_{9/2}$	7.016 (7.643)	10.58 (10.05)
$^4F_{7/2}$ $^4S_{3/2}$	8.301 (8.033)	10.75 (11.21)
$^4F_{9/2}$	0.574 (0.581)	0.630 (0.778)
$^4G_{5/2}$ $^2G_{7/2}$	19.95 (19.99)	15.11 (15.12)
$^4G_{7/2}$	4.728 (4.201)	4.470 (4.531)
$^4G_{9/2}$	2.850 (1.516)	2.880 (1.820)
$^2G_{9/2}$ $^2(D,P)_{3/2}$	0.389 (0.247)	2.580 (1.544)
$^4G_{11/2}$	0.623 (0.223)	
$^2P_{1/2}$	0.507 (0.621)	0.476 (0.688)
rms $\times 10^7$	6.39	8.31
Ω_λ		
$\Omega_2 \times 10^{20}$ (cm^2)	5.84	3.09
$\Omega_4 \times 10^{20}$ (cm^2)	5.00	5.41
$\Omega_6 \times 10^{20}$ (cm^2)	6.60	4.30

strength values of the hypersensitive transition ($^4I_{9/2} \rightarrow {}^4G_{5/2}, {}^2G_{7/2}$) and Ω_2 parameter values of methanol and aqueous solution of the complex. The values of P_{HYP} and Ω_2 for methanol solution are greater than that for aqueous solution, P_{HYP} and Ω_2 are the most sensitive for the change in environment around lanthanide ion. The results show that the changes of P_{HYP} and Ω_2 can be related to the difference of Nd^{III} species in methanol and aqueous solutions.

Molar conductance data indicate that the complex in methanol behave as 1 : 1 electrolyte (Λ_m : 78 s mol^{-1} cm^2) and in aqueous solution behave as 2 : 1 electrolyte (Λ_m : 240 s mol^{-1} cm^2) [16]. The results present the possibility of coordination of solvent molecules, which

Table 3. Peak position and molar extinetion coefficient values of the hypersensitive transition (${}^4G_{9/2} \rightarrow {}^4G_{5/2}, {}^2G_{7/2}$) of the neodymium complex

	λ_{max}(nm)	ε(cm^{-1} mol^{-1}l)
Solid	574.4	
	578.5	
	584.9	
Methanol	577.0	11.3
Solution	586.5	17.4
Aqueous	575.2	8.3
Solution	580.0	8.9
	584.2	9.7

can exchange the nitrate ions in first coordinated sphere of the neodymium ion, and Nd^{III} species in the methanol solution is different from that in the aqueous solution. This is also confirmed by Table 3, where the distinct changes in the shape, energy and intensity of the hypersensitive transition are observed for both the solutions. This fact also demonstrates a change in environment about Nd^{III} in methanol and aqueous solution.

Acknowledgements—This work was supported by the National Natural Science Foundation of China.

REFERENCES

1. Alexander, V., *Chem. Rev.*, 1995, **95,** 273.
2. Kumar, D. S., Alexander, V., *Inorg. Chim. Acta.*, 1995, **238,** 63.
3. Ziessel, R., Maestri, M., Prodi, L., Balzani, V. and Dorsselaer, A. V., *Inorg. Chem.*, 1993, **32,** 1237.
4. Kodama, M., Koike, T., Mahatma, A. B. and Kimura, E., *Inorg. Chem.*, 1991, **30,** 1270.
5. Kodama, M., Kimura, E. and Yamaguchi, S., *J. Chem. Soc., Dalton Trans.*, 1980, 2536.
6. Richman, J. E. and Atkins, T. J., *J. Am. Chem. Soc.* 1974, **96,** 2268.
7. Judd, B. R., *Phys. Rev.* 1962, **127,** 750.
8. Ofelt, G. S., *J. Chem. Phys.* 1962, **37,** 511.
9. Stephens, E. M., Davis, S., Reid, M. F. and Richardson, F. S., *Inorg. Chem.*, 1984, **23,** 4607.
10. Carnall, W. T., Fields, P. R. and Rajnak, K., *J. Chem. Phys.*, 1968, **49,** 4424.
11. Shannon, R. D., *Acta Cryst.* 1976, **A32,** 751.
12. Nakamoto, K., *Infrared and Raman Spectra of Inorganic and Coordination Compounds*, John Wiley & Sons, New York (1978).
13. Jørgensen, C. K., *Prog. Inorg. Chem.*, 1962, **4,** 73.
14. Henrie, D. E. and Choppin, G. R., *J. Chem. Phys.*, 1968, **49,** 477.
15. Sinha, S. P., *Spectrochim. Acta.*, 1966, **22,** 57.
16. Geary, W. J., *Coord. Chem. Rev.*, 1971, **7,** 81.