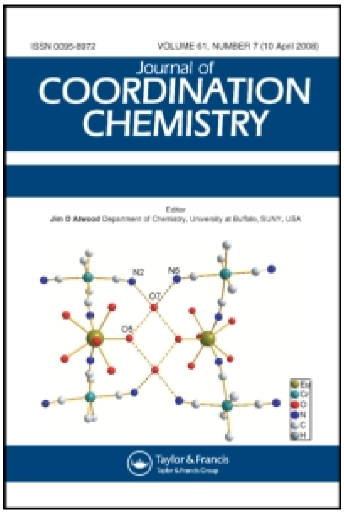

**Journal of Coordination Chemistry**
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713455674

# Synthesis and crystal structure of a new neodymium cryptate of a ligand derived from 2,6-diformylpyridine

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**To cite this Article** Hu, Xue-Lei , Li, Yi-Zhi and Luo, Qin-Hui(2003) 'Synthesis and crystal structure of a new neodymium cryptate of a ligand derived from 2,6-diformylpyridine', Journal of Coordination Chemistry, 56: 15, 1277 — 1283
**To link to this Article: DOI:** 10.1080/00958970310001650349
**URL:** http://dx.doi.org/10.1080/00958970310001650349

*J. Coord. Chem.* Vol. 56, No. 15, 15 October 2003, pp. 1277–1283

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# SYNTHESIS AND CRYSTAL STRUCTURE OF A NEW NEODYMIUM CRYPTATE OF A LIGAND DERIVED FROM 2,6-DIFORMYLPYRIDINE

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*(Received 29 April 2003; In final form 11 August 2003)*

A new neodymium cryptate $[NdL](NO)_3 \cdot H_2O$ (L = 1,4,12,15,18,26,31,39,42,43,44-undecaazapentacyclo-[13.13.13.$1^{6,10}$.$1^{20,24}$.$1^{33,37}$]-tetratetraconta-4,6,8,10(44)11,18,20,22,24(43),25,31,33,35,37(42),38-pentadecaene) was synthesized by the reaction of free ligand L with neodymium nitrate and characterized by physical methods and X-ray crystallography. It crystallizes in space group $R\bar{3}c$ with $a = 14.623(2)$, $c = 32.682(3)$ Å, Z = 6. Final refinement of the structure gave $R = 0.042$ and $Rw = 0.132$ . The crystal structure of Nd(III) cryptate shows a tricapped prismatic structure with coordination number nine.

*Keywords:* Neodymium; Cryptate; Crystal structure; ES-MS

## INTRODUCTION

The design and synthesis of lanthanide complexes is an interesting area of research [1,2] due to significance in both basic and applied chemistry. Cryptand ligands possess spherical cavities, appropriate recognition sites and suitable sizes for metal ions. They may be designed to form lanthanide cryptates [3–5].

Among the most interesting lanthanide cryptates, neodymium(III) cryptates have novel photophysical properties and may be used as fluorescence probes in biological systems [6]. A polyazacryptand ligand derived from (2 + 3) condensation of pyridyl dicarboxylaldehyde (dfp) with tris(2-aminoethyl)amine tren has been actively investigated due to its good complexing properties [7–9], but its other lanthanide cryptates and their structure have received less attention. Generally the lanthanide cryptates were obtained by means of template synthesis involving alkali, alkali-earth metal ions [10] or lanthanide ions as templating agents [11] and by nontemplate reaction of the free ligand with lanthanide ions [12]. Herein we report a new neodymium cryptate $[NdL](NO_3)_3 \cdot H_2O$ (Scheme 1) by nontemplate reaction of free ligand with

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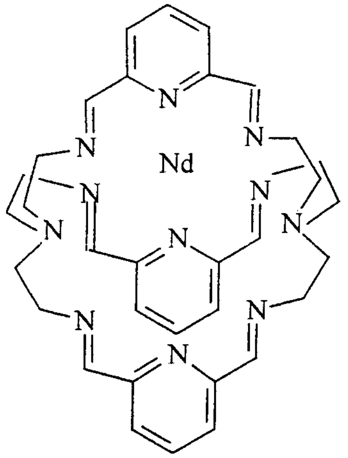
ISSN 0095-8972 print: ISSN 1029-0389 online
DOI: 10.1080/00958970310001650349



SCHEME 1. The schematic chemical formula of the complex cation $[NdL]^{3+}$.

neodymium nitrate, characterized by physical methods. Its X-ray crystal structural analysis shows that the complex cation has a tricapped prismatic structure with nine-coordination, different from the asymmetrical structure of the sodium cryptate with the same ligand [9] and the neodymium cryptate based phenol [11].

## EXPERIMENTAL

### Materials

All starting chemicals were of reagent grade. Hydrated lanthanide nitrate was prepared by dissolving $Nd_2O_3$ (99.99%) in an excess of nitric acid; tris(2-aminoethyl)amine [13] and 2,6-diformylpyridine [14] were prepared by the literature method, respectively. Cryptand L was prepared by condensation of dfp with tren by the literature method [7]. Physical constants and spectroscopic data are in agreement with literature values.

### Preparation of the Compounds

$[NdL](NO_3)_3 \cdot H_2O$: $Nd(NO_3)_3 \cdot 6H_2O$ (0.048 g, 0.11 mmol) in 20 $cm^3$ of MeCN was added to a boiling solution of L (0.059 g 0.1 mmol) in 100 $cm^3$ of MeCN. After refluxing the mixture for 12 h, the yellow solid was filtered off and washed with MeCN and $Et_2O$, and then dried. Yield: 0.083 g (85%). Anal. Calcd. for $C_{33}H_{41}N_{14}O_{10}Nd$ (%): C, 42.26; H, 4.41; N, 20.90. Found: C, 42.63; H, 4.25; N, 21.21. IR ($cm^{-1}$): 1641 (s, $\nu$(C=N)); 1384 (s, $\nu(NO_3^-)$). UV-Vis ($\lambda_{max}$/nm ($\varepsilon$/$dm^3$ $mol^{-1}$ $cm^{-1}$), $H_2O$): 209 (136400), 247 (40500), 316 (21000), 330 (17000). $\Lambda_M$($H_2O$, 293 K): 404 $S \cdot cm^2 \cdot mol^{-1}$. Red blocky crystals of $[NdL](NO_3)_3 \cdot 0.5H_2O$ suitable for X-ray diffraction were obtained by diffusion of $Et_2O$ into an MeOH/DMF solution over 1 week.

### Physical Measurements

Elemental analyses were performed on a Perkin-Elmer 240c instrument. Molar electrical conductivities in $H_2O$ solution containing $10^{-4}$ M l complex were measured at

25°C ± 0.1°C using a BSD-A conductmeter (Jangsu, China). Electronic spectra were recorded on a UV-3100 spectrophotometer. IR spectra were measured using KBr discs with a Vector 22 FI-IR spectrophotometer. Electrospray mass spectra (ES-MS) were determined on a Finnigan LCQ ES-MS mass spectrometer using methanol as mobile phase with sample concentration about 1.0 mmol dm$^{-3}$. The dilute solution was electrosprayed at a flow rate of $5 \times 10^{-6}$ dm$^3$ min$^{-1}$ with a needle voltage of +4.5 kV. The temperature of the heated capillary in the interface was 200°C and a fused silica sprayer was used.

### Crystal Structure Determination

Diffraction intensity data were collected on a SMART CCD area-detector diffractometer at 293 K using graphite-monochromated Mo K$\alpha$ radiation ($\lambda = 0.71073$ Å). Data reduction and cell refinement were performed by SMART and SAINT Program [15]. The structure was solved by direct methods (Bruker SHELXTL) and refined on $F^2$ by full-matrix least-squares (Bruker SHELXTL) using all unique data [16]. The non-H atoms in the structure were treated as anisotropic. Hydrogen atoms were located geometrically and refined in riding mode. A summary of crystallographic data and data collection parameters is given in Table I. Final atomic coordinates and equivalent isotropic displacement parameters are listed in Table II. Full lists of crystallographic data are available from the authors.

## RESULTS AND DISCUSSION

### Synthesis and Characterization

Attempts to synthesize the cryptate by the condensation of dfp with tren in the presence of Nd$^{3+}$ ion or alkali-earth metal ions as template ions were unsuccessful.

TABLE I A summary of crystallographic data and data collection parameters for the cryptate $[NdL](NO_3)_3 \cdot 0.5H_2O$

| | |
|---|---|
| Empirical formula | $C_{33}H_{40}N_{14}O_{9.5}$ Nd |
| Crystal system | Trigonal |
| Space group | $R\bar{3}c$ |
| a, c (Å) | 14.623(2), 32.682(3) |
| $V$(Å$^3$) | 6052.2(1) |
| $D_{calcd}$. (g/cm$^3$) | 1.529 |
| $F$(000) | 2832 |
| Crystal size (mm) | 0.20 × 0.20 × 0.30 |
| Temperature (K) | 293 |
| $\mu$(Mo-K$\alpha$)/mm$^{-1}$ | 1.357 |
| $2\theta$ range (°) | 2–25 |
| Reflections collected | 9790 |
| Independent reflections | 1196 ($R_{int} = 0.049$) |
| Observed reflections | 877 |
| Index ranges | $-17 \leq h \leq 17k$; $-16 \leq k \leq 17$; $-38 \leq 1 \leq 28$ |
| $w^{-1}$ | $1/[\sigma^2(Fo^2) + (0.0923P)^2]P = (Fo^2 + 2Fc^2)/3$ |
| Goodness of fit on $F^2$ | 1.07 |
| Final $R1$ $wR(2)[I > 2\sigma I]$ | 0.0418, 0.1318 |
| Largest diff. peak and hole [eÅ$^3$] | 0.88, −0.35 |

TABLE II Atomic coordinates and equivalent isotropic displacement parameters for the cryptate (Å$^2$)

| *Atom* | $x/a$ | $y/b$ | $z/c$ | $U$(eq) |
|---|---|---|---|---|
| Nd 1 | 2/3 | 1/3 | 1/12 | 0.0414(2) |
| N1 | 2/3 | 1/3 | −0.0310(3) | 0.057(2) |
| N2 | 0.7905(3) | 0.4794(3) | 0.03036(13) | 0.0528(16) |
| N3 | 2/3 | 0.5109(4) | 1/12 | 0.0504(18) |
| C1 | 0.7672(4) | 0.4250(5) | −0.04031(18) | 0.062(2) |
| C2 | 0.8426(4) | 0.4616(5) | −0.00407(16) | 0.0554(17) |
| C3 | 0.8005(4) | 0.5701(5) | 0.0323(2) | 0.0589(19) |
| C4 | 0.7333(4) | 0.5916(4) | 0.05999(17) | 0.0557(17) |
| C5 | 0.7352(5) | 0.6869(4) | 0.0595(2) | 0.066(2) |
| C6 | 2/3 | 0.6996(6) | 1/12 | 0.072(3) |
| O4 | 0 | 0 | 0 | 1.4(4) |
| O1 | 0.720(3) | 0.620(3) | 0.8842(8) | 0.229(19) |
| O2 | 0.700(3) | 0.626(4) | 0.9569(15) | 0.33(3) |
| O3 | 0.7143(12) | 0.7484(13) | 0.9057(7) | 0.151(8) |
| N5 | 0.7119(8) | 2/3 | 0.91667 | 0.161(12) |

TABLE III Selected bond distances (Å) and angles (°) for the complex[a]

| | | | |
|---|---|---|---|
| Nd1–N2 | 2.640(4) | Nd1–N3 | 2.597(5) |
| Nd1–N2A | 2.640(4) | Nd1–N3A | 2.596(5) |
| Nd1–N2B | 2.640(4) | Nd1–N3B | 2.596(6) |
| Nd1–N2C | 2.640(4) | Nd1 · · · N1 | 3.738 |
| Nd1–N2D | 2.640(4) | Nd1 · · · N1A | 3.738 |
| Nd1–N2E | 2.640(4) | | |
| N2–Nd1–N3 | 62.22(11) | N2-Nd1-N2B | 81.66(13) |
| N2–Nd1–N3A | 138.37(14) | N2-Nd1-N2C | 83.26(13) |
| N2–Nd1–N3B | 73.66(11) | N2–Nd1–N2E | 124.43(14) |
| N2A–Nd1–N3 | 73.64(12) | N2–Nd1–N2D | 147.33(17) |
| N2B–Nd1–N3 | 138.37(9) | N2A–Nd1–N2B | 81.66(16) |
| N2C–Nd1–N3 | 73.64(11) | N2A–Nd1–N2C | 147.30(14) |
| N2E–Nd1–N3 | 62.21(12) | N2A–Nd1–N2E | 83.26(15) |
| N2D–Nd1– N3 | 138.35(10) | N2A–Nd1–N2D | 124.44(16) |
| N2A–Nd1–N3A | 62.21(14) | N2B–Nd1–N2E | 147.32(15) |
| N2A–Nd1–N3B | 138.37(10) | N2B–Nd1–N2D | 83.28(14) |
| N2B–Nd1–N3A | 73.67(15) | N2B–Nd1–N2C | 124.46(16) |
| N2C–Nd1–N3A | 138.37(9) | N2C–Nd1–N2E | 81.65(15) |
| N2E–Nd1–N3A | 73.66(15) | N2C–Nd1–N2D | 81.67(13) |
| N2D–Nd1–N3A | 62.22(15) | N2E–Nd1–N2D | 81.66(16) |
| N2C–Nd1–N3B | 62.24(10) | N3–Nd1–N3A | 119.99(16) |
| N2E–Nd1–N3B | 138.38(10) | N3–Nd1–N3B | 120.00(8) |
| N2D–Nd1–N3B | 73.67(13) | N3A–Nd1–N3B | 120.01(14) |
| N2–Nd1–N2A | 81.66(15) | N2B–Nd1–N3B | 62.22(13) |

[a] Symmetry transformations used to generate equivalent atoms are i: is $1-y$, $x-y$, $z$ (N2A, N3A); ii: $1-x+y$, $1-x$, $z$ (N2B, N3B); iii: $1/3+y$, $-1/3+x$, $1/6-z$ (N2C, N1A); iv: $1/3+x-y$, $2/3-y$, $1/6-z$ (N2D); v: $4/3-x$, $2/3-x+y$, $1/6-z$ (N2E).

Based on the conductivity of the cryptate, it behaves as a 1 : 2 electrolyte [17], consistent with the chemical formula predicated by elemental analysis. The IR spectrum shows characteristic C=N (1641 cm$^{-1}$) and ionic nitrate (1384 cm$^{-1}$) bonds. Because of coordination of neodymium (III) ion, the frequency of the C=N band shifts to longer wavelengths by 6 cm$^{-1}$ compared to the free ligand (1647 cm$^{-1}$ [7]. Intense absorptions in electronic spectra of the cryptate at 200–250 and 310–330 nm are assigned to $\pi$-$\pi$ transitions of the pyridyl and C=N groups, respectively.

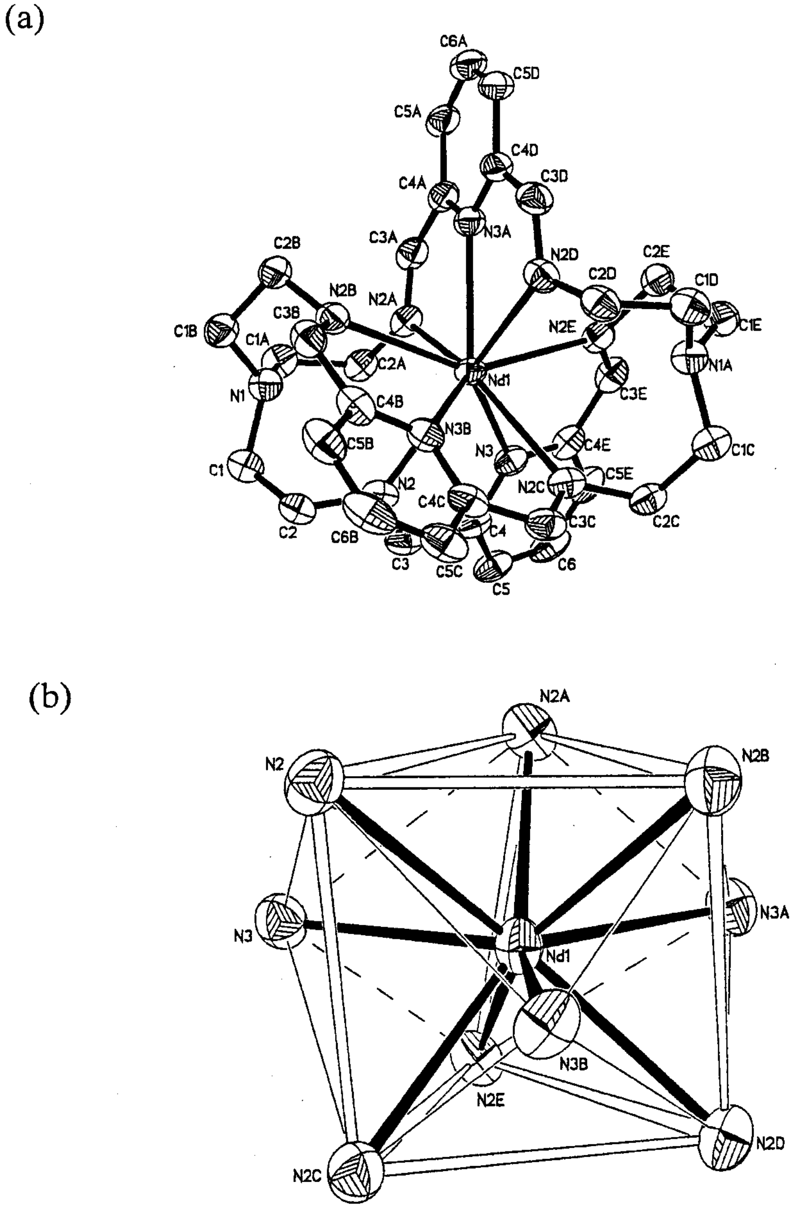


FIGURE 1 (a) A perspective view of the cation $[NdL]^{3+}$ and (b) the structure of the coordination polyhedron. Symmetry transformations used to generate equivalent atoms are i: $1-y$, $x-y$, $z$ (N2A, N3A); ii: $1-x+y$, $1-x$, $z$ (N2B, N313); iii: $1/3+y$, $-1/3+x$, $1/6-z$ (N2C, N1A); iv: $1/3+x-y$, $2/3-y$, $1/6-z$ (N2D); v: $4/3-x$, $2/3-x+y$, $1/6-z$ (N2E).

## Electrospray Mass Spectra

The positive-ion ES mass spectrum of the title cryptate in methanol shows a base peak at $m/z=244.7$ assigned to $[NdL]^{3+}$. Peaks at $m/z=397.3$ and 856.1 can be assigned to $NdL(NO_3)]^{2+}$ and $[NdL(NO_3)_2]^2$, respectively. Besides these, two peaks at $m/z=612.5$

and 696.3 are assigned to $[NaL]^+$ and $[Na_2L(NO_3)]^+$, respectively, implying that the cryptand can bind $Na^+$ ion to form an inclusion complex. The $Na^+$ ion is present in trace amount. The dissociation of $Nd^{3+}$ implies that the cryptate is somewhat unstable in methanol solution. No fragment of the cryptand is observed, showing the cryptand is very stable.

## Crystal Structure of the Cryptate

Selected bond distances and angles are listed in Table III. In the complex cation (Fig. 1 (a)), Nd7 is located in the centre of the macrocycle and coordinated by three pyridyl nitrogen atoms (N3, N3A and N3B) and six imino nitrogens (N2, N2A, N2B, N2C, N2D and N2E). The complex cation has a three-fold axis through Nd1 and the two bridgehead nitrogen atoms (N1, N1A). The average bondlength between Nd1 and nitrogen atoms of the pyridine groups is 2.596 Å, slightly shorter than those for the imino groups (2.640 Å). The separation of Nd1 and N (bridgehead) is 3.738 Å. No interation between Nd1 and N (bridgehead) is observed. The coordination polyhedron of complex cation can be described approximately as a tricapped prism (Fig. 1 (b)). The upper and basal planes of the prism are composed of the imino nitrogen atoms (N2, N2A, N2B and N2C, N2D, N2E, respectively). The distance between two parallel planes is 3.462 Å and the average distance between Nd1 and the upper (or basal) plan 1.731 Å; three pyridyl nitrogen atoms are located at capping positions and Nd1 is located in the symmetrical centre of the prism. The distance from Nd1 to each of the three least-squares prism planes is 0.987 Å. This symmetrical tricapped prism structure is different from the structures of the sodium cryptate with the same ligand [9] and that of neodymium cryptate based on phenol [11], in which the central ions are located at one side of the macrocycle. Nd1 in this cryptate locates in the symmetrical centre in order to make best use of the nine nitrogens donors and to satisfy the requirements of higher co-ordination numbers for lanthanide ion.

## *Acknowledgements*

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

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