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## Hydrated neodymium(III) and europium(III) picrate complexes with pyrazine-*N*-oxide

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### Abstract

Compounds with composition  $\text{Ln}(\text{pic})_3 \cdot 2\text{pyzNO} \cdot 7\text{H}_2\text{O}$  ( $\text{Ln}=\text{Nd}, \text{Eu}$ ;  $\text{pic}=\text{picrate}$ ;  $\text{pyzNO}=\text{pyrazine-}N\text{-oxide}$ ) were obtained by reaction of the hydrated lanthanide picrate with pyrazine-*N*-oxide in ethanol (molar ratio 1:4). The adducts were characterized by elemental analyses and IR spectra. X-ray single crystal data for the neodymium complex indicate that the crystal system is triclinic, space group  $P \bar{1}$ . Nd unit cell dimensions are:  $a=7.930(1) \text{ \AA}$ ;  $b=12.869(1) \text{ \AA}$ ;  $c=20.833(1) \text{ \AA}$ ;  $\alpha=106.414(7)^\circ$ ;  $\beta=92.574(7)^\circ$ ;  $\gamma=92.202(9)^\circ$ ;  $V=2034.4(3) \text{ \AA}^3$ ;  $Z=2$ . Europium cell parameter are  $a=7.882(1) \text{ \AA}$ ,  $b=12.880(1) \text{ \AA}$ ,  $c=20.788(2) \text{ \AA}$ ,  $\alpha=106.224(8)^\circ$ ,  $\beta=92.055(7)^\circ$ ,  $\gamma=93.140(7)^\circ$ . One picrate is bidentate, coordinated through the phenoxo oxygen and one oxygen of an *o*-nitro group and two are not coordinated. One pyrazine-*N*-oxide is bonded through the oxygen and the other is out of sphere. Six water molecules are bonded and a seventh is not coordinated. The coordination polyhedron is a distorted tricapped trigonal prism. © 2000 Elsevier Science S.A. All rights reserved.

**Keywords:** Neodymium(III); Europium(III); Pyrazine-*N*-oxide; Structure

### 1. Introduction

The possibility of utilizing pyrazine-*N*-oxide (pyzNO) in substitution and rearrangement reactions similar to those developed for pyridine-*N*-oxide in biological systems led to a growing interest in this ligand [1].

Addition compounds of trivalent lanthanide perchlorates [2], chlorides, hexafluorophosphates [3], hydrated iodides [4], nitrates [5], isothiocyanates [6] and trifluoroacetates [7] with compositions:  $\text{La}(\text{ClO}_4)_3 \cdot 7\text{pyzNO} \cdot 2\text{H}_2\text{O}$ ,  $\text{Ln}(\text{ClO}_4)_3 \cdot 8\text{pyzNO}$  ( $\text{Ln}=\text{Pr}, \text{Eu}, \text{Er}, \text{Y}$ );  $\text{LaCl}_3 \cdot 2\text{pyzNO}$ ,  $\text{LnCl}_3 \cdot 2.5\text{pyzNO}$  ( $\text{Ln}=\text{Pr}, \text{Eu}, \text{Y}$ ),  $\text{LnCl}_3 \cdot 3\text{pyzNO}$  ( $\text{Ln}=\text{Er}, \text{Y}$ );  $\text{Ln}(\text{PF}_6)_3 \cdot 8\text{pyzNO}$  ( $\text{Ln}=\text{La}, \text{Pr}, \text{Eu}, \text{Er}, \text{Y}$ );  $\text{LnI}_3 \cdot 3\text{pyzNO} \cdot 8\text{H}_2\text{O}$  ( $\text{Ln}=\text{Ce}, \text{Nd}, \text{Eu}, \text{Tb}, \text{Yb}, \text{Y}$ );  $\text{Ln}(\text{NO}_3)_3 \cdot 3\text{pyzNO}$  ( $\text{Ln}=\text{La-Lu}, \text{Y}$ );  $\text{Ln}(\text{NCS})_3 \cdot 4\text{pyzNO}$  ( $\text{Ln}=\text{La-Lu}, \text{Y}$ ) and  $\text{Ln}(\text{TFA})_3 \cdot 2\text{pyzNO} \cdot \text{H}_2\text{O}$  ( $\text{Ln}=\text{La}, \text{Pr-Dy}, \text{Er}, \text{Yb}, \text{Y}$ ) have been described.

In this article we report the preparation of the addition

compounds obtained by reaction of trivalent lanthanide hydrated picrates ( $\text{Ln}=\text{Nd}, \text{Eu}$ ) and this ligand (pyzNO), with the objective to correlate structure and spectra of the complexes.

### 2. Experimental

Pyrazine mono-oxide was prepared according to Koelsch and Gumprecht [8] by oxidation of pyrazine with hydrogen peroxide and was characterized by its melting point (110–112°C) and IR spectrum.

The neodymium compound was obtained by reaction of the hydrated picrate [9] in ethanol with an ethanolic solution of the ligand (molar ratio 1:4). The precipitate obtained was separated and the filtrate left to slow evaporation at room temperature in order to obtain single crystals.

The europium compound was prepared by the same procedure, but in this case the mixture was maintained in the refrigerator for 1 day.

Infrared absorption spectra were recorded on a FT-IR

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Table 1

Summary of the analytical results of the compounds with composition  $\text{Ln}(\text{pic})_3 \cdot 2(\text{pyzNO}) \cdot 7(\text{H}_2\text{O})$

| Ln | % C    |       | % H    |      | % N    |      |
|----|--------|-------|--------|------|--------|------|
|    | Theor. | Exp.  | Theor. | Exp. | Theor. | Exp. |
| Nd | 27.2   | 27.3  | 2.4    | 2.5  | 15.9   | 15.7 |
| Eu | 27.0   | 27.90 | 2.4    | 2.6  | 15.8   | 15.9 |

Prospect R Midac using Nujol mulls, between KBr plates. The absorption spectrum (visible range) of the neodymium compound was obtained at room temperature in a Carl Zeiss DMR-10 spectrophotometer, using a silicone mull in a 0.5 mm path cell. The emission spectrum of the europium compound at 77 K was recorded on a Hitachi Perkin-Elmer MPF-4 spectrofluorimeter.

### 2.1. Crystal structure determination

Data were collected on a CAD-4 Mach 3 Enraf-Nonius diffractometer in  $\omega/2\theta$  scan mode, using graphite-monochromated Mo  $K\alpha$  radiation. These data were corrected for Lorentz, polarization and absorption effects. The structure

of the Nd compound was solved by the standard Patterson heavy-atom method followed by normal difference Fourier techniques. H-atoms were refined with fixed geometry, each riding on a carrier atom, with an isotropic displacement parameter amounting to 1.2 times (1.5 for water hydrogens) the values of the equivalent isotropic displacement parameters of the atoms they are attached. The programs used were SHELXL-97 [10], SHELXL-86 [11] and ZORTEP [12]. Further details were deposited at the Cambridge Crystallographic Data Centre.

### 3. Results and discussion

The complexes with composition  $\text{Ln}(\text{pic})_3 \cdot 2(\text{pyzNO}) \cdot 7(\text{H}_2\text{O})$ , where  $\text{Ln}=\text{Nd}$  and  $\text{Eu}$ , were characterized by CHN microanalytical procedures, confirming the stoichiometry proposed (Table 1).

The main bands obtained in the infrared spectra are presented in Table 2.

Fig. 1 contains the absorption spectrum of the neodymium compound at room temperature for  ${}^4\text{G}_{5/2}$ ,  ${}^2\text{G}_{7/2} \leftarrow {}^4\text{I}_{9/2}$  transitions. The baricenter of such transitions

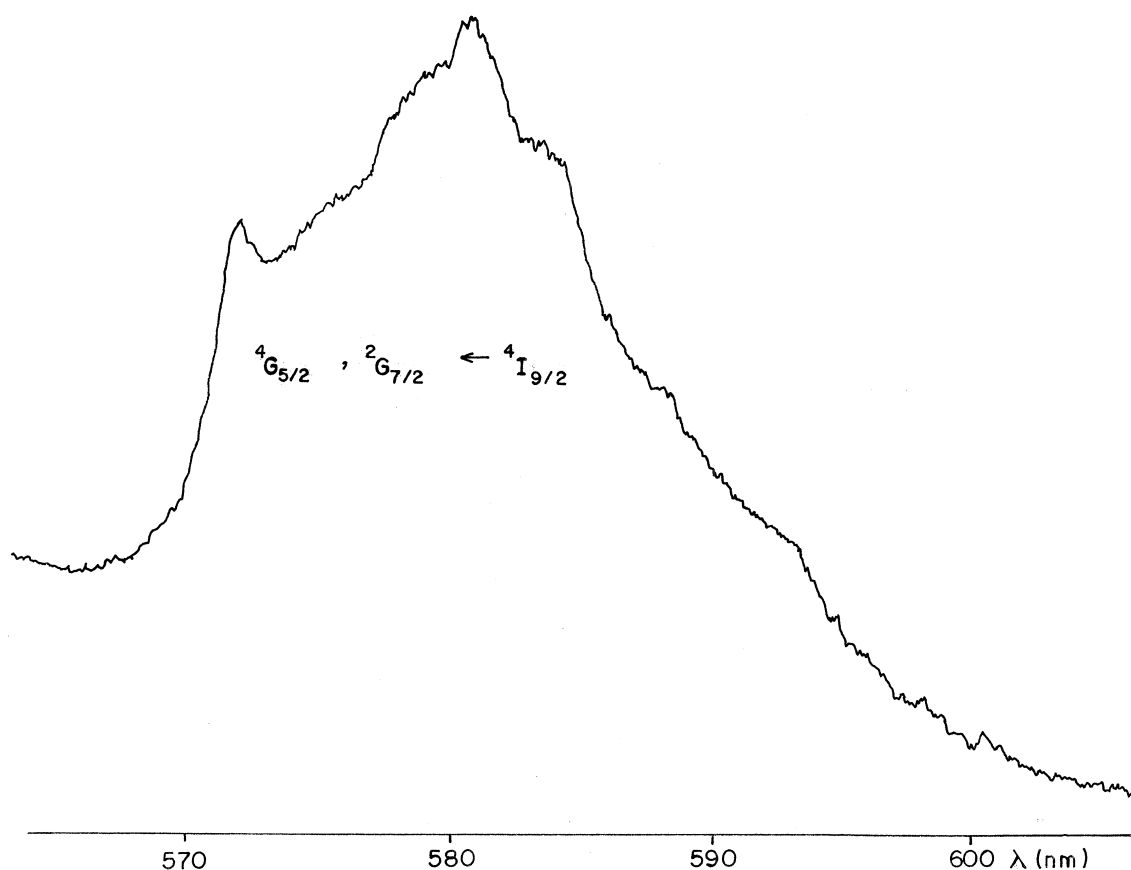


Fig. 1. Absorption spectrum of neodymium compound, at room temperature in silicone mull.

Table 2  
IR frequencies ( $\text{cm}^{-1}$ ) of the complexes

| Ln                 | $\nu\text{C-C}$ | $\nu_{\text{as}}\text{NO}_2$ | $\nu_{\text{s}}\text{NO}_2$ | $\delta\text{NO}_2$ | $\nu\text{C-N}$<br>(pyzNO) | $\nu\text{NO}$<br>(pyzNO) |
|--------------------|-----------------|------------------------------|-----------------------------|---------------------|----------------------------|---------------------------|
| Nd                 | 1617s           | 1570–1541s                   | 1363–1335s                  | 860m                | <sup>a</sup>               | 1278s                     |
| Eu                 | 1617s           | 1571–1542s                   | 1369–1341s                  | 860m                | <sup>a</sup>               | 1272s                     |
| PyzNO <sup>a</sup> | –               | –                            | –                           | –                   | 1591m                      | 1309s                     |

<sup>a</sup> Enveloped by  $\nu\text{C-C}$ . s=shoulder, m=medium.

was calculated by applying Simpson's rule [13]. The value obtained ( $17\,192\text{ cm}^{-1}$ ) was compared to that of the standard  $\text{Nd}^{3+}:\text{LaF}_3$  ( $17\,156\text{ cm}^{-1}$ ) [14] in order to calculate the nephelauxetic parameter  $\beta=0.992$  [15], the covalent factor  $b^{1/2}=0.063$  [16] and Sinha's parameter  $\delta=0.806$  [17]. They are indicative of an essentially ionic but with some covalent character.

The emission spectrum of the europium complex at 77 K is presented in Fig. 2. The  ${}^5\text{D}_0 \rightarrow {}^7\text{F}_0$  transition is extremely weak. The  ${}^5\text{D}_0 \rightarrow {}^7\text{F}_1$  transition contains three



Fig. 2. Emission spectrum of the europium compound, at 77 K. Excitation wavelength 394 nm.

peaks one  $A'_2$  species, magnetic dipole allowed and two peaks due to  $E''$  species (electrically and magnetically allowed). The  ${}^5\text{D}_0 \rightarrow {}^7\text{F}_2$  transition shows an intense peak with a shoulder and two peaks due to  $E'$  (electrically allowed levels) and two  $E''$  (magnetically allowed levels). The spectrum was interpreted in terms of a  $D_{3h}$  distorted to  $C_{3v}$  symmetry [18].

Table 3 presents the crystal collection and refinement data of the Nd compound together with the cell constants of the Eu complex. Table 4 presents distances and angles around the  $\text{Nd}^{3+}$  ion. Fig. 3 shows a ZORTEP view of the coordination polyhedron.

In Fig. 4, the  $\text{Nd}^{3+}$  ion achieves a coordination number of nine by the bonding of one bidentate picrate via the phenoxo-oxygen and an oxygen of the adjacent nitro moiety an oxygen of one pyrazine-*N*-oxide molecule and six oxygens of water molecules, in a distorted tricapped

Table 3  
Crystallographic data and details of the structure refinement

|                                                    |                                                          |
|----------------------------------------------------|----------------------------------------------------------|
| Empirical formula                                  | $\text{C}_{26}\text{H}_{28}\text{N}_{13}\text{NdO}_{30}$ |
| Formula weight                                     | 1146.85                                                  |
| Crystal system, space group                        | Triclinic, $P\bar{1}$                                    |
| Unit cell dimensions <sup>a</sup>                  |                                                          |
| $a$ (Å)                                            | 7.930(1)                                                 |
| $b$ (Å)                                            | 12.869(1)                                                |
| $c$ (Å)                                            | 20.833(1)                                                |
| $\alpha$ (°)                                       | 106.414(7)                                               |
| $\beta$ (°)                                        | 92.574(7)                                                |
| $\gamma$ (°)                                       | 92.202(9)                                                |
| Volume (Å <sup>3</sup> )                           | 2034.4(3)                                                |
| Molecules per cell, $Z$                            | 2                                                        |
| Calculated density, $D_c$ ( $\text{g cm}^{-3}$ )   | 1.872                                                    |
| Absorption coefficient, $\mu$ ( $\text{mm}^{-1}$ ) | 1.401                                                    |
| $F(000)$                                           | 1150                                                     |
| Crystal size (mm)                                  | $0.25 \times 0.20 \times 0.20$                           |
| $\theta$ range for data collection (°)             | 2.57 to 25.50                                            |
| Limiting indices                                   | $-9 \leq h \leq 9, -15 \leq k \leq 14, 0 \leq l \leq 25$ |
| Reflections collected/unique                       | 7793/7571 [ $R_{\text{int}}=0.0201$ ]                    |
| Refinement method                                  | Full-matrix least-squares on $F^2$                       |
| Data/restraints/parameters                         | 7571/0/631                                               |
| Goodness-of-fit (S) on $F^2$                       | 1.029                                                    |
| Final $R$ indices [ $I > 2\sigma(I)$ ]             | $R1=0.0357, wR2=0.0893$                                  |
| $R$ indices (all data)                             | $R1=0.0567, wR2=0.0970$                                  |
| Max., min. residual $\rho$ ( $\text{e Å}^{-3}$ )   | 0.22 and $-0.25$                                         |

<sup>a</sup> Cell parameters of the Eu-complex:  $a=7.882(1)$  (Å),  $b=12.880(1)$  (Å),  $c=20.788(2)$  (Å),  $\alpha=106.224(2)^\circ$ ,  $\beta=92.055(7)^\circ$ ,  $\gamma=93.140(7)^\circ$ .

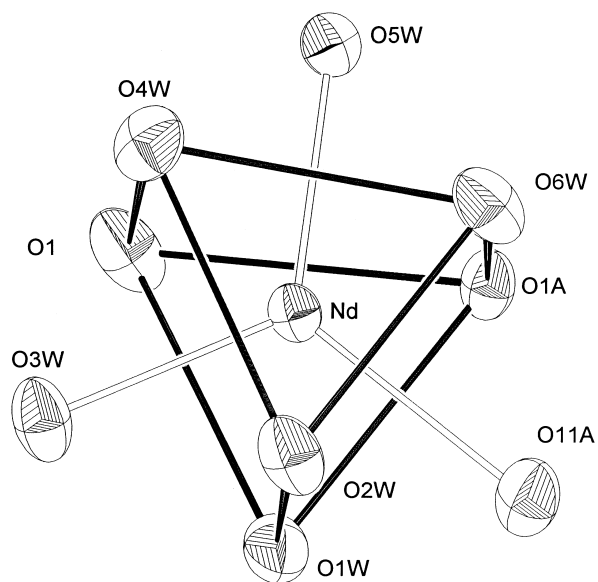


Fig. 3. ZORTEP view of the coordination polyhedron.

trigonal prism fashion. The formula can be written  $[\text{Nd}(\text{pic})(\text{pyzNO})(\text{H}_2\text{O})_6](\text{pic})_2(\text{pyzNO})(\text{H}_2\text{O})$  with two picrates, one pyzNO and one water molecule that are out of sphere.

Several geometric parameters to quantify the deformation of the coordination polyhedra, introduced by Balic Zunic and Makovicky [19] and implemented in IVTON [20], are given. These parameters are calculated in relation to the 'centroid of coordination polyhedron', which is the point in the coordination polyhedron for which the variance of squares of distances to ligands is minimum. These are the central atom-centroid distance ( $\Delta$ ) of 0.055 Å, the average distance from the centroid to the ligands ( $r$ ) is 2.478 Å, and the 'sphericity' ( $1 - \sigma_r/r$ ) is of 0.967 ( $\sigma_r$  is the standard deviation of the distances from the centroid to the ligands). Moreover, the bond-valence parameter calculated for this structure is 2.097 (the tabulated value is 2.105 [21]).

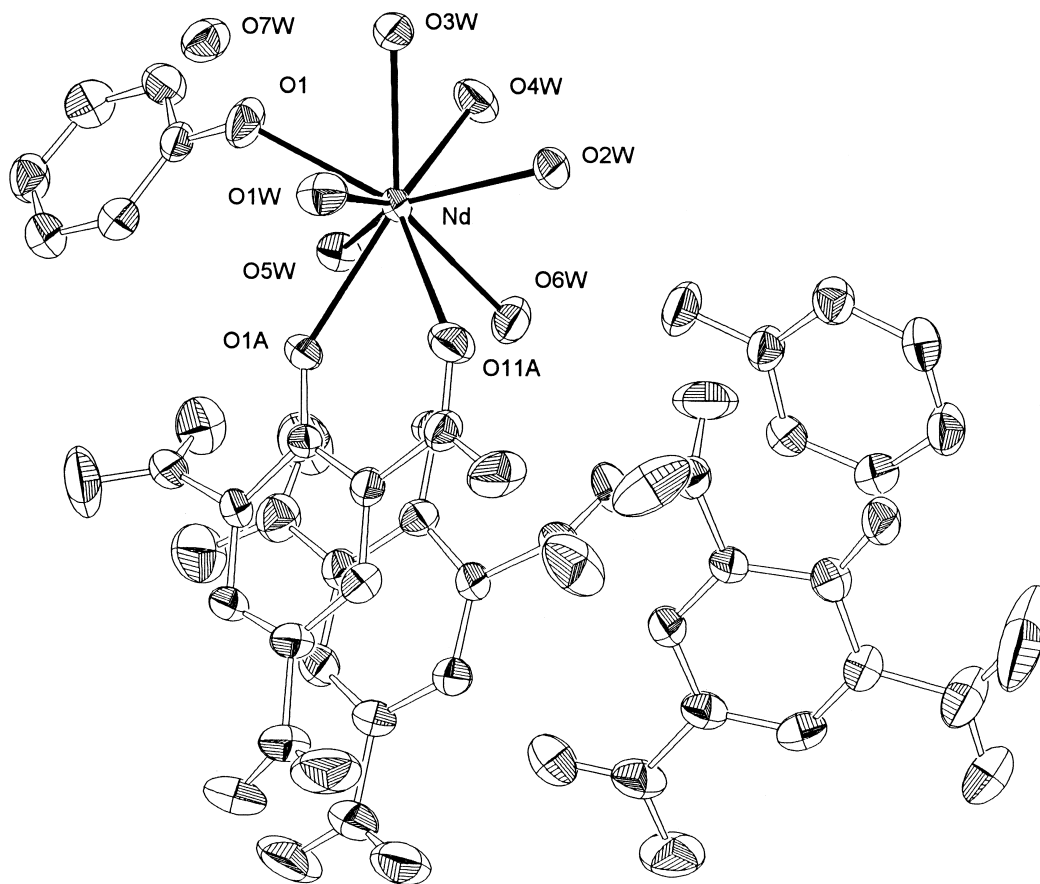


Fig. 4. Structure of neodymium complex.

Table 4  
Distances (Å) and angles (°) around the Nd<sup>3+</sup> ion

|                 |            |
|-----------------|------------|
| Nd–O(1A)        | 2.393(3)   |
| Nd–O(1)         | 2.430(3)   |
| Nd–O(2W)        | 2.441(3)   |
| Nd–O(6W)        | 2.450(3)   |
| Nd–O(1W)        | 2.458(3)   |
| Nd–O(3W)        | 2.499(3)   |
| Nd–O(5W)        | 2.503(3)   |
| Nd–O(4W)        | 2.520(3)   |
| Nd–O(11A)       | 2.694(3)   |
| O(1A)–Nd–O(1)   | 85.96(11)  |
| O(1A)–Nd–O(2W)  | 129.69(10) |
| O(1)–Nd–O(2W)   | 138.42(10) |
| O(1A)–Nd–O(6W)  | 79.53(10)  |
| O(1)–Nd–O(6W)   | 141.93(11) |
| O(2W)–Nd–O(6W)  | 74.13(10)  |
| O(1A)–Nd–O(1W)  | 78.46(11)  |
| O(1)–Nd–O(1W)   | 77.09(12)  |
| O(2W)–Nd–O(1W)  | 88.84(11)  |
| O(6W)–Nd–O(1W)  | 132.56(11) |
| O(1A)–Nd–O(3W)  | 141.81(10) |
| O(1)–Nd–O(3W)   | 66.38(10)  |
| O(2W)–Nd–O(3W)  | 72.04(10)  |
| O(6W)–Nd–O(3W)  | 138.27(11) |
| O(1W)–Nd–O(3W)  | 70.30(11)  |
| O(1A)–Nd–O(5W)  | 68.54(10)  |
| O(1)–Nd–O(5W)   | 70.88(10)  |
| O(2W)–Nd–O(5W)  | 135.96(10) |
| O(6W)–Nd–O(5W)  | 71.07(10)  |
| O(1W)–Nd–O(5W)  | 134.88(11) |
| O(3W)–Nd–O(5W)  | 121.03(10) |
| O(1A)–Nd–O(4W)  | 136.64(10) |
| O(1)–Nd–O(4W)   | 89.18(12)  |
| O(2W)–Nd–O(4W)  | 78.06(11)  |
| O(6W)–Nd–O(4W)  | 78.23(11)  |
| O(1W)–Nd–O(4W)  | 141.79(11) |
| O(3W)–Nd–O(4W)  | 71.52(11)  |
| O(5W)–Nd–O(4W)  | 69.19(10)  |
| O(1A)–Nd–O(11A) | 63.06(9)   |
| O(1)–Nd–O(11A)  | 133.92(12) |
| O(2W)–Nd–O(11A) | 67.50(10)  |
| O(6W)–Nd–O(11A) | 68.14(11)  |
| O(1W)–Nd–O(11A) | 64.44(11)  |
| O(3W)–Nd–O(11A) | 118.29(10) |
| O(5W)–Nd–O(11A) | 120.54(10) |
| O(4W)–Nd–O(11A) | 136.84(10) |

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