

КРАТКИЕ СООБЩЕНИЯ

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CRYSTAL STRUCTURE OF DIGUANIDINIUM DIAQUAPENTAKIS(NITRATO)NEODYMIATE(III)

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The crystal structure of the $C_2H_{16}N_{11}NdO_{17}$ complex (**I**) is established by X-ray crystallography. Compound (**I**) crystallizes in the monoclinic system, space group $C2/c$, $a = 10.8926(6)$ Å, $b = 9.0003(6)$ Å, $c = 20.4621(11)$ Å, $\alpha = 90^\circ$, $\beta = 94.535(3)^\circ$, $\gamma = 90^\circ$, $V = 1999.8(2)$ Å³, and $Z = 4$. The guanidinium N—H and water H atoms are engaged in hydrogen bonds with an oxygen atom of the nitrate groups attached on neodymium (Nd). This has resulted in the formation of a three dimensional network. Based on the Cambridge Structural Database, this is the first structurally-characterized neodymium nitrate anion bonded to the $[(NH_2)_3C]^+$ cation.

Keywords: crystal structure, neodymium nitrate complex, guanidinium cation, hydrogen bonding.

The novel crystal structure of diguanidinium diaquapentakis(nitrato)neodymiate(III) reported herein is a result of the study of the coordination of electron-deficient lanthanide and guanidinium tetrafluoroborate salts. The symmetric $[(NH_2)_3C]_2Nd(NO_3)_5 \cdot (H_2O)_2$ compound is composed of one $[Nd(NO_3)_5(H_2O)_2]^{2-}$ anion and half of the guanidinium cation $[(NH_2)_3C]^+$. Neodymium (Nd) is coordinated to twelve oxygen atoms: ten from five nitrate ions and two from water molecules. Some of already investigated neodymium nitrate complexes containing cationic species are $Na_2[Nd(NO_3)_5(H_2O)]$ (Vigdorchik *et al.*, 1990) [1], $K_2[Nd(NO_3)_5(H_2O)_2]$ (Held *et al.*, 2000) [2], $Cs_2[Nd(NO_3)_5(H_2O)_2]$ (Vigdorchik *et al.*, 1989) [3], $[C_3H_5N_2]_2[Nd(NO_3)_5(H_2O)]$ (Zhang *et al.*, 2006) [4]. In addition, there is scant or no information about a lanthanide complex with the guanidinium cation in the literature.

Experimental. All the chemicals and solvents used were of analytical grade. Neodymium nitrate hexahydrate (0.01 g, 0.22 mmol) was dissolved in 8 ml of methanol and added to a 25 ml flask with a magnetic stirrer in the dry box. Guanidinium tetrafluoroborate (0.03 g, 0.23 mmol) was dissolved in 5 ml of methanol and added to the reaction, and the colorless mixture was stirred at room temperature overnight. The following day this mixture was concentrated using an argon stream, producing a suspension of white crystals. Further evaporation at room temperature resulted in white single crystals suitable for X-ray analysis.

The X-ray crystallography was measured at 228 K temperature with a Bruker ApexII K-axis diffractometer with a graphite monochromator (MoK_α radiation, $\lambda = 0.71073$ Å) and a charged coupled device (CCD) camera. The intensity data were collected for Lorentz and polarization effects.

The Bruker SHELXTL package was used for the structure solution and cell refinement. In accomplishing the integration and scaling of the intensity data the SAINT-*plus* software package was used [5]. The structure was solved by direct approach methods and refined by a matrix least-squares procedure based on F^2 [6]. All non-hydrogen atoms were refined anisotropically and the hydrogen atoms were refined in idealized position in the riding model approximation, with N—H = 0.81 Å; isotropic displacement parameters were refined freely. Table 1 summarizes the crystal data and structure

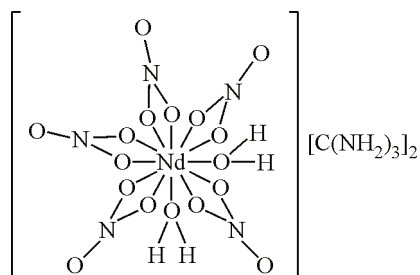
T a b l e 1

Summary of crystal data and structure refinement results for compound (I)

Parameter	Compound
Chemical formula	C ₂ H ₁₆ N ₁₁ NdO ₁₇
<i>M</i>	610.50
Crystal system	Monoclinic
Space group	<i>C</i> 2/ <i>c</i>
Unit cell dimensions <i>a</i> , <i>b</i> , <i>c</i> , Å	10.8926(6), 9.0003(6), 20.4621(11)
α, β, γ, deg.	90, 94.535(3), 90
<i>V</i> , Å ³	1999.8(2)
<i>Z</i>	4
Calculated density, g/cm ³	2.028
Crystal dimensions, mm	0.621×0.23×0.184
Crystal shape and color	Colorless and plates
Absorp. coefficient, mm ⁻¹	2.071
<i>F</i> (000)	1204
θ range for data collection, deg.	3.47 to 36.37
Reflections collected	32236
Independent reflections	4846 [<i>R</i> (int) = 0.0196]
Completeness to θ, %	99.7
Data / restraints / parameters	4846 / 0 / 174
GOOF on <i>F</i> ²	1.655
Final <i>R</i> indices [<i>I</i> > 2σ(<i>I</i>)]	<i>R</i> 1 = 0.0206, <i>wR</i> 2 = 0.0464
<i>R</i> indices (all data)	<i>R</i> 1 = 0.0207, <i>wR</i> 2 = 0.0465
Largest diff. peak and hole, e/Å ⁻³	1.689 and -2.734
CCDC	941141

refinement for compound (I). For molecular graphics DIAMOND was used [7], and the SHELXTL XCIF software package was used to prepare the publication [6].

Results and discussion. The novel crystal structure of compound (I) was established by the single crystal X-ray analysis as shown in Fig. 1. It was confirmed after a thorough search of the Cambridge Structural Database [8] (version 5.32, November 2011 update), which indicates that there is no compound (I) that has been structurally characterized. This was the result of the reaction of electron-deficient lanthanide salts with guanidinium tetrafluoroborate salts in the 1:1 stoichiometry ratio and the compound in Scheme 1 was isolated.



The nitrate ligand coordination around the neodymium atom in Fig. 1 does not seem to vary from other similar Nd complexes in terms of bond distances for Nd—O and N—O, which are in the range 2.4917(10)—2.7109(11) Å and 1.219(2)—1.2573(16) Å respectively. The O—N—O bond angles are

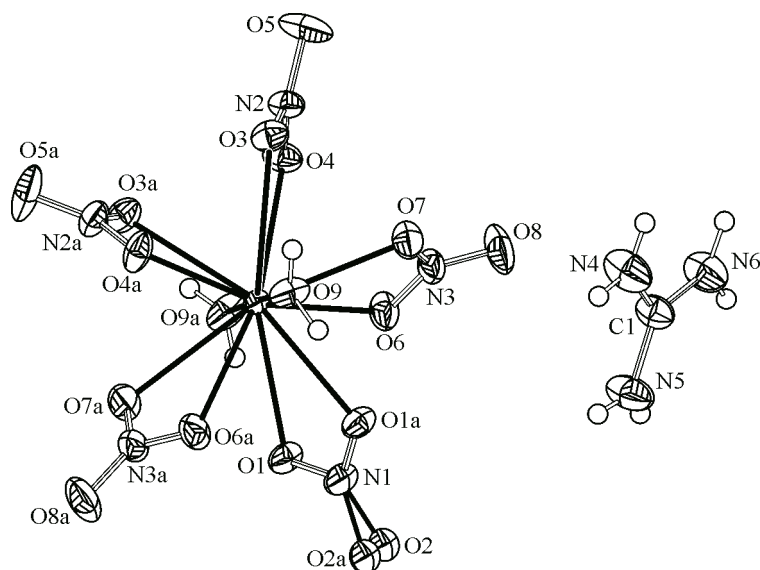


Fig. 1. Molecular structure of $C_2H_{16}N_{11}NdO_{17}$ showing the atomic numbering scheme. Displacement ellipsoids are drawn at the 50 % probability level. Hydrogen atoms on the guanidinium cation are shown as small spheres of arbitrary radius compared to carbon, nitrogen, and oxygen spheres

in the range $116.41(14)$ – $122.59(14)^\circ$ (Table 2). These results are in good agreement with those of $A_2[Nd(NO_3)_5(H_2O)]$ ($A = Na, K, Cs$) complexes, as we have seen earlier, also with $[Me_4N]_3[Nd(NO_3)_6]$ (Chesman *et al.*, 2007) [9] and $[(C_3H_5N_2)_2Nd(NO_3)_5(H_2O)]$ (Zhang *et al.*, 2006) [4].

In Fig. 1 nitrate ligands in the $[Nd(NO_3)_5(H_2O)_2]^{2-}$ anion are positioned in a pseudo-octahedron around the metal center in the arrangement which minimizes repulsion between the ligands; this has also been observed by Chesman *et al.* 2006 [10]. The nitrate ligands are oriented perpendicular to each other around the metal center.

In the crystal structure shown in Fig. 1, the ions are held together by N—H...O hydrogen bonds as indicated in Table 3. The hydrogen bond distances for OH^- (from water) with O (from nitrate) and N—H (from the guanidinium cation) with O (from nitrate) are $2.9078(16)$ Å— $3.066(3)$ Å and $2.852(2)$ — $3.057(3)$ Å, respectively. The latter hydrogen bond lengths are similar to those ($2.945(6)$ —

Table 2

Selected bond distances d , Å
and angles φ , deg. for compound **I**

Bond	d
Nd1—O1	2.6049(11)
Nd1—O3	2.6820(12)
Nd1—O6	2.6584(12)
Nd11—O7	2.7109(11)
O2—N1	1.218(2)
O1—N1	1.2711(14)
O2—N1	1.2460(3)
Angle	φ
O1—N1—O1	116.76(17)
O3—N2—O4	116.41(14)
O2—N1—O1	121.97(16)
O5—N2—O3	122.59(14)
O8—N3—O7	121.77(15)
O8—N3—O6	120.42(15)

Table 3

Hydrogen bond geometry (Å, deg.)

D—H...A	D—H	D—H	D—A	D—H
O9—H9B...O2#2	0.77(3)	2.56(3)	3.066(3)	124(3)
O9—H9B...O1	0.77(3)	2.15(3)	2.917(16)	175(3)
O9—H9B...O3#3	0.83(3)	2.08(3)	2.9078(16)	172(3)
N5—H5A...O8#4	0.82(3)	2.27(4)	3.057(3)	161(3)
N6—H6A...O6#4	0.80(3)	2.20(3)	2.982(2)	169(3)
N5—H5A...O5#5	0.82(3)	2.56(3)	2.869(2)	104(3)
N6—H6B...O7#6	0.86(3)	2.20(3)	3.022(2)	162(3)
N4—H4B...O8#6	0.81(3)	2.10(3)	2.907(3)	173(3)
N4—H4A...O4#7	0.79(3)	2.08(3)	2.852(2)	168(3)

Symmetry code: (i) $-x+1, y, -z+3/2$; (ii) $x+1/2, y+1/2, z$; (iii) $-x+3/2, y-1/2, -z+3/2$; (iv) $-x+1, -y+1, -z+1$; (v) $x, y-1, z$; (vi) $-x+3/2, -y+3/2, -z+1$; (vii) $x+1/2, y-1/2, z$.

2.968(6) Å) observed by Katrusiak, 1994 [11] in $[(\text{NH}_2)_3\text{C}]^+\text{NO}_3^-$. The hydrogen bonding in Fig. 1 is fairly strong based on the bond angles which are in the range $104(3)$ – $73(3)^\circ$ for the N—H...O bond (nitrate) and $124(3)$ – $75(3)^\circ$ for the O—H...O bond (nitrate). These two types of angles presented in Table 3 approach 180° , which signifies the existence of a strong hydrogen stretching in complex (I).

Conclusions. Novel complex compound (I), which is a result of the reaction of the guanidinium cation and electron-deficient lanthanide salts is prepared and fully characterized. This was made as part of the coordination chemistry investigation on scanty lanthanide salts-guanidinium cation complexes. The complex in Fig. 1 is held together by hydrogen bonds which bind the guanidinium cation N—H and water H atoms with oxygen atoms of the nitrate groups attached on the Nd metal atom.

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CIF file containing complete information on the studied structural (I) was deposited with CCDC, deposited number 941141, and is freely available upon request from the following web site: www.ccdc.cam.ac.uk/data_request.cif.

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