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Significant impact of lanthanide contraction on the structure of the phenanthroline complexes

Pavel S. Lemport,[a] Mariia V. Evsiunina,[a] Yulia V. Nelyubina,[b] Kseniya L. Isakovskaya,[b,c] Victor N. Khrustalev,[d,e] Valentine S. Petrov,[a] Anton S. Pozdeev,[a] Petr I. Matveev,[a] Yuri A. Ustynyuk[a] and Valentine G. Nenajdenko*[a]

[a] *Department of Chemistry, M. V. Lomonosov Moscow State University, 119991 Moscow, Russian Federation.*
E-mail: nenajdenko@gmail.com
[b] *A. N. Nesmeyanov Institute of Organoelement Compounds, Russian Academy of Sciences, 119991 Moscow, Russian Federation*
[c] *D. I. Mendeleev University of Chemical Technology of Russia, 125047 Moscow, Russian Federation*
[d] *Peoples Friendship University of Russia (RUDN University), 117198 Moscow, Russian Federation*
[e] *N. D. Zelinsky Institute of Organic Chemistry, Russian Academy of Sciences, 119991 Moscow, Russian Federation*

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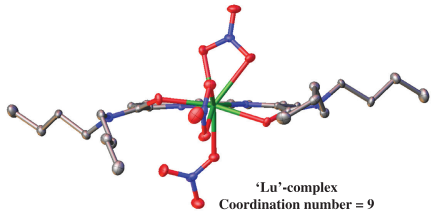
The structure of La, Nd, Eu and Lu complexes with *N*,*N*,*N′*,*N′*-tetrabutyl-1,10-phenanthroline-2,9-dicarboxamide ligand was examined using X-ray diffraction analysis. Due to the effect of lanthanide contraction, lutetium forms unique type of complex having the coordination number 9 in contrast to other 10-coordinated lanthanides.



Keywords: phenanthrolinediamide, polydentate ligand, lanthanide, complex, lutetium complexes, X-ray, coordination number.

Diamides of 1,10-phenanthroline-2,9-dicarboxylic acids (DAPhenA) are intensively studied as polydentate N,O-donor ligands that form strong complexes with lanthanides (Ln) and actinides (An). These substances have moderate Brønsted basicity but high Lewis basicity and are capable of forming stable complexes with cations of transition and post-transition metals, which are soluble in polar organic solvents. High selectivity and efficiency of DAPhenA in the binding of cations that are similar in their chemical properties makes them useful as extractants in the separation of Ln and An in two-phase water/organic solvent systems.[1] The intra- and intergroup separation of trivalent Ln and An is challenging. This task is one of the most difficult in the development of technologies for processing highly radioactive waste in nuclear energetics.[2,3] Solving such problems requires obtaining accurate data on the structure and properties of Ln and An complexes during extraction. DAPhenA can form 1 : 1 and 2 : 1 complexes with lanthanides and actinides. X-ray study of several complexes of both types are documented.[4–12] It is very important to identify patterns in the changes in these parameters with increasing atomic numbers in the series of DAPhenA complexes with Ln and minor An, however scarce data available in the literature is insufficient to solve this problem. Therefore, systematic study of structural peculiarities of DAPhenA complexes is highly desirable.

Trying to fill this gap, in this work we synthesized complexes of Ln, Nd, Eu, and Lu nitrates ligated with *N*,*N*,*N′*,*N′*-tetrabutyl-1,10-phenanthroline-2,9-dicarboxamide (L) and studied their structure in the crystalline state by X-ray analysis.†

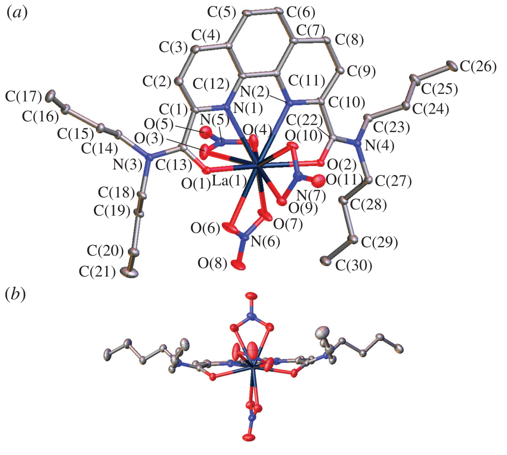


Figure 1 General view of (*a*) complex **1** and (*b*) its perpendicular projection in representation of atoms *via* thermal ellipsoids ($p = 50\%$). Hydrogen atoms and solvent acetonitrile molecules are omitted for clarity.

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† Single crystals of complexes **1**–**4** were obtained upon slow isothermal (25 °C) recrystallization of corresponding substances from CD_3CN.

Crystal data for **1**. $C_{34}H_{48}LaN_9O_{11}$, $M = 897.72$, triclinic, space group $P\bar{1}$, at 120 K: $a = 12.8066(15)$, $b = 13.1723(15)$ and $c = 14.0055(16)$ Å, $\alpha = 74.188(2)°$, $\beta = 67.870(3)°$, $\gamma = 66.735(2)°$, $V = 1989.3(4)$ Å^3, $Z = 2$, $d_{\mathrm{calc}} = 1.499$ g cm^{-3}, $F(000) = 920$. Intensities of 67046 reflections were measured [$\lambda(\mathrm{MoK\alpha}) = 0.71073$ Å, $\mu(\mathrm{MoK\alpha}) = 11.42$ cm^{-1}, ω-scans, $2\theta < 62°$], and 12112 independent reflections were used for the structure solution and refinement. Final R factors: $R_1 = 0.0498$ for 9758 observed reflections with $I > 2\sigma(I)$, $wR_2 = 0.0940$ and GOF = 1.065 for all the independent reflections.

Crystal data for **2**. $C_{34}H_{48}N_9NdO_{11}$, $M = 903.05$, triclinic, space group $P\bar{1}$, at 100 K: $a = 12.7265(2)$, $b = 13.0852(3)$ and $c = 13.9425(3)$ Å, $\alpha = 74.1023(7)°$, $\beta = 68.3360(6)°$, $\gamma = 66.7703(6)°$, $V = 1960.38(7)$ Å^3, $Z = 2$, $d_{\mathrm{calc}} = 1.530$ g cm^{-3}, $F(000) = 926$. Intensities of 47825 reflections were measured [$\lambda(\mathrm{MoK\alpha}) = 0.71073$ Å, $\mu(\mathrm{MoK\alpha}) = 13.93$ cm^{-1}, ω-scans, $2\theta < 56°$], and 9429 independent reflections were used for the structure solution and refinement. Final R factors: $R_1 = 0.0178$ for 9010 observed reflections with $I > 2\sigma(I)$, $wR_2 = 0.0444$ and GOF = 1.038 for all the independent reflections.

Table 1 Basic geometrical parameters of coordination nodes of complexes **1**–**4**.

Parameter	**1**	**2**	**3**	**4**
	Bond length/Å			
$R_{M–O(1)}$	2.481(2)	2.4341(10)	2.4088(12)	2.333(3)
$R_{M–O(2)}$	2.483(2)	2.4385(10)	2.4068(12)	2.315(3)
$R_{M–N(1)}$	2.704(3)	2.6431(14)	2.6152(14)	2.419(4)
$R_{M–N(2)}$	2.708(3)	2.6500(12)	2.6054(17)	2.446(4)
$R_{M–ONO_2}$	2.587(3)–2.609(2)	2.522(2)–2.590(6)	2.447(4)–2.578(5)	2.298(3)–2.490(3)
	Angles (°)			
N(1)–C(1)–C(13)–O(1)	25.6(4)	25.07(17)	21.9(2)	21.6(5)
N(2)–C(10)–C(22)–O(2)	22.5(4)	22.10(18)	24.6(2)	18.1(5)
C(14)–N(3)–C(13)–O(1)	6.8(3)	7.94(13)	15.45(16)	16.8(4)
C(18)–N(3)–C(13)–O(1)	1.7(5)	2.0(2)	1.6(3)	2.1(6)
C(23)–N(4)–C(22)–O(2)	15.0(3)	15.45(13)	8.94(15)	–13.6(4)
C(27)–N(4)–C(22)–O(2)	2.0(5)	2.0(2)	2.4(2)	1.9(6)
Out-of-plane angle of metal	5.3	5.1	5.2	2.3
Ion-plane distance	0.256(3)	0.2339(14)	0.2209(17)	0.081(3)

Complexes L*La(NO_3)$_3$ **1**, L*Nd(NO_3)$_3$ **2** and L*Eu(NO_3)$_3$ **3** were obtained as isostructural solvates with acetonitrile as a lattice solvent in a ratio 1 : 2. Complex L*Lu(NO_3)$_3$ **4** does not contain solvent molecules. Analytical and spectral characteristics confirming the composition and structure of the obtained complexes and all details of X-ray experiments and data processing are given in Online Supplementary Materials. Two projections of structure of complex **1** are shown in Figure 1. Very similar data for complexes **2** and **3** are given in Online Supplementary Materials. The main geometric parameters of the coordination nodes of all complexes are presented in Table 1.

The phenanthroline nucleus acts as a tetradentate ligand in all complexes. Coordination of Ln^{3+} cations occurs by binding to two amide oxygen atoms and two nitrogen atoms of the heterocyclic nucleus. In accordance with the HSAB principle, the Ln^{3+} acts as hard Lewis acid. The Ln–O bonds in all complexes are stronger and shorter by 0.2 Å than the Ln–N bonds with softer nitrogen centers. The structure of the coordination nodes of the three complexes **1**–**3** (Ln = La, Nd, Eu) is very similar. These complexes have flat phenanthroline and almost planar amide fragments (C–CO–N–C dihedral angles below 2°). The atoms that deviate mostly from the mean plane of the phenanthroline ligand are N(2), C(5) and C(8) in **1**, C(5), C(7), C(10) and C(12) in **2** and C(2), C(6), C(11) and C(12) in **3**; the largest deviations are as low as 0.018(4), 0.016(1) and 0.017(2) Å, respectively. However, both amide groups in complexes **1**–**3** are removed from the plane of the phenanthroline nucleus towards the metal cation. It is noteworthy that the dihedral angles N(2)–C(10)–C(22)–O(2) and N(1)–C(1)–C(13)–O(1) are different (22.9 and 25.6°) in complex **1**. As a result, carbonyl oxygen atoms are located at slightly different distances from the ligand plane [0.714(4) and 0.748(4) Å]. Such rotation partially disrupts the conjugation of amide groups with an electron-deficient aromatic system. In this case, the negative charges on oxygen atoms increase in comparison with their values in the completely planar conformation of the ligand, which leads to an increase in the strength of the Ln–O coordination bonds that have an electrostatic ionic character.[16,17] As a result, the lanthanide ions in complexes **1**–**3** leave the ligand plane by 0.256(3), 0.2339(14) and 0.2209(17) Å, respectively.[8,10] The coordination number of lanthanide ions is supplemented to 10 by three bidentate nitrate anions. The Ln–ONO_2 bond lengths (see Table 1) are typical of other lanthanide nitrate complexes. In the structures of complexes **1**–**3**, there is a sequential reduction in the lengths of La–O and La–N bonds, which is largely determined by the effect of lanthanide contraction.

Unique structure was observed for lutetium complex **4** (Figure 2). It is significantly different from the structures of the three complexes described above. A decrease in ionic radius of La^{3+} (1.14 Å) to Lu^{3+} (0.95 Å)[18] leads to a significant increase in strain in the coordination sphere. As a result, one bond Lu–ONO_3 breaks and this nitrate becomes a monodentate ligand. Such behaviour has been never observed previously in any of lanthanide complexes ligated to DAPhenA. The Lu–O and Lu–N bond lengths have the minimum known values for the complexes of Lu with DAPhenA. The decrease in Lu coordination number is a typical phenomenon when moving along the lanthanide series from La^{3+} to Lu^{3+}.[19] The organic ligand remains tetradentate and flat, however its conformation changes significantly. Both amide groups in complex **4** are turned in different directions from the plane of the phenanthroline nucleus, the dihedral angles N(1)–C(1)–C(13)–O(1) and N(2)–C(10)–C(22)–O(2) being equal to 18.2 and 21.6°. The lutetium cation is located almost in the plane of the phenanthroline nucleus. Such conformation has been observed earlier in complexes of Nd and Gd.[8]

Crystal data for **3**. $C_{34}H_{48}N_9O_{11}Eu$, $M = 910.77$, triclinic, space group $P\bar{1}$, at 100 K: $a = 12.7052(2)$, $b = 13.0357(2)$ and $c = 13.9381(2)$ Å, $\alpha = 74.0920(10)°$, $\beta = 68.5940(10)°$, $\gamma = 66.6940(10)°$, $V = 1951.00(6)$ Å^3, $Z = 2$, $d_{calc} = 1.550$ g cm^{-3}, $F(000) = 932$. Intensities of 41028 reflections were measured [λ(MoKα) = 0.71073 Å, μ(MoKα) = 16.77 cm^{-1}, ω-scans, $2\theta < 56°$], and 9406 independent reflections were used for the structure solution and refinement. Final R factors: $R_1 = 0.0206$ for 8852 observed reflections with $I > 2\sigma(I)$, $wR_2 = 0.0474$ and GOF = 1.037 for all the independent reflections.

Crystal data for **4**. $C_{30}H_{42}LuN_7O_{11}$, $M = 851.67$, monoclinic, space group $P2_1/n$, at 120 K: $a = 12.5387(9)$, $b = 13.2104(9)$ and $c = 20.5389(14)$ Å, $\beta = 94.300(2)°$, $V = 3392.5(4)$ Å^3, $Z = 4$, $d_{calc} = 1.667$ g cm^{-3}, $F(000) = 1720$. Intensities of 38724 reflections were measured [λ(MoKα) = 0.71073 Å, μ(MoKα) = 29.79 cm^{-1}, ω-scans, $2\theta < 56°$], and 8199 independent reflections were used for the structure solution and refinement. Final R factors: $R_1 = 0.0377$ for 5767 observed reflections with $I > 2\sigma(I)$, $wR_2 = 0.0742$ and GOF = 1.002 for all the independent reflections.

Data for **1** and **4** were collected on a Bruker APEX2 DUO CCD and for **2** and **3**, on a Bruker D8 QUEST PHOTON-III CCD diffractometers. Using Olex2,[13] the structures were solved with the ShelXT[14] structure solution program using Intrinsic Phasing and refined with the XL[15] refinement package using Least-Squares minimisation. Positions of hydrogen atoms were calculated, and they all were refined in the isotropic approximation within the riding model.

CCDC 2072995 (for **1**), 2073000 (for **2**), 2073001 (for **3**) and 2072996 (for **4**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre *via* http://www.ccdc.cam.ac.uk.

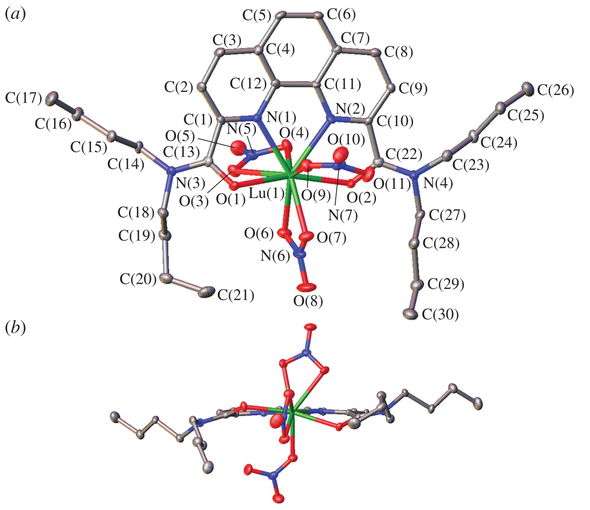

Figure 2 General view of (*a*) complex **4** and (*b*) its perpendicular projection in representation of atoms *via* thermal ellipsoids ($p = 50\%$). Hydrogen atoms are omitted for clarity.

In the solvent-free crystal of complex **4**, the molecules are assembled into infinite chains along the crystallographic axis *b* so that the ligand's phenanthroline cores locate perfectly parallel to each other within the chains but are tilted by 60.5(5)° in the neighbouring chains [Figure 3(*b*)]. This results from stacking interactions of the parallel-displaced type formed between the two pyridine moieties of the phenanthroline core and their symmetry-generated counterparts with the centroid-centroid distances of 3.698(5) and 3.742(5) Å and the shift distance of 1.484(6) and 1.688(5) Å, respectively. The other three complexes **1–3** (La, Nd, Eu) which include lattice solvent molecule in their crystals feature somewhat similar. However, they possess very different overall supramolecular organization governed by significantly weaker stacking interactions of the same parallel-displaced type [Figure 3(*a*)]. The appropriate centroid-centroid distances in them are 4.206(2)–4.266(1) and 5.129(3)–5.167(2) Å and the shift distances are 2.513(7)–2.627(4) and 2.254(8)–2.299(4) Å. They produce infinite intermolecular chains that run along the diagonal of the crystallographic plane *ac* with the phenanthroline nuclei perfectly parallel to each other within and between these chains. Solvent acetonitrile molecules occur somewhere in between.

In summary, the structural features and tendencies can be revealed for DAPhenA complexes with lanthanides. Phenanthroline bis-amide acts as an *N*,*N*,*O*,*O*-tetradentate ligand having both amide oxygens removed from the plane of the phenanthroline nucleus. However, when in the complexes of the cations from the beginning (La, Nd) and the middle (Eu) of the series both carbonyls are turned in the same direction from the plane, then in the lutetium complex they are turned in opposite directions. In the La, Nd and Eu complexes, metal ions are located below the plane of the phenanthroline core. In this case, the distances between them and this plane decrease in the series La > Nd > Eu. In the lutetium complex, the Lu^{3+} ion is located practically in the plane of the nucleus. As expected, when moving along the series La, Nd, Eu, Lu, the lengths of the Ln–N and Ln–O coordination bonds in the complexes decrease in accordance with a decrease in the ionic radii of the cations. As a result, the coordination number of the lutetium complex decreases to 9 due to the transformation of one of the nitrates into a monodentate ligand, which is observed for the first time for complexes of this type.

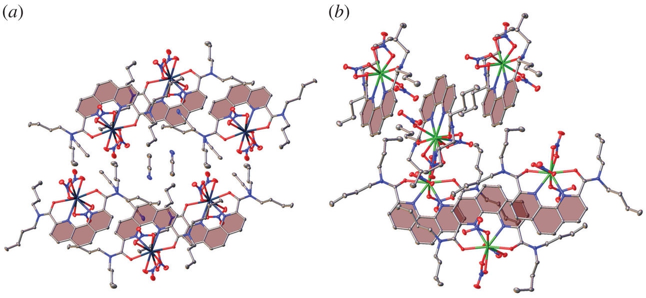

Figure 3 Fragment of the crystal packing in complexes (*a*) **1–3** and (*b*) **4** illustrating infinite chains formed by intermolecular stacking interactions between phenanthroline moieties of the ligand (shown by pink planes). Hydrogen atoms are omitted for clarity.

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Online Supplementary Materials

Supplementary data associated with this article can be found in the online version at doi: 10.1016/j.mencom.2021.11.028.

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