Coordination Compounds of Lanthanide Nitrates with Dimorpholido-N-trichloroacetylphosphorylamide. The Structure of Di(dimorpholido-N-trichloroacetylphosphorylamide)-diaqua Neodymium(III)trinitrate

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Lanthanide, Carbacylamidophosphate

The coordination compounds of the general formula \( \text{Ln(NO}_3)_3(\text{HL})_2(\text{H}_2\text{O})_2 \cdot \text{H}_2\text{O} \), where \( \text{Ln} = \text{La}, \text{Ce} - \text{Nd}, \text{Sm} - \text{Dy}, \) \( \text{HL} = \text{CCl}_3\text{C}(\text{O})\text{NHP(O)[N(CH}_2\text{CH}_2\text{)}_2\text{O}]_2} \), dimorpholido-N-trichloroacetylphosphorylamide, have been synthesized. The complexes were studied by IR, \(^1\)H and \(^31\)P NMR and UV-VIS absorption spectroscopies. X-ray diffraction analyses indicate that all synthesized compounds are isostuctural. The crystal structure of \( \text{Nd(NO}_3)_3(\text{HL})_2(\text{H}_2\text{O})_2 \cdot \text{H}_2\text{O} \) was solved (monoclinic, \( a = 11.0467(3) \text{Å}, b = 15.9080(5) \text{Å}, c = 24.1921(7) \text{Å}, \gamma = 96.4080(10)° \)).

It was shown that these compounds in methanol solution are 1:1 electrolytes, and in acetone solution weak electrolytes. According to NMR data in acetone solution the complexes of the lanthanides with the ligand \{HL\} have axial symmetry.

Introduction

This work is a continuation of the systematic investigations of complexes of lanthanides with carbacylamidophosphates, compounds of the general formula \( \text{RC(O)NHP(O)R}_2 \). Many compounds of this type show biological activity [1]. The presence of the phosphoryl group, which shows high affinity to lanthanide ions in carbacylamidophosphates, makes them particularly interesting for the coordination chemistry of rare earth metals.

Coordination compounds of lanthanides with \( \text{N',N'-tetraethyl-N''-trichloroacetylphosphorictriamide CCl}_3\text{C(O)NHP(O)[NEt}_2\text{]}_2 \) in neutral [2 - 4] and acid forms [5] were studied earlier.

In this paper we report the syntheses, properties and structures of coordination compounds of lanthanides with dimorpholido-N-trichloroacetylphosphorylamide of composition \( \text{Ln(NO}_3)_3(\text{HL})_2(\text{H}_2\text{O})_2 \cdot \text{H}_2\text{O} \).

Experimental

Dimorpholido-N-trichloroacetylphosphorylamide was prepared as described previously [6]. Its complexes were synthesized by the reaction:

\[ \text{Ln(NO}_3)_3 \cdot \text{nH}_2\text{O} + 2\text{HL} \rightarrow \text{Ln(NO}_3)_3(\text{HL})_2(\text{H}_2\text{O})_2 + (n-3)\text{H}_2\text{O} \]

Hydrated rare earth nitrate (1 mmol) was dissolved in methanol (15 ml). The solution was heated to the boiling point to dissolve the rare earth salt completely, and the resulting solution was added to the solution of HL (2 mmol) in methanol (15 ml). The solution was allowed to stand in a vacuum desiccator over CaCl\(_2\). The crystals precipitated from the solution, were filtered off, washed with cooled methanol, and dried over CaCl\(_2\) (yield 80 - 90%).

According to powder X-ray diffraction, the prepared complexes are isostuctural crystalline compounds. They are stable in air, slightly colored depending of the color.
UV-VIS spectra were recorded on a KSVU-23 “LOMO” adapted for an IBM PC and a SPECTROD M40 spectrometer.

The single crystal of Nd(NO₃)₃·(HL)₂·(H₂O)₂·H₂O was prepared by slow crystallization from methyl alcohol.

For the X-ray diffraction study a crystal of the dimension 0.15x0.20x0.25 mm was used. Crystallographic measurements were made at 22 °C using a SMART CCD area detector diffractometer (Siemens). Table 1 lists the cell parameters and details of data acquisition and structure refinement. The structure was solved by direct methods and subsequent Fourier difference techniques and refined using the programs SHELXS and SHELXL-93 [7, 8]. All non hydrogen atoms were refined anisotropically. All hydrogen atoms were localized by difference Fourier techniques without further refinement (except hydrogen atoms of the non-coordinated molecule of water). Full crystallographic data have been deposited at the Cambridge Crystallographic Data Center [9]. E-mail: deposit@ccdc.cam.ac.uk.

**Results and Discussion**

The values of the main vibrational frequencies in the IR spectra of the compounds are comparable with the data for neutral dimorpholido-N-trichloroacetylphosphorylamide.

In the IR spectra of HL the broad absorption band at 3030 cm⁻¹ may be assigned to ν(NH) of the N-H groups, which are hydrogen-bonded to the oxygen atoms of the phosphoryl groups of neighboring molecules in the crystal [6]. The coordination of the lanthanide ion to the ligand leads to a frequency shift of ν(NH) to 3150 cm⁻¹. This result suggests that the hydrogen bond of N-H…O=P type disappears upon complex formation. Hydrogen bonds are formed between hydrogen atoms of amide groups and oxygen atoms of a water molecule. The formation of such intramolecular hydrogen bonds was observed for complexes of europium nitrate with dioxouranium nitrate with N,N'-tetraethyl-N"-trichloroacetylphosphoric triamide [2, 10].

The shift of ν(PO) from 1170 to 1200 cm⁻¹ in the spectra of the complexes and the free ligand, respectively demonstrates the coordination of the ligand HL via the oxygen atom of the phosphoryl group. The vibrations of the carbonyl groups of the complexes [ν(CO)=1725-1730 cm⁻¹] and the free ligand [ν(CO) = 1730 cm⁻¹] are very similar. This suggests that the carbonyl group does not take part in the formation of coordinative bonds [2, 3].
The absorption bands of the NO$_3^-$ ions appear at 1480 - 1485 and 1300 - 1305 cm$^{-1}$. The splitting of the values of the high frequency vibration of the NO$_3^-$ ions in the IR spectra of the complexes (180 cm$^{-1}$) reflects that the coordination of nitrate groups to lanthanide ions is realized in a bidentate chelate manner [11].

Judging from the positions of the absorption bands and the intensity ratios in the regions of hypersensitive transitions $^4$I$_{9/2} - ^4$G$_{5/2}, ^4$G$_{7/2}$ in the spectra of Nd(NO$_3$)$_3$·(H$_2$O)$_2$·H$_2$O, the nearest environment of the central atom is changed in methanol solutions (Fig. 1). The results of measurements of electroconductivity of methanol solution of this compound demonstrated that in the range of concentrations 2.5·10$^{-3}$ - 9·10$^{-4}$ mol/l it is a strong 1:1 electrolyte. The function of electroconductivity from concentration is $\lambda = A\sqrt{C} + B$, where $A = 715.14$ and $B = 93.15$, with a correlation coefficient $R = 0.997$.

The comparison of the diffuse reflectance spectrum of the complex of Nd(III) and its absorption spectrum in acetone solution allows to assume identity of structure of the coordination spheres of this compound in solid state and in acetone solution. The solution of Nd(NO$_3$)$_3$·(H$_2$O)$_2$·H$_2$O in acetone is a weak electrolyte (C = $1.2 \times 10^{-3}$ - $4 \times 10^{-4}$ mol/l, $\lambda = 20$ - 30 ohm$^{-1}$cm$^2$mol$^{-1}$), therefore very probability the structure of the coordination unit is preserved in acetone.

Table 2 lists the oscillator strength of f-f transitions for solutions of Nd(NO$_3$)$_3$·(HL)$_2$(H$_2$O)$_2$ in acetone at room temperature.

Table 3. $^1$H and $^{31}$P chemical shifts for the lanthanide compounds with dimorpholido-N-trichloroacetylphosphoryl-}

<table>
<thead>
<tr>
<th>Ln(III)</th>
<th>F(d,j)*</th>
<th>$^1$H O(CH$_2$)$_2$</th>
<th>$^1$H N(CH$_2$)$_2$</th>
<th>$^{31}$P</th>
</tr>
</thead>
<tbody>
<tr>
<td>La</td>
<td></td>
<td>3.65</td>
<td>3.27</td>
<td>7.15</td>
</tr>
<tr>
<td>Ce</td>
<td>-11.8</td>
<td>4.20</td>
<td>1.56</td>
<td>28.8</td>
</tr>
<tr>
<td>Pr</td>
<td>-20.7</td>
<td>4.80</td>
<td>1.15</td>
<td>32.4</td>
</tr>
<tr>
<td>Nd</td>
<td>-8.02</td>
<td>4.07</td>
<td>1.05</td>
<td>115.4</td>
</tr>
<tr>
<td>Sm</td>
<td>0.94</td>
<td>3.73</td>
<td>0.08</td>
<td>6.7</td>
</tr>
<tr>
<td>Eu</td>
<td>-3.65</td>
<td>1.53</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Tb</td>
<td>-157.5</td>
<td>15.0</td>
<td>11.35</td>
<td>382.5</td>
</tr>
<tr>
<td>Dy</td>
<td>-187.0</td>
<td>48.3</td>
<td>44.65</td>
<td>16.23</td>
</tr>
</tbody>
</table>

*F(d,j) = $g^2J(J+1)(2J-1)(2J+3)\alpha(2J)$.

The positions of methylene signals in the spectra of a mixture of Ce(NO$_3$)$_3$·(HL)$_2$(H$_2$O)$_2$·H$_2$O and the free ligand in molar ratio 1:2 have average values between the chemical shifts of the signals in the spectra of the complex and the free ligand in acetone solutions ($\delta = 3.22$ and $3.61$ in free ligand, 3.90 and 4.19 for the mixture). This fact proves
the lability of the coordination sphere: in acetone solution rapid exchange between coordinated and non-coordinated ligand takes place (on the NMR time scale).

The NMR $^{31}$P spectra of acetone solutions of the complexes show only one broad signal.

Table 3 summarizes the NMR spectroscopic data for all compounds under study. We have used the approaches described in [13].

Fig. 2 presents chemical shifts of the methylene protons of the complexes of the paramagnetic lanthanides plotted vs. $F(d, j)$ values. One can see that the compounds of Ce, Pr, Nd, Sm, Tb satisfy a linear relation [13]. Linear least squares approximations for the series of these complexes give the equations of a straight line $y = 0.07284 x + 0.16098$ (with the correlation coefficient $K = 0.999$) for the methylene protons at the oxygen atom, and $y = 0.20398 x + 0.51406$ (with $K = 0.999$) for the methylene protons at the nitrogen atom (without data for Dy).

The calculation of the hyperfine coupling constant by methods described in [14] was not successful, because the averaged geometry of the investigated complexes in acetone solutions is not isomorphous.

The coordination sphere of Nd in Nd(NO$_3$)$_3$·(HL)$_2$(H$_2$O)$_2$·H$_2$O is a sphenocorona (coordination number ten) (Fig. 4). Four oxygen atoms from two bidentately coordinated nitrate groups O(4), O(5), O(7), O(8) and two oxygen atoms O(14), O(15) from coordinated molecules of water form a corrugated hexagon in the equatorial plain of the polyhedron. These nitrate groups are located opposite to one other in one plane (deviations of the neodymium ion and all atoms of the nitrate groups from the mean plane are less than 0.086 Å). The angle of the plane of the third (axial) nitrate group with the previous plane is 87°. A similar disposition of nitrate groups was observed in the structure of [Nd(NO$_3$)$_3$(urea)$_2$(H$_2$O)$_2$] [15]. The edges of the coordination polyhedron formed by the two oxygen atoms O(10), O(20) of the monodentate ligand HL and the oxygen atoms O(1), O(2) of the third bidentate nitrate group have a bisphenoid arrangement in axial positions. The symmetry of such a coordination environment is roughly $C_{2v}$.

In the planar four membered NdO$_2$N chelate rings, the average Nd-O-N angle is 96.9°, and the average Nd-O bond length for nitrate groups is 2.572 Å. This agrees well with literature data for other lanthanide nitrate complexes [2, 16]. The coordinated nitrate groups have virtually planar triangular structures. The tightening effect of the coordination center leads to a decrease of the average O-N-O angle of the chelate ring (116.3°) in comparison with other angles (average 121.8°). The average N-O distance is 1.248 Å.

As in the majority of complexes with phosphoryl ligands the Nd-O and O-P bonds in
Nd(NO$_3$)$_3$(HL)$_2$(H$_2$O)$_2$·H$_2$O are not colinear. The Nd-O-P angles range within 151.5(3)$^\circ$ - 159.8(3)$^\circ$, which is somewhat smaller than typical angles in the lanthanide compounds with hexamethylphosphoryltriamide (Hmpt) [17]. This difference can be explained by hydrogen bonding of amide hydrogen atoms with oxygen atoms of the coordinated water molecule.

The average Nd-O bond length for the phosphoryl ligand is 2.40 Å.

The phosphoryl and carbonyl groups of the coordinated ligands HL are in anti position to one other. The same configuration is typical for the free ligand HL. The phosphorus atoms have a slightly distorted tetrahedral configuration. The phosphoryl group forms an OPN angle (104$^\circ$) with the nitrogen atom of the trichloroacetylamide group. The small value of this angle is probably caused by the hydrogen bond N-H···OH$_2$ (Table 5). The coordinated water molecules take part in the formation of hydrogen bonds with oxygen atoms of the morpholine rings of neighbouring molecules.

Although it was not possible to locate the hydrogen atoms of the non-coordinated water molecule in the structure, the intramolecular contacts with oxy-
There is a close contact between the electrophilic N(3)-O(8) 1.249(8) N(l)-O(2) 1.276(8)
terminated complexes, and donor atoms on the nitrate groups (Table 5) can be interpreted as hydrogen bonds.

The morpholine rings have a chair conformation. There is a close contact between the electrophilic phosphorus and the nucleophilic oxygen atoms of carbonyl groups. The distances between these atoms (O(11)-P(1) 3.06, O(21)-P(2) 3.09 Å) are slightly smaller than the sum of the van-der-Waals radii of phosphorus and oxygen atoms (3.3 Å). Similar contacts were found in the free ligand [6].

<table>
<thead>
<tr>
<th>Table 5. Geometry of hydrogen bonding.</th>
</tr>
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<tbody>
<tr>
<td>Donor Hydrogen Acceptor (D) (H) (A)</td>
</tr>
<tr>
<td>----------------------------------------</td>
</tr>
<tr>
<td>N(10) H(1) O(14) 0.769(6) 2.148(4) 2.888(7) 161.7(4)</td>
</tr>
<tr>
<td>N(20) H(2) O(15) 0.821(6) 2.119(5) 2.914(8) 163.2(4)</td>
</tr>
<tr>
<td>O(16) - O(9) - 3.04(2) -</td>
</tr>
<tr>
<td>O(16) - O(3)c - 3.01(2) -</td>
</tr>
<tr>
<td>O(16) - O(6)d - 3.02(2) -</td>
</tr>
<tr>
<td>O(14) H(3) O(22)a 0.669(5) 2.296(5) 2.885(7) 148.0(4)</td>
</tr>
<tr>
<td>O(14) H(4) O(23)b 0.900(5) 1.789(6) 2.682(7) 170.9(4)</td>
</tr>
<tr>
<td>O(15) H(5) O(12)a 0.680(5) 2.169(5) 2.820(7) 160.5(4)</td>
</tr>
<tr>
<td>O(15) H(6) O(13)b 0.781(4) 2.005(5) 2.761(7) 162.7(4)</td>
</tr>
</tbody>
</table>

Symmetry transformation used to generate equivalent atom: a 0.5 - x, -0.5 + y, 0.5 - z; b -0.5 - x, -0.5 + y, 0.5 - z; c 0.5 - x, 0.5 + y, 0.5 - z; d 1 + x, y, z.

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