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¹H- AND ³¹P-NMR SPECTROSCOPY STUDY OF PARAMAGNETIC LANTHANIDE COORDINATION COMPOUNDS [LnL₃ · Phen] (L = CCl₃C(O)NP(O)(OCH₃)₂)

A series of lanthanide coordination compounds with dimethyl-*N*-trichloroacetylamidophosphate CCl₃C(O)N(H)P(O)(OCH₃)₂ (HL) [HL = CCl₃C(O)N(H)P(O)(OCH₃)₂ is a ligand of the carbacylamidophosphate (CAPH) type], whose compositions are described by the formula [LnL₃ · Phen], where Ln = La, Ce, Pr, Nd, Sm, Tb, Dy, Ho, and Er; L is the deprotonized form of HL; and Phen is 1,10-Phenanthroline, has been synthesized. Acetonic solutions of HL and complexes synthesized on its basis are studied by means of ¹H- and ³¹P-NMR spectroscopy at room temperature (298 K). Since the chemical shifts of ¹H signals have the pseudocontact origin, the isotropic shifts of ³¹P signals are managed to be decomposed into the contact and pseudocontact components. It is found that there are two series of complexes in the solution of [LnL₃ · Phen] compounds with the same structure of the coordination sphere within each of the series Ln = (Ce, Pr, Nd, Sm) (series L1) and Ln = (Tb, Dy, Ho, Er) (series L2). The values of the constant of superfine interaction for those complexes are calculated: 0.18 MHz (series L1) and 0.13 MHz (series L2).

Keywords: lanthanide coordination compounds, carbacylamidophosphates, NMR spectroscopy, isotropic chemical shift.

1. Introduction

Specific magnetic properties of lanthanide (III) ions and the effects induced by them in the NMR spectra of organic ligands coordinated to them make them valuable objects for the application as lanthanide shifting reagents (LSRs). Lanthanide (III) complexes, in particular, of the chelate type, are used as tools in the structural analysis with the help of NMR spec-

troscopy [1, 2]. The LSRs are widely applied when studying the structure of organic compounds, their conformations in solutions, and the enantiomeric purity, as well as to detect the chirality, and so forth [3].

It is known that Ln (III) ions can isomorphically substitute Ca (II) ones. Therefore, paramagnetic lanthanide cations can be used as magnetic and optical probes to study calcium-containing compounds [4]. The application of Ln (III) chelates becomes more and more important in medical diagnostic methods with spin NMR imaging and magnetic resonance

imaging [5, 6]. Taking the aforesaid into account, the development of methods for evaluating the structure of lanthanide complexes in solutions seems to be important and challenging [7].

The object of our research is to consider the intracomplex coordination compounds of lanthanides on the basis of dimethyl-N-trichloroacetylamidophosphate ($\text{CCl}_3\text{C}(\text{O})\text{N}(\text{H})\text{P}(\text{O})(\text{OCH}_3)_2$), a ligand of the carbacylamidophosphate (CAPH) type. A particular advantage of the CAPH compounds with respect to other chelating oxygen-donor ligands – e.g., β -diketones [8] – consists in the presence of phosphorus atoms in the CAPH ligand composition, which are known to be a convenient ^{31}P -NMR probe. A high affinity of those ligands to lanthanide (III) ions, a synthetic possibility of introducing substituents, different in their steric characteristics and electron structures, near the functional chelating fragment $-\text{C}(\text{O})\text{N}(\text{H})\text{P}(\text{O})=$ led to a systematic study of lanthanide complexes with CAPH ligands [9–15].

In this work, two series of lanthanide coordination compounds with dimethyl-N-trichloroacetylamidophosphate (HL), which compositions are described by the formula $[\text{LnL}_3 \cdot \text{Phen}]$, where Ln = (La–Nd, Sm–Yb), L is the deprotonized form of HL, and Phen is 1,10-Phenanthroline, were synthesized and studied with the help of NMR spectroscopy of the ^1H and ^{31}P nuclei. In the content of complexes, the ligand HL exists in the deprotonated state (L) (see the synthesis scheme below).

2. Research Methods

The synthesized coordination compounds were identified by analyzing their metal contents [16] and IR spectra.

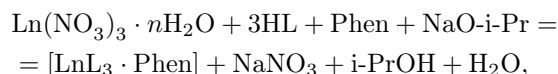
The IR spectra were registered in an interval of 400–4000 cm^{-1} on an FT-IR Spectrophotometer BX-II (Perkin Elmer). The specimens were prepared in the form of tablets with potassium bromide (an extra-high purity degree).

The ^1H -NMR spectra (solutions in $(\text{CD}_3)_2\text{CO}$) and ^{31}P -NMR spectra of acetonetic solutions were registered on an AVANCE 400 Bruker NMR spectrometer at a temperature of 298 K.

3. Experimental Results and Their Discussion

Dimethyl-N-trichloroacetylamidophosphate (HL) and its sodium salt (NaL) were synthesized and identified according to the method described in work [17], and

lanthanide complexes of the $[\text{LnL}_3 \cdot \text{Phen}]$ composition according to the method described in works [18–20]. The general scheme of complex synthesis was as follows:



where HL is the molecular form of the ligand ($\text{CCl}_3\text{C}(\text{O})\text{N}-\text{P}(\text{O})(\text{OCH}_3)_2$), L is its deprotonated form ($\text{CCl}_3\text{C}(\text{O})\text{N}^-\text{P}(\text{O})(\text{OCH}_3)_2$), Phen is 1,10-phenanthroline, Ln = (La, Ce, Pr, Nd, Sm, Tb, Dy, Ho, Er), NaO-i-Pr is sodium isopropylate, and i-PrOH is isopropyl alcohol.

For the compounds with the $[\text{LnL}_3 \cdot \text{Phen}]$ composition, two types of the coordination environment for the central atom are realized in the crystalline state: a distorted two-cap trigonal prism (TCTP) and a distorted square antiprism (AP) [21].

4. NMR Spectroscopic Research

Table 1 demonstrates the chemical shifts (δ , ppm) in the ^1H - [the solution in $(\text{CD}_3)_2\text{CO}$] and ^{31}P - [the solution in $(\text{CH}_3)_2\text{CO}$] NMR spectra of the $[\text{LnL}_3 \cdot \text{Phen}]$ complexes. The NMR spectra of ^1H -complexes with Ln = La–Sm and Yb reveal one signal from every methyl proton in the doublet (d) form, whereas, for complex compounds of other lanthanides, the signal of methyl proton is registered as a broadened singlet. In the ^{31}P -NMR spectra of acetonetic solutions of the complexes (see Table 1), one singlet is observed, which testifies to a magnetic equivalence of all phosphorus atoms in the molecule.

Table 2 demonstrates the values of isotropic chemical shifts for the phosphorus atoms and protons (Δ^{P} and Δ^{H} , respectively), which are equal to the difference between the chemical shifts in the NMR spectra for the paramagnetic and analogous diamagnetic complex compounds [22].

It is known that the isotropic shift reflects nuclear resonance variations that emerge as a result of two different interactions: a hypersensitive “contact” Fermi interaction and the electron-nuclear “dipole” (or “pseudocontact”) interaction. The total observed isotropic shift is the algebraic sum of the shifts induced through the contact ($\Delta\nu_c$) and pseudocontact ($\Delta\nu_{pc}$) mechanisms: $\Delta\nu_i = \Delta\nu_c + \Delta\nu_{pc}$. The contact, or scalar, contribution to the isotropic shift is associated with the delocalization of the unpaired electron

Table 1. Chemical shifts (δ , ppm) in the ¹H- and ³¹P-NMR spectra of lanthanide complex compounds [LnL₃ · Phen]

Ln	³¹ P		¹ H					
			Proton type in L		Proton type in 1,10-Phen			
			-CH ₃		H _a	H _b	H _c	H _d
	δ , ppm	$\delta_{\text{La}} - \delta_{\text{Ln}}$ (Δ), ppm	δ , ppm	$\delta_{\text{La}} - \delta_{\text{Ln}}$ (Δ), ppm	δ , ppm	δ , ppm	δ , ppm	δ , ppm
La	-9.81	—	3.48(d)	—	9.77(d)	7.97(dd)	8.67(d)	8.1(s)
Ce	29.3	-39.11	5.33(d)	-1.85		7.84. 7.34. 6.29		
Pr	60.1	-69.91	7.66(d)	-4.18		5.63. 3.76. 3.29. 2.79		
Nd	50.8	-60.61	4.71(d)	-1.23	8.21	7.45	6.77	7.74
Sm	10.7	-20.51	3.80	-0.32	9.07	7.87	8.63	8.08
Tb	-88.8	78.99	19.54	-16.06		-1.48. -3.62		
Dy	29.8	-39.61	33.84	-30.36		-19.65. -23.31		
Ho	-81	71.19	10.56	-7.08		16.24. -0.31. -5.32. -42.5		
Er	-127.84	118.03	-0.23	3.71		13.6. 12.6		
Tm	-82.36	72.55	4.61	-1.13		11.64. 7.78		
Yb	-16.38	6.57	1.55(d)	1.93		13.05. 12.7. 11.7		

Table 2. Isotropic chemical shifts in the ¹H- and ³¹P-NMR spectra of lanthanide complex compounds [LnL₃ · Phen] at the temperature $T = 298$ K

Ln	C_J^*	$10^6 \Delta^{\text{H}}$	$10^6 \Delta^{\text{P}}$	$10^{-4} \frac{\Delta^{\text{H}}}{KJg}$, Hz	$10^{-4} \frac{\Delta^{\text{P}}}{KJg}$, Hz	$10^8 TKJg$, Hz ⁻¹ K
Ce	-11.8	-1.85	-39.11	4.10644	8.68123	-1.32
Pr	-20.7	-4.18	-69.91	2.94621	5.57867	-4.157
Nd	-8.02	-1.23	-60.61	0.56514	2.78481	-6.377
Sm	0.94	-0.32	-24.65	0.40414	3.1776	-2.32
Tb	-157.5	-16.06	73.99	-1.15003	0.52983	40.917
Dy	-187	-30.36	-39.61	-2.41699	-0.31534	36.804
Ho	-71.2	-7.08	63.19	-0.70977	0.63348	29.227
Er	58.8	3.71	118.03	0.54696	1.7401	19.874
Tm	95.3	-1.13	72.55	-0.31211	2.00388	10.608
Yb	39.2	1.93	6.57	1.69308	0.57635	3.34

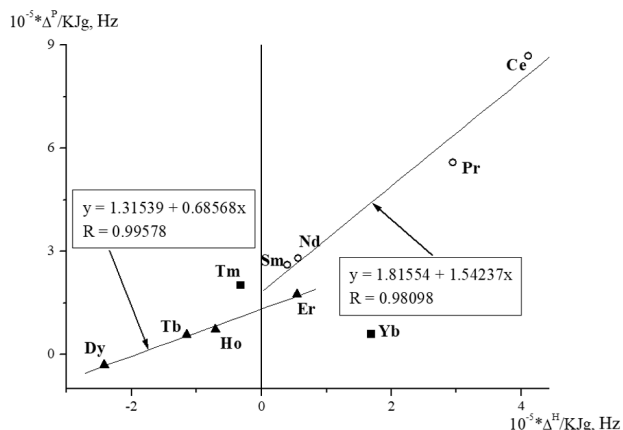
* $C_J = g^2 J(J+1)(2J-1)(2J+3) \langle J || \alpha || J \rangle$ is the Bleaney factor [23–25].

density at the resonating nucleus and is proportional to the squared value of the electron wave function at the examined nucleus. In order to calculate the contact shift, Reuben and Fiat [22] have proposed the following equation:

$$\Delta_c = \frac{\Delta\nu_c}{\nu_0} = \frac{2\pi\mu_B J(J+1)g(g-1)}{3kT\mu_N} \cdot \frac{A}{h}, \quad (1)$$

where μ_B is the electron Bohr magneton, J the total momentum of the electron motion [19], g the electron Lande factor, μ_N the nuclear Bohr magneton, k the Boltzmann constant, T the absolute temperature, and A/h is the superfine interaction (SFI) constant.

If the ligand is bound to the complex, the contact contribution is possible, only if the metal-ligand bond is covalent. Therefore, the SFI constant magni-



Dependence of the quantity Δ^P/KJg on Δ^H/KJg for $[LnL_3 \cdot Phen]$ compounds at a temperature of 298 K

tude reflects the fraction of covalency in the binding. The pseudocontact (dipole) shift $\Delta\nu_{pc}$ characterizes the spatial interaction between the ligand nuclei and unpaired electrons at the metal ion [26]. Its value depends on the geometry of the central atom environment rather than on the bond type. Dipole shifts are relevant only for complexes with magnetic anisotropy. Therefore, as an example, for magnetoisotropic octahedral Ni (II) and tetrahedral Co (II) complexes, we have $\Delta\nu_{pc} = 0$. For most coordination compounds, the both contributions to the isotropic shift are substantial. However, in the case of lanthanide coordination compounds, unpaired electrons are located at deep-lying $4f$ orbitals, so that their delocalization at the ligands (and, hence, the $\Delta\nu_c$ magnitude) is very small.

The method for obtaining the value of the SFI constant is based on the assumption that this value should not change significantly along the series of isomorphous lanthanide complexes with identical ligands [27]. An equation for calculating the SFI constant A/h is derived from the ratio between the pseudocontact shifts for two different nuclei in the same complex (e.g., for phosphorus nuclei and protons in the examined complexes):

$$\Delta_{pc}^P : \Delta_{pc}^H = \frac{3 \cos^2 \theta_P - 1}{r_P^3} : \frac{3 \cos^2 \theta_H - 1}{r_H^3} = R, \quad (2)$$

where r_i is the length of the vector \mathbf{r}_i between the paramagnetic ion and the P or H nucleus, and θ_i the angle between the vector \mathbf{r}_i and the principal magnetic axis of the complex. This ratio does not depend on the selected lanthanide, but is a function of only

the structural parameters θ and r . Hence, it is constant for the isomorphous series of complexes,

$$\Delta_{pc}^P = R \Delta_{pc}^H. \quad (3)$$

If the contact shift for the ligand protons is considered to be insignificant, then, for the isotropic shift at the ^{31}P nucleus, we have (at $\Delta^H = \Delta_{pc}^H$)

$$\Delta^P = \Delta_c^P + \Delta_{pc}^P = \Delta_c^P + R \Delta_{pc}^H = \Delta_c^P + R \Delta^H, \quad (4)$$

where Δ^P and Δ^H are the isotropic chemical shifts of phosphorus and protons, respectively. Introducing the notation

$$\frac{2\pi\mu_B J(J+1)g(g-1)}{3kT\mu_N} = KJg,$$

Eq. (1) for the contact shift can be rewritten in the simplified form

$$\Delta_c^P = KJg \cdot \frac{A}{h}. \quad (5)$$

Substituting Eq. (5) into Eq. (4), we obtain the final expression

$$\Delta^P = \Delta_c^P + R \Delta^H = KJg \cdot \frac{A}{h} + R \Delta^H$$

or

$$\frac{\Delta^P}{KJg} = \frac{A}{h} + R \frac{\Delta^H}{KJg}.$$

Hence, the plot of the dependence of the quantity Δ^P/KJg on the quantity Δ^H/KJg should be a straight line for a number of isomorphous complexes. The slope of the plot equals R , and the plot intersection with the OY axis determines the value of the SFI constant.

The dependence of $y = \Delta^P/KJg$ on $x = \Delta^H/KJg$ plotted for the $[LnL_3 \cdot Phen]$ complexes is depicted in Figure. From the data obtained, it follows that, in the case of acetonic solutions, there are two series of complexes with the same structure of a coordination sphere within each series: $Ln = (Ce, Pr, Nd, Sm)$ and $Ln = (Tb, Dy, Ho, Er)$. Since the points corresponding to the lanthanides of the yttrium subgroup drastically deviate from the common dependence, they were not taken into account. Linear approximations using the mean-least-square method

gave rise to the following equations for the series of [LnL₃·Phen] complexes:

- for Ln = Ce, Pr, Nd, and Sm:

$$y = 1.81554 + 1.54237x, \quad R = 0.98098;$$

- for Ln = Tb, Dy, Ho, and Er:

$$y = 1.31539 + 0.68568x, \quad R = 0.99578.$$

The SFI constant values determined for those series of compounds equal 0.18 and 0.13 MHz, respectively.

The results obtained testify that the covalent contribution to the metal-ligand bond in the analyzed compounds is significantly lower for heavy lanthanides than for light ones, which completely correlates with the change in ionic radii and the polarizability of electron shells. A comparison of the SFI constant values with literature data – see, e.g., similar studies using the ¹⁷O-NMR method [28, 29] – demonstrates the fruitfulness of this approach for evaluating the strength of the metal-ligand bond not only in the case of kinetically inert systems, but also in the case of systems characterized by intra- and intermolecular chemical exchange processes.

5. Conclusions

In this work, a series of lanthanide coordination compounds with dimethyl-N-trichloroacetylamidophosphate, whose compositions are described by the formula [LnL₃·Phen], were synthesized. The structure of the complexes in the solution is studied using the polynuclear NMR spectroscopy method. The isotropic shifts of protons and phosphorus, as well as the superfine interaction constants, are calculated. By separating the isotropic chemical shift into the contact and pseudocontact components, it is found that, in acetonic solutions of [LnL₃·Phen] complexes, there are two series of isomorphous complexes, and the lanthanide-phosphorus SFI constant amounts to 0.18 MHz for light lanthanides (Ce, Pr, Nd, and Sm) and 0.13 MHz for heavy ones (Tb, Dy, Ho, and Er).

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1. A.J. Roche, S.A. Rabinowitz, K.A. Cox. Efficient NMR enantiodiscrimination of bridge fluorinated paracyclophanes using lanthanide tris beta-diketonate complexes. *Tetrahedron: Asymmetry*. **24**, 1382 (2013).

2. S. Spiliadis, A.A. Pinkerton. Paramagnetic nuclear magnetic resonance study of the lanthanide complexes [Ln(SPR)₃]; R=OMe, OiPr. Determination of phosphorus hyperfine coupling and solution structures. *Inorg. Chim. Acta*. **75**, 125 (1983).
3. A.V. Turov, S.P. Bondarenko, A.A. Tkachuk, V.P. Khilya. Study of the conformational mobility of substituted 2-methoxychalcones under the influence of lanthanide shift reagents. *Zh. Org. Khim.* **41**, 51 (2005) (in Russian).
4. V.F. Zolin, L.G. Koreneva. *Rare-Earth Probe in Chemistry and Biology* (Nauka, Moscow, 1980) (in Russian).
5. M. Woods, D.E. Woessner, A. Dean Sherry. Paramagnetic lanthanide complexes as PARACEST agents for medical imaging. *Chem. Soc. Rev.* **35**, 500 (2006).
6. M.D. Organ, R.C. Brasch. Contrast enhancing agents in NMR imaging. *Annu. Rep. Med. Chem.* **20**, 277 (1985).
7. J.A. Peters, M.S. Nieuwenhuizen, A.P.G. Kieboom, D.J. Raber. Analysis of multinuclear lanthanide induced shifts. Part 5'. The coordination polyhedron of 1:3 lanthanide(III)-glycolate complexes in aqueous solution. *J. Chem. Soc. Dalton Trans.* **3**, 717 (1988).
8. V.V. Skopenko, V.M. Amirkhanov, T.Yu. Sliva, I.S. Vasilchenko, E.L. Anpilova, A.D. Garnovskii. Various types of metal complexes based on chelating β-diketones and their structural analogues. *Russ. Chem. Rev.* **8**, 737 (2004).
9. V.M. Amirkhanov, V.A. Ovchinnikov, V.A. Trush, P. Gawryszewska, L.B. Jerzykiewicz. Powerful new ligand systems: Carbacylamidophosphates (Caph) and sulfonylamidophosphates (Saph). In *Ligands. Synthesis, Characterization and Role in Biotechnology* (NOVA Publishers, 2014) [ISBN: 978-1631171437].
10. O.O. Litsis, I.O. Shatrava, V.M. Amirkhanov, V.A. Ovchinnikov, T.Yu. Sliva, S.V. Shishkina, V.V. Dyakonenko, O.V. Shishkin, V.M. Amirkhanov. New carbacylamidophosphates (CAPH) and CAPH-containing coordination compounds: structural peculiarities. *Struct. Chem.* **27**, 341 (2016).
11. N.S. Kariaka, J.A. Rusanova, S.S. Smola, S.V. Kolotilov, K.O. Znovjyak, M. Weselski, T.Yu. Sliva, V.M. Amirkhanov. First examples of carbacylamidophosphate pentanuclear hydroxo-complexes: Synthesis, structure, luminescence and magnetic properties. *Polyhedron*. **106**, 44 (2016).
12. O. Litsis, V. Ovchinnikov, T. Sliva, S. Shishkina, V. Amirkhanov. Lanthanide coordination compounds with monodentate coordinated β-diketone heteroanalogue-(2,2,2-trichloro-N-(dipiperidin-1-yl-phosphoryl)acetamide: synthesis and spectral investigations. *Chem. J. Moldova* **13**, 15 (2018).
13. V. Amirkhanov, A. Rauf, T.B. Hadda, V. Ovchinnikov, V. Trush, M. Saleem, M. Raza, T. Rehman, H. Zgou, U. Shaheen, T. Farghaly. Pharmacophores modeling in terms of prediction of theoretical physico-chemical properties and verification by experimental correlations of carbacylamidophosphates (CAPH) and sulfonylamidophosphates (SAPH) tested as new carbonic anhydrase inhibitors. *Mini-Rev. Med. Chem.* **19**, 20 (2019).

14. I.I. Grynyuk, S.V. Prylutska, N.S. Kariaka, T.Yu. Sliva, O.V. Moroz, D.V. Franskevych, V.M. Amirkhanov, O.P. Matyshevska, M.S. Slobodyanik. Computer prediction of biological activity of dimethyl-n-(benzoyl)amidophosphate and dimethyl-n-(phenylsulfonyl)amidophosphate, evaluation of their Cytotoxic activity against leukemia cells *invitro*. *Ukr. Biochem. J.* **87**, 154 (2015).
15. Iu. Shatrava, V. Ovchynnikov, K. Gubina, S. Shishkina, O. Shishkin, V. Amirkhanov. Varieties in structures of Co(II), Ni(II) and Cu(II) coordination compounds based on dimethyl pyridine-2-ylcarbamoylphosphoramidate. *Struct. Chem.* **27**, 1413 (2016).
16. S.J. Lyle, Md.M. Rahman. Complexometric titration of yttrium and lanthanoids. *Talanta* **10**, 1177 (1963).
17. V.M. Amirkhanov, V.A. Trush. Properties and structure of dimethyl ester of trichloroacetyl-amidophosphoric acid. *Zh. Org. Khim.* **7**, 1120 (1995) (in Russian).
18. J. Cybin'ska, J. Legendziewicz, V. Trush, R. Reisfeld, T. Saraidarov. The orange emission of single crystals and solgels based on Sm³⁺ chelates. *J. Alloy. Compd.* **451**, 94 (2008).
19. M. Puchalska, I. Turowska-Tyrk, V. Trush, J. Legendziewicz. Structural characteristic and luminescence properties of first known example of a pair of europium(III) complexes of phosphoroazo-derivative of β -diketone with inner and both inner and outer sphere 2,2'-bipyridine. *J. Alloy. Compd.* **451**, 264 (2008).
20. V. A. Trush, O.O. Litsis, T.Yu. Sliva, V.M. Amirkhanov. Heteroleptic lanthanide complexes with the CAPH-type ligand dimethyl-N-trichloroacetylamidophosphate. *Visn. Odes. Nats. Univ. Khim.* **22**, 62 (2017).
21. G. Oczko, J. Legendziewicz, V. Trush, V. Amirkhanov. X-ray analysis and excited state dynamics in a new class of lanthanide mixed chelates of the type LnPh β ₃-Phen (Ln = Sm, Eu, Gd, Tb). *New J. Chem.* **27**, 948 (2003).
22. J. Reuben, D. Fiat. Nuclear magnetic resonance studies of solutions of the rare earth ions and their complexes. *J. Chem. Phys.* **51**, 4909 (1969).
23. K.A. Gschneidner, J.-C.G. Bunzli, V.K. Pecharsky. *Handbook on the Physics and Chemistry of Rare Earths*, (Elsevier, 2003) [ISBN: 978-0-444-51323-6].
24. A.M. Funk, K.-L.N. A. Finney, P. Harvey, A.M. Kenwright, E.R. Neil, N.J. Rogers, P.K. Senanayake and D. Parker. Critical analysis of the limitations of Bleaney's theory of magnetic anisotropy in paramagnetic lanthanide coordination complexes. *Chem. Sci.* **6**, 1655 (2015).
25. B.B. Bleaney. Nuclear magnetic resonance shifts in solution due to lanthanide ions. *J. Magn. Reson.* **8**, 91 (1972).
26. R.S. Drago, J.I. Zink, R.M. Richman, W.D. Perry. Theory of isotropic shifts in the NMR of paramagnetic materials: Part I. *J. Chem. Educ.* **51**, 371 (1974).
27. A.A. Pinkerton, W.L. Earl. A nuclear magnetic resonance investigation of bis(O,O'-diethyldithiophosphato)-complexes of the lanthanids: Separation of contact and pseudo-contact contributions to the chemical shifts. *J. Chem. Soc. Dalton Trans.* **3**, 267 (1978).
28. L. Fusaro. An ¹⁷O NMR study of diamagnetic and paramagnetic lanthanide-tris(oxydiacetate) complexes in aqueous solution. *Magn. Reson. Chem.* **56**, 1168 (2018).
29. K. Djanashvili, J.A. Peters. How to determine the number of inner-sphere water molecules in lanthanide(III) complexes by ¹⁷O NMR spectroscopy. A technical note. *Contr. Media Mol. Imag.* **2**, 67 (2007).

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ДОСЛІДЖЕННЯ ПАРАМАГНІТНИХ
КООРДИНАЦІЙНИХ СПОЛУК ЛАНТАНОЇДІВ
СКЛАДУ [LnL₃ · Phen] (L = CCl₃C(O)NP(O)(OCH₃)₂)
МЕТОДОМ ЯМР-СПЕКТРОСКОПІЇ
НА ЯДРАХ ¹H ТА ³¹P

Резюме

Синтезовано ряд координаційних сполук лантаноїдів з диметил-N-трихлорацетиламідифосфатом HL [HL = CCl₃C(O)N(H)P(O)(OCH₃)₂, ліганд карбаціламідифосфатного (CAPH) типу] складу [LnL₃ · Phen], де Phen – 1,10 фенантролін, Ln = La, Ce, Pr, Nd, Sm, Tb, Dy, Ho, Er. Розчини ліганду HL та синтезованих на його основі комплексів в ацетоні досліджені методом ЯМР ¹H та ³¹P при кімнатній температурі 298 К. Оскільки хімічні зсуви сигналів ¹H мають псевдоконтактну природу, то ізотропні зсуви сигналів ³¹P вдалося розкласти на контактну та псевдоконтактну складові. Було встановлено існування у розчині сполук [LnL₃ · Phen] двох серій комплексів, що мають однакову будову координаційної сфери в межах кожної серії: Ln = Ce, Pr, Nd, Sm (L1) та Ln = Tb, Dy, Ho, Er (L2). Для цих комплексів було розраховано значення константи надтонкої взаємодії: 0,18 МГц (L1) та 0,13 МГц (L2).