IR and ^{31}P NMR spectroscopic study of complexation of carbamoyl methyl phosphinates with U^{VI} and Th^{IV} in nitric acid solutions

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The composition of complexes formed upon the extraction of U^{VI} and Th^{IV} nitrates with *O*-*n*-nonyl(*N*,*N*-dibutylcarbamoylmethyl) methyl phosphinate (**L**) from solutions of nitric acid without additional solvent was determined by ^{31}P NMR spectroscopy. The structures of the complexes formed were studied by IR spectroscopy. Uranium(vi) is extracted from 3 and 5 *M* solutions of HNO_3 as the $[UO_2(\mathbf{L})_2(NO_3)_2]$ complex, while thorium(iv) is extracted from 5 *M* HNO_3 as the $[Th(\mathbf{L})_3(NO_3)_3]^+ \cdot NO_3^-$ complex. In both cases, ligand L has bidentate coordination. Ligand **L** contacts with 3 and 5 *M* nitric acid to form adducts $\mathbf{L} \cdot HNO_3$ and $\mathbf{L} \cdot (HNO_3)_2$, respectively.

Key words: carbamoyl methyl phosphinates, carbamoylmethylphosphine oxides, extraction, uranium(vi), thorium(iv), complexation, complexes, NMR and IR spectroscopies.

N,*N*-Dialkylamides of phosphorylacetic acids (carbamoylmethylphosphine oxides, phosphinates, and phosphonates) are widely used for extraction of uranium and transuranium metals from radioactive waste of different composition by liquid extraction. The study of the extraction properties of diphenyl(*N*,*N*-dibutylcarbamoylmethyl)phosphine oxide $Ph_2P(O)CH_2C(O)NBu_2$ (**1**) in solutions of 1—8 *M* nitric acid in the absence of organic solvents found the formation of $\mathbf{1} \cdot HNO_3 \cdot nH_2O$ complexes ($n = 2$—3) and a change in the stoichiometry of extracted forms of metal ions and their solvate number with an increase in the partition coefficients ($>10^3$).[1—4] A highly efficient sorption method for concentrating radionuclides was proposed using this ligand.[3] Extraction of actinides with neutral organophosphorus compounds from nitric acid solutions without additional organic solvent have great advantages over standard liquid extraction. This circumstance stimulated searching for and studying other extraction systems involving neutral organophosphorus compounds.

Continuing our studies[5,6] of the use of carbamoyl methyl phosphinates as bidentate neutral complexing extragents, it seemed of interest to study their behavior in extraction systems without additional solvent. In the present work, we report the results of studying the system **L**—HNO_3—An (**L** is *O*-*n*-nonyl(*N*,*N*-dibutylcarbamoylmethyl) methyl phosphinate (**2**); An = Th^{IV}, U^{VI}) by NMR and IR spectroscopies, which made it possible to determine both the compositions and structures of the complexes formed.

Complexes of bidentate neutral complexing extragents with nitric acid and metal ions are known[4] to be stable and remain unchanged after dissolving in organic solvents, which allows their NMR study. We showed that, unlike the published results,[1,7] the composition of the complexes formed by U^{VI} and Th^{IV} extraction with methyl phosphinate **2** without additional solvent can be determined by ^{31}P NMR using the metal in amounts substantially lower than stoichiometry demands.

Experimental

^{31}P{^{1}H} NMR spectra were recorded in 1,2-dichloroethane (DCE) (85% H_3PO_4 as external standard) on a Bruker AMX-400 instrument. IR spectra were obtained on a Nikolet MAGNA-IR 750 FT-IR spectrometer as a thin film between CaF_2 plates or as a solution in $CHCl_3$. The standard interval of studies was 1000—4000 cm^{-1}, and NaCl plates were used to extend the interval to 700 cm^{-1}.

Nitric acid solutions of ^{232}Th and ^{238}U and nitric acid (special purity grade) were used.

Synthesis of *O*-*n*-nonyl(*N*,*N*-dibutylcarbamoylmethyl) methyl phosphinate, $Me(n\text{-}C_9H_{19}O)P(O)CH_2C(O)N(Bu^n)_2$ (2). Chloroacetic acid *N*,*N*-dibutylamide (4.52 g, 0.022 mol) was added to

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a solution of *O*,*O*-di-*n*-nonyl methyl phosphonite (6.66 g, 0.02 mol) in anhydrous xylene (50 mL), and the resulting mixture was refluxed for 5 h in an argon flow. Xylene was distilled off *in vacuo*, and the residue was purified by chromatography on silica gel (60 mesh). Compound **2** was obtained in 70% yield (5.25 g) as a viscous oil. ^{31}P NMR ($CDCl_3$), δ: 51.1. Found (%): C, 63.26; H, 11.19; P, 7.72. $C_{20}H_{42}NO_3P$. Calculated (%): C, 63.97; H, 11.27; P, 8.25.

Determination of the composition of complex of phosphinate 2 with nitric acid. The ligand was stirred for 10 min with HNO_3 at a phase ratio of 1 : 100, and the phases were separated by centrifugation. To equilibrate the extraction of nitric acid to the organic phase, the procedure was repeated twice. The concentration of HNO_3 was varied in a range of 0.5—7 mol L^{-1}. The phosphorus and nitrogen contents in the organic phase were determined by elemental analysis data. These data were used to calculate the ratio of **2** to nitric acid. The organic phase after contact with HNO_3 was studied by ^{31}P NMR and IR spectroscopies.

Actinides were extracted without additional solvent with ligand **2** using a previously described method,[1] and U^{VI} and Th^{IV} were used in amounts of 5—15 mol.%. An exact weighed sample of methyl phosphinate **2** was stirred for 10 min with a solution of nitric acid with the corresponding concentration at a phase ratio of 1 : 50, and the calculated amount of U^{VI} or Th^{IV} was added as a 0.025 *M* solution in nitric acid of the same concentration. The mixture was stirred for 10 min, and the phases were separated by centrifugation. The content of uranium(VI) and thorium(IV) in the aqueous phase before and after extraction was determined spectrophotometrically with the reagent Arsenazo III on a Specord M-40 instrument. The organic phase, which represented a mixture of the H-bonded ligand (see below) and its complex with metal, was studied by ^{31}P NMR (solvent 1,2-dichloroethane) and IR spectroscopies.

The composition of the complexes formed was determined by the formula

$$n_{\mathrm{L}} = \frac{I_{\mathrm{C}}}{(I_{\mathrm{C}} + I_{\mathrm{L}})M\%}\cdot 100\%,$$

where n_{L} is the number of ligand molecules in the complex, I_{C} is the integral intensity of the signal from the complex in the ^{31}P NMR spectrum, I_{L} is the integral intensity of the signal from the noncoordinated ligand in the ^{31}P NMR spectrum, and *M* (%) is the mole percentage of the metal used.

Results and Discussion

Study of the interaction of methyl phosphinate 2 with HNO_3. To determine the form in which ligand **2** interacts with actinide ions during their extraction without solvent, at first we studied the compositions and structures of complexes formed on contact of **2** with nitric acid. Based on the elemental analysis data, we determined the ratio of nitric acid to the ligand in the liquid adduct formed upon this contact (Fig. 1). It follows from the data obtained that the 1 : 1 adducts ($\mathbf{2}\cdot HNO_3$) are formed on contact of phosphinate **2** with 3 *M* nitric acid in the organic phase, whereas the contact with 5 *M* nitric acid produces the 1 : 2 adducts ($\mathbf{2}\cdot 2HNO_3$). The ^{31}P NMR spectrum of the adduct exhibits a downfield shift of the signal of Δδ 2.9 compared to the signal of the starting phosphinate (δ$_P$ 51.1), which is caused by the formation of a complex of ligand **2** with nitric acid, most likely, due to hydrogen bonding at the oxygen atom of the P=O phosphoryl group.

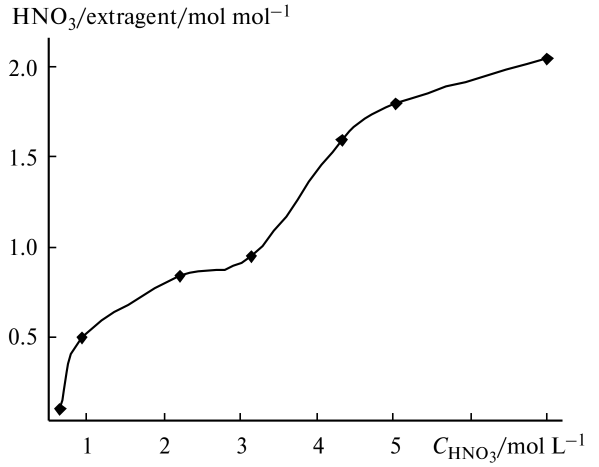

Fig. 1. Extraction curve of nitric acid with methyl phosphinate **2**.

The coordination mode of phosphinate **2** with HNO_3 was studied by IR spectroscopy. In the spectrum of the initial ligand **2** (Fig. 2, *a*), the absorption band of the phosphoryl group ν(P=O) is observed at 1230 cm^{-1} and the vibration frequency of the carbonyl group ν(C=O) lies at 1640 cm^{-1}, while the interaction of phosphinate **2** with 3 and 5 *M* HNO_3 shifts the absorption band of the P=O group to 1165 cm^{-1}, indicating the formation of a hydrogen bond by the phosphoryl group. In this case, the absorption band of the C=O group is not shifted, and a weak low-frequency shoulder could indicate a small fraction of a complex with participation of the carbonyl group only in hydrogen bonding. Note that this shoulder becomes more pronounced after the contact with a solution of the acid of a higher concentration. However, it should be taken into account that the bending vibration of water and $\nu_{as}(NO_2)$ of the coordinated nitric acid molecule[8] appear in the same region (1620—1645 cm^{-1}), which does not allow us to attribute reliably the appeared shoulder to the vibration of the C=O group.

The previous study[9] of the interaction of carbamoylmethylphosphine oxides and carbamoyl methyl phosphonates with nitric acid in organic solvents by thermometric titration and IR spectroscopy showed that a hydrogen bond is formed between the phosphoryl group and acid at the 1 : 1 ratio of the components, whereas the carbonyl group is involved in hydrogen bonding in a fourfold excess of nitric acid only. However, the studies of the interaction of the phosphine oxides with nitric acid,[9] including that during extraction,[10] found that different forms

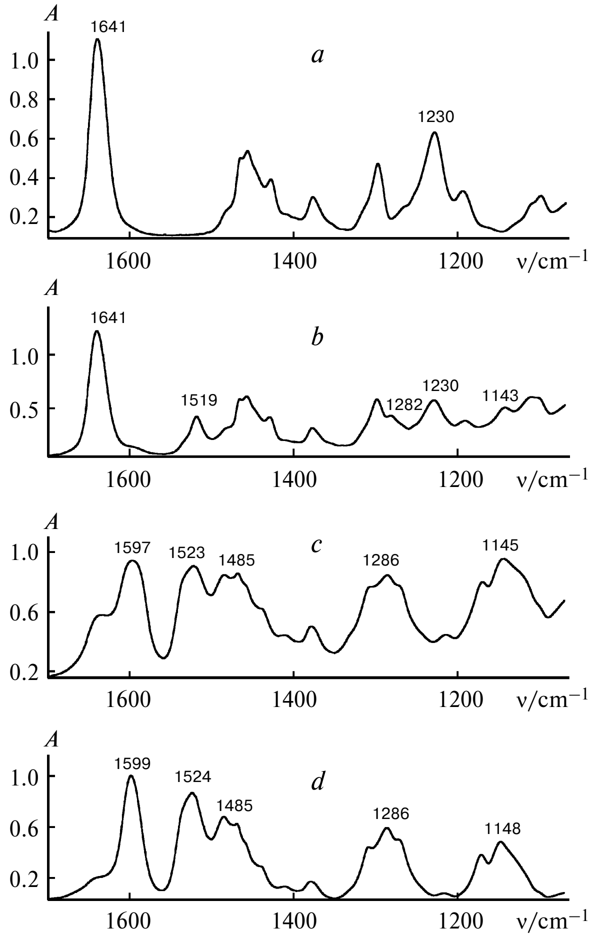

Fig. 2. IR spectra of phosphinate **2** and the products of the organic phase after U^{VI} extraction from nitric acid: *a*, initial methyl phosphinate **2**; *b—d*, organic phase after U^{VI} extraction from an aqueous solution (*b*), from 3 *M* HNO_3 (*c*), and from 5 *M* HNO_3 (*d*).

of the complex can be formed depending on the acid concentration, namely, molecular $PO \cdots HONO_2$ and ionic $POH^+(NO_3)^-$ and $P—O \cdots (H_3O)^+(NO_3)^-$.

Comparison of the IR spectroscopic data for the samples obtained after the contact of ligand **2** with 3 and 5 *M* nitric acid to published data[9,10] shows that the main reaction product of these compounds is a molecular complex formed due to a hydrogen bond between the P=O group and the hydrogen atom of an HNO_3 molecule.

Thus, the interaction of ligand **2** with solutions of nitric acid results in the successive formation of the mono- and diadducts with an increase in the concentration of nitric acid similarly to the interaction of carbamoylmethylphosphine oxides and carbamoyl methyl phosphonates with HNO_3 in organic solvents[8,11] and during liquid extraction.[12]

^{31}P NMR determination of compositions of the uranium(VI) and thorium(IV) complexes with methyl phosphinate 2 upon extraction from nitric acid without solvent. To determine the compositions of the U^{VI} and Th^{IV} complexes with ligand **2** upon extraction without additional solvent, the organic phase was studied by ^{31}P NMR after the contact of phosphinate **2** with nitric acid solutions of $UO_2(NO_3)_2$ and $Th(NO_3)_4$. Since methyl phosphinate **2** forms the 1 : 1 and 1 : 2 adducts upon the interaction with 3 and 5 *M* HNO_3, respectively, it seemed of interest to estimate the effect of solvation on the composition of the complexes extracted into the organic phase. For a considerable excess of ligand **2** in the reaction mixture, the ratio of the integral intensity of a signal from the complex (I_C) to the total intensity of signals of the free ligand (and/or its H-bonded form) (I_L) and the complex is proportional to the content of the complex, *i.e.*, corresponds to its mole percentage in the mixture. The division of this value into the mole percentage of the initially introduced metal amount (5—15 mol.%) makes it possible to determine the number of ligand molecules involved in complexation (An : **2** ratio). Note that the low solubility of phosphinate **2** in nitric acid solutions ($<10^{-5}$ mol L^{-1}, 4 mg L^{-1}), which was determined by ^{31}P NMR spectroscopy using a 0.01 *M* solution of NaH_2PO_4 as reference, exerts no effect on the accuracy of determination of the composition of the complexes.

The signal of the complex in the ^{31}P NMR spectrum of the organic phase after the interaction of ligand **2** with uranyl nitrate dissolved in both 3 *M* and 5 *M* HNO_3 exhibits a downfield shift relative to the signal of the H-bonded ligand and lies at δ 63.1. Upon the interaction of ligand **2** with $Th(NO_3)_4$ dissolved in 3 *M* HNO_3, the broadened signal of the thorium(IV) complex in the ^{31}P NMR spectrum is partially overlapped with the signal of the H-bonded ligand. This does not allow the correct integration of the signals to be performed. At the same time, when a solution of thorium nitrate in 5 *M* HNO_3 is used, the signal of the complex is shifted to a greater extent relative to the signal of the H-bonded ligand (Δδ 6.6) and is observed at δ 57.7. Table 1 contains the integral intensities of the resonance signals of the coordinated ligands obtained when different metal amounts were used.

The data obtained show that without solvent uranium(VI) is extracted with methyl phosphinate **2** from both 3 *M* and 5 *M* HNO_3 as a complex with the composition close to 1 : 2. When the amount of U^{VI} changes from 5 to 15 mol.% of the stoichiometric value, the composition of the complex extracted from nitric acid in the indicated concentration interval remains unchanged. A similar calculation for the extraction of thorium(IV) shows that the complex extracted in this case has the composition Th^{IV} : **2** = 1 : 3.

Determination of the coordination mode of phosphinate 2 with uranium(VI) and thorium(IV) by IR spectroscopy. To determine the coordination mode of ligand **2** in the complexes with U^{VI} and Th^{IV} extracted from nitric acid solu-

Table 1. Integral intensity of signals from the U^{VI} and Th^{IV} complexes with methyl phosphinate **2** in the ^{31}P NMR spectra[a] of the extraction products from 3 and 5 *M* HNO_3 and the number of molecules of ligand **2** in the extracted complexes

M[b] (mol. %)	U^{VI}				Th^{IV}	
	3 *M* HNO_3		5 *M* HNO_3		(5 *M* HNO_3)	
	I_C[c]	n_L	I_C[c]	n_L	I_C[c]	n_L
5	9.53	1.90	12.70	2.2	—	—
10	24.09	1.94	25.70	2.04	47.55	3.22
15	57.30	2.4	47.00	2.03	—	—

[a] 1,2-Dichloroethane was used as solvent for recording the ^{31}P NMR spectra.

[b] M is metal.

[c] Integral intensity of the signal from the complex; the signal of noncoordinated ligand **2** in the ^{31}P NMR spectrum was conventionally taken as 100 for simplicity of calculation.

tions, the products formed on contact of excess ligand with solutions of $UO_2(NO_3)_2$ and $Th(NO_3)_4$ in HNO_3 of different concentrations were studied by IR spectroscopy. Note that an increase in the content of actinides in a solution exerts no effect on the general view and character of the detected IR spectra, except for the decreased intensity of absorption bands in the spectra of the noncoordinated ligand. When interpreting the spectra of the extraction products, we used the data[13—16] obtained for the individual complexes of carbamoylmethylphosphine oxides and carbamoyl methyl phosphonates with lanthanides. Thus, in the case of the chelate complexes, a decrease in vibration frequencies of the P=O and C=O bonds due to coordination was 50—70 and 25—45 cm^{-1}, respectively, depending on the substituents at the P and C atoms. The bidentate coordination mode of the nitrate group was determined from absorption bands at 1520—1530, 1270—1300, and 1030—1105 cm^{-1}, which were assigned[16] to the $\nu_{as}(NO_2)$, $\nu_s(NO_2)$, and $\nu(NO)$ vibrations, respectively. Analysis of published data[13—15] shows that in the complexes under study the phosphoryl group is coordinated to the metal atom, which is accompanied by a regular decrease in the $\nu(P=O)$ vibration frequency by at least 50 cm^{-1}. The carbonyl can be not involved in coordination, and the assignment of its absorption band is not so unambiguous. However, the shift of the $\nu(C=O)$ group to 1590—1600 cm^{-1} can serve as an indicator of its coordination by actinide or lanthanide atoms. In this case, the nitrate groups are not displaced, as a rule, from the coordination sphere of the metal, and the carbamoylmethylphosphoryl ligands are incorporated into a polyhedron, thus increasing the coordination number to 9—12.

The IR spectra of the reaction products of ligand **2** with uranyl nitrate dissolved in water or nitric acid of different concentrations (0.5—7 mol L^{-1}) are shown in Fig. 2, *b—d*. Uranyl nitrate is insignificantly extracted from a neutral aqueous solution with ligand **2**: the spectrum exhibits weak absorption bands of the NO_3^- ion at 1519 and 1299 cm^{-1} (see Fig. 2, *b*), an intense absorption band with a weak shoulder of the free C=O groups (1641 cm^{-1}), and a band corresponding to the coordinated P=O group at 1143 cm^{-1}. Probably, under these conditions, uranium(VI) is insignificantly extracted through the formation of a complex only due to the phosphoryl group (monodentate coordination).

When the ligand interacts with the uranyl ion dissolved in 2—5 *M* HNO_3, bidentate ligand binding occurs, which is indicated by bands of the coordinated functional groups P=O at 1145 cm^{-1} and C=O at 1597 cm^{-1} (see Fig. 2, *c*,*d*). The absorption bands at 1523 and 1286 cm^{-1} correspond, according to published data,[14] to the bidentate-bonded nitrate groups. A complicated character of the band at 1523 cm^{-1} is related, probably, to the superposition of two components: the band belonging to the vibration of the NO_3 group and the band caused by the vibration of the N—C(O) bond in the amide group, whose frequency increases because of C=O bond weakening.[16] When the acidity of the medium increases from 0.5 to 6 mol L^{-1}, the spectral bands at 1485 and 1310 cm^{-1}, which can also be attributed to the bonded nitrate groups, become more intense. No absorption band of the free nitrate anion is observed in the spectra, *i.e.*, the uranyl ligand continues to retain the nitrate anions during complexation with ligand **2**.

Based on the IR spectroscopic data, we can conclude that, unlike uranium, thorium is extracted by phosphinate **2** without solvent already in a neutral medium. In this case, a complex with bidentate ligand coordination and retention of the nitrate groups in the coordination sphere is formed. The spectrum of the product obtained by the contact of thorium nitrate with phosphinate **2** in an aqueous solution (Fig. 3, *a*) exhibits absorption bands of the coordinated ligand: $\nu(P=O)$ at 1143 cm^{-1} and $\nu(C=O)$ at 1591 cm^{-1}, as well as bands of the nitrate anion at 1519 cm^{-1} and 1284 cm^{-1}. Thorium is extracted from 3 and 5 *M* solutions of HNO_3 due to the formation of the same complex but containing additionally the free nitrate ion, which is indicated by a weak band at 1400 cm^{-1} (see Fig. 3, *b—d*). In a more acidic medium (6—7 *M* HNO_3), the reaction product contains free nitric acid, which appears in the IR spectrum as bands at 1670 and 3500 cm^{-1} (see Fig. 3, *d*)[15].

Comparison of the results of ^{31}P NMR and IR spectroscopic studies of the complexation of U^{VI} and Th^{IV} with ligand **2** suggests that U^{VI} is extracted from 3 and 5 *M* HNO_3 as the neutral complex $UO_2(\mathbf{2})_2(NO_3)_2$, whereas thorium is extracted as the cationic complex $[Th(\mathbf{2})_3(NO_3)_3]^+\cdot NO_3^-$.

We have previously[5] shown that the liquid extraction of the analog of ligand **2**, *viz.*, *O*-(2-ethylhexyl)(*N*,*N*-di-

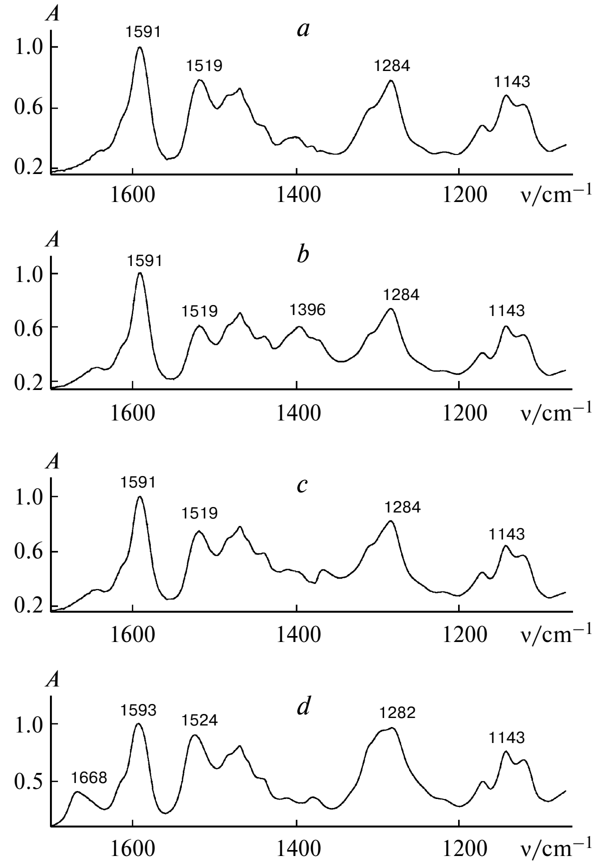

Fig. 3. IR spectra of the organic phase after Th^{IV} extraction from nitric acid: *a*, from an aqueous solution; *b*, from 3 *M* HNO_3; *c*, from 5 *M* HNO_3; and *d*, from 6 *M* HNO_3.

ethylcarbamoylmethyl) phenyl phosphonate (**3**), with uranium affords a complex with the composition metal : ligand = 1 : 1. As can be seen from the results of the present work, the solvate number increases from 1 to 2 for extraction without solvent. This difference can be explained by the fact that during liquid extraction the ligand interacts with actinide ions as an individual compound, while during solvent-free extraction it reacts as a complex with nitric acid,[1] which finally affords complexes of different compositions.

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References

1. Y. M. Kulyako, D. A. Malikov, M. K. Chmutova, M. N. Litvina, and B. F. Myasoedov, *J. All. Comp.*, 1998, 760.
2. Y. M. Kulyako, D. A. Malikov, M. K. Chmutova, and B. F. Myasoedov, *Mendeleev Commun.*, 1997, 135.
3. Y. M. Kulyako, D. A. Malikov, M. K. Chmutova, M. N. Litvina, and B. F. Myasoedov, *Mendeleev Commun.*, 1997, 193.
4. Y. M. Kulyako, T. I. Trofimov, and B. F. Myasoedov, *Proc. of International Conf. on Hazardous Waste; Sources, Effects and Management*, Cairo, Egypt, 1998, 85.
5. V. P. Morgalyuk, G. A. Pribylova, D. E. Drozhko, L. I. Ivanova, R. M. Kalyanova, O. I. Artyushin, M. V. Logunov, I. G. Tananev, T. A. Mastryukova, and B. F. Myasoedov, *Radiokhimiya*, 2004, **46**, 128 [*Sov. Radiochem.*, 2004, **46** (Engl. Transl.)].
6. V. P. Morgalyuk, N. P. Molochnikova, G. V. Myasoedova, E. V. Sharova, and O. I. Artyushin, *Radiokhimiya*, 2005, **47**, 167 [*Sov. Radiochem.*, 2005, **47** (Engl. Transl.)].
7. M. K. Chmutova, Yu. M. Kulyako, M. N. Litvina, D. A. Malikov, and B. F. Myasoedov, *Radiokhimiya*, 1998, **40**, 241 [*Sov. Radiochem.*, 1998, **40** (Engl. Transl.)].
8. E. I. Matrosov, V. V. Tkachev, L. O. Atovmyan, and M. I. Kabachnik, *Izv. Akad. Nauk SSSR*, *Ser. Khim.*, 1985, 320 [*Bull. Acad. Sci. USSR, Div. Chem. Sci.*, 1985, **34**, 292 (Engl. Transl.)].
9. E. I. Matrosov, N. P. Nesterova, A. I. Zarubin, I. A. Komolova, T. Ya. Medved´, and M. I. Kabachnik, *Izv. Akad. Nauk SSSR*, *Ser. Khim.,* 1988, 1070 [*Bull. Acad. Sci. USSR, Div. Chem. Sci.*, 1988, **37**, 935 (Engl. Transl.)].
10. V. M. Vdovenko, L. S. Bulyanitsa, and G. P. Savoskina, *Radiokhimiya,* 1970, **12**, 658 [*Sov. Radiochem.*, 1970, **12** (Engl. Transl.)].
11. H. F. Aly, A. T. Kandl, M. Raieh, and E. Hallaba, *Z. Anorg. Allg. Chem.,* 1973, **397**, 314.
12. A. M. Rozen, A. S. Nikiforov, Z. I. Nikolotova, N. A. Kartasheva, Yu. N. Studnev, V. A. Chauzov, and A. V. Fokin, *Dokl. Akad. Nauk*, 1985, **285**, 16 [*Dokl. Chem.*, 1985 (Engl. Transl.)].
13. T. Ya. Medved´, M. K. Chmutova, N. P. Nesterova, O. E. Koiro, N. E. Kochetkova, B. F. Myasoedov, and M. I. Kabachnik, *Izv. Akad. Nauk SSSR*, *Ser. Khim.,* 1981, 2121 [*Bull. Acad. Sci. USSR, Div. Chem. Sci.*, 1981, **30** (Engl. Transl.)].
14. S. M. Bowen, E. N. Duesler, and R. T. Paine, *Inorg. Chim. Acta*, 1982, **61**, 155.
15. W. E. Steward and T. H. Siddall, *J. Inorg. Nucl. Chem.*, 1970, **32,** 3599.
16. (a) L. J. Bellamy, *The Infrared Spectra of Complex Molecules,* Methuen and Co., Ltd., London, 1960; (b) K. Nakamoto, *Infrared and Raman Spectra of Inorganic and Coordination Compounds*, Wiley-Intersci., New York—Chichester—Brisbane—Toronto—Singapoure, 1978.

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