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Extraction of Rare Earth Elements(III) from Nitric Acid Solutions with Binary Extractants Based on Dialkylamino Derivatives of Carbamoylmethylphosphine Oxides and Dinonylnaphthalenesulfonic Acid

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Abstract—Interphase distribution of La, Ce, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, Lu, and Y between aqueous HNO_3 solutions and solutions of binary extractants obtained by reaction of equimolar amounts of dialkylamino derivatives of carbamoylmethylphosphine oxides and dinonylnaphthalenesulfonic acid in organic solvents has been studied. Stoichiometry of extracted complexes has been determined, effect of HNO_3 concentration in aqueous phase and organic solvent nature on the efficiency of metal ion recovery into organic phase has been considered. On the formation of extractable REE(III) complexes, the cationic moiety of binary extractant provides coordination solvation of REE(III) ions, while anionic moiety offers their high hydrophobicity, which favors to the efficient transition of metal ions into organic phase.
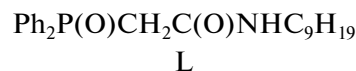
INTRODUCTION

Extraction methods are widely used for recovery, preconcentration, and separation of actinides and rare earth elements (REE) from solutions obtained on the processing of spent nuclear fuel [1]. High extraction ability toward these elements is shown by polydentate organophosphorus compounds [2−9], diamides of malonic [10], diglycolic [11] and N-heterocyclic carboxylic acids [12], organophosphorus acids [13], salts of quaternary ammonium bases (QAB) [14], as well as binary extractants: salts of amines and QAB with organic acid anions [15−21]. The latter can be classified as functionalized ionic liquids (FIL) whose anionic moiety participates in complexation with metal ion. In recent time, there is growing interest in the use of FIL in extraction practice for preconcentration and separation of actinides and REE(III) [22].

Extraction properties were studied for FIL synthesized by introducing thioether [23], monoaza crown ether [24], phosphoryl [25], calixarene−phosphine oxide [26], malonamide [27], diglycolamide [28], carbamoylphosphone oxide (CMPO) [29−31] and other

coordinating groups into cationic (1-alkyl-3-methylimidazolium) moiety of ionic liquid molecule. The anionic moiety of these FIL were mainly hexafluorophosphate or bis[(trifluoromethyl)sulfonyl]imide anions.

The aim of this work is to study extraction of REE(III) ions from nitric acid solutions with solutions of binary extractants based on cations of dialkylamino derivatives of CMPO L^1 and L^2 and anions of dinonylnaphthalenesulfonic acid.

$$Ph_2P(O)CH_2C(O)NH(CH_2)_3N(C_2H_5)_2$$
$$L^1$$
$$Ph_2P(O)CH_2C(O)NH(CH_2)_2N(CH_3)_2$$
$$L^2$$
$$Ph_2P(O)CH_2C(O)NHC_9H_{19}$$
$$L$$

EXPERIMENTAL

Compound L previously described by us was obtained by reaction of ethyl diphenylphosphorylace-

tate with *n*-nonylamine on heating in ethanol solution [32]. Compounds L^1 and L^2 were obtained in similar manner using 3-(diethylamino)propylamine-1 and 2-(dimethylamino)ethylamine-1, respectively. NMR spectra were recorded on a Bruker AV 300 spectrometer.

N-(3-(diethylamino)propyl)diphenylphosphorylacetamide (L^1). Yield 60%, mp = 140−141°C (toluene). ^1H NMR (300 MHz, $CDCl_3$), δ, ppm, *J*, Hz: 7.85−7.75 m, 4H (*m*-CH in Ph); 7.75−7.45 m, 7H (*o*- and *p*-CH in Ph + NH); 3.34 d, $^2J_{P-H} = 12.0$, 2H, P−CH_2; 3.28 t, $^3J_{H-H} = 6.0$, $NHCH_2$; 2.48 q, $^3J_{H-H} = 6.0$, 4H, N−CH_2; 2.41 t, $^3J_{H-H} = 6.0$, 2H, CH_2−NEt_2; 1.59 quin, $^3J_{H-H} = 6.0$, 2H, CH_2−CH_2−CH_2; 1.01 t, $^3J_{H-H} = 6.0$, 6H, CH_3. ^{31}P NMR (121 MHz, $CDCl_3$), δ, ppm: 29.43 s.

For $C_{21}H_{29}N_2O_2P$ anal. calcd. (%): C, 67.72; H, 7.85; N, 7.52.

Found (%): C, 67.74; H, 7.77; N, 7.52.

N-(2-(dimethylamino)ethyl)diphenylphosphorylacetamide (L^2). Yield 61%, mp = 151−152°C (acetonitrile). ^1H NMR (300 MHz, $CDCl_3$), δ, ppm, *J*, Hz: 7.90−7.75 m, 4H (*m*-CH in Ph); 7.75−7.55 m, 7H (*o*- and *p*-CH in Ph + NH); 3.38 d, $^2J_{P-H} = 12.0$, 2H, P−CH_2; 3.33 t, $^3J_{H-H} = 6.0$, $NHCH_2$; 2.38 q, $^3J_{H-H} = 6.0$, 2H, N−CH_2; 2.25 s, 6H, NMe_2. ^{31}P NMR (121 MHz, $CDCl_3$), δ, ppm: 29.21 s. IR, ν, cm^{-1}: 3269 (NH), 3081 (NH), 1663 (C=O), 1564 (C−N), 1185 (P=O).

For $C_{18}H_{23}N_2O_2P$ anal. calcd., %: C, 65.44; H, 7.02; N, 8.48; P, 9.38.

Found, %: C, 65.35; H, 7.05; N, 8.44; P, 9.39.

Dinonylnaphthalenesulfonic acid (DNNSA, Sigma-Aldrich) was purified by procedure [33]. Solutions of binary extractants were prepared by dissolution of equimolar amounts of L^1 or L^2 and DNNSA in organic solvent followed by washing with water. Organic solvents used were 1,2-dichloroethane, *o*-xylene, and chloroform of reagent grade without additional purification. Initial aqueous solutions containing 2×10^{-6} mol/L of each REE(III) were obtained by dissolution of the corresponding nitrates in water followed by addition of HNO_3 solution to required concentration. Chemicals used were of reagent grade.

Extraction experiments were conducted in test tubes with ground stoppers at 21 ± 2°C and volume ratio of organic and aqueous phase of 1 : 1. Phases were contacted on a rotary apparatus for mixing with rotation speed of 60 rpm for 1 h. It was found preliminary that this time is sufficient to reach constant values of distribution ratios for REE(III) (D_{Ln}). After extraction, the phases were separated by centrifugation.

Rare earth element concentration in initial and equilibrium aqueous solutions was determined by mass spectral method with inductively coupled plasma ionization of sample (ICP-MS) using a Thermo Sci-

entific X-7 mass spectrometer (USA). The concentration of elements in organic phase was determined by material balance equation. The value of D_{Ln} was calculated as the ratio of element concentrations in equilibrium organic and aqueous phases. Determination error for D_{Ln} was not larger 5%. Concentration of HNO_3 in equilibrium aqueous phases was determined by potentiometric titration with NaOH solution.

RESULTS AND DISCUSSION

Compounds L^1 and L^2 contain in molecules bidentate coordinating fragment $Ph_2P(O)CH_2C(O)NH-$ and amino group attached to the amide nitrogen atom through alkylene bridge as distinct from CMPO L. To assess the possibility of amino group to participate in complexation with Ln^{3+} ions, we studied extraction of REE(III) from ammonium nitrate solutions with solutions of compounds L, L^1, and L^2 in dichloroethane. Compounds L^1 and L^2 were found to extract REE(III) ions more efficiently than CMPO L (Fig. 1). It may be due to participation of the nitrogen atom of the amino group in complexation with Ln^{3+} ions. The efficiency of REE(III) extraction with compounds L^1 and L^2 increases from La(III) to Lu(III) as the atomic number (*Z*) of element increases. The opposite character of $\log D_{Ln}-Z$ dependence is observed for REE(III) extraction with CMPO L solutions, which can be due to the different character of coordination of Ln^{3+} ions to CMPO L and ligands L^1 and L^2. The difference in the extraction ability of CMPO L and L^1 or L^2 increases with *Z*.

The extraction ability of compounds L^1 and L^2 sharply decreases in the system with nitric acid, which is associated with protonation of nitrogen atom of the amino groups and transition of salts L^1HNO_3 and L^2HNO_3 into aqueous phase. However, L^1 and L^2 react with DNNSA in organic phase to form binary extractants L^1HA and L^2HA according to equations:

$$L^1_{(org)} + HA_{(org)} \leftrightarrows L^1HA_{(org)}, \qquad (1)$$

$$L^2_{(org)} + HA_{(org)} \leftrightarrows L^2HA_{(org)}, \qquad (2)$$

where A^- is DNNSA anion. The high hydrophobicity of DNNSA anion determines the small transition of components of these binary extractants into aqueous phase.

The binary extractants L^1HA and L^2HA efficiently extract REE(III) ions from nitric acid solutions of low and moderate concentration. Under comparable conditions, D_{Ln} values on extraction with L^1HA solution are slightly higher than on extraction with L^2HA (Fig. 2), which can be due to higher hydrophobicity of compound L^1, the component of binary extractant. Under these conditions, DNNSA extracts REE(III) less efficiently than the binary extractants on its basis, while
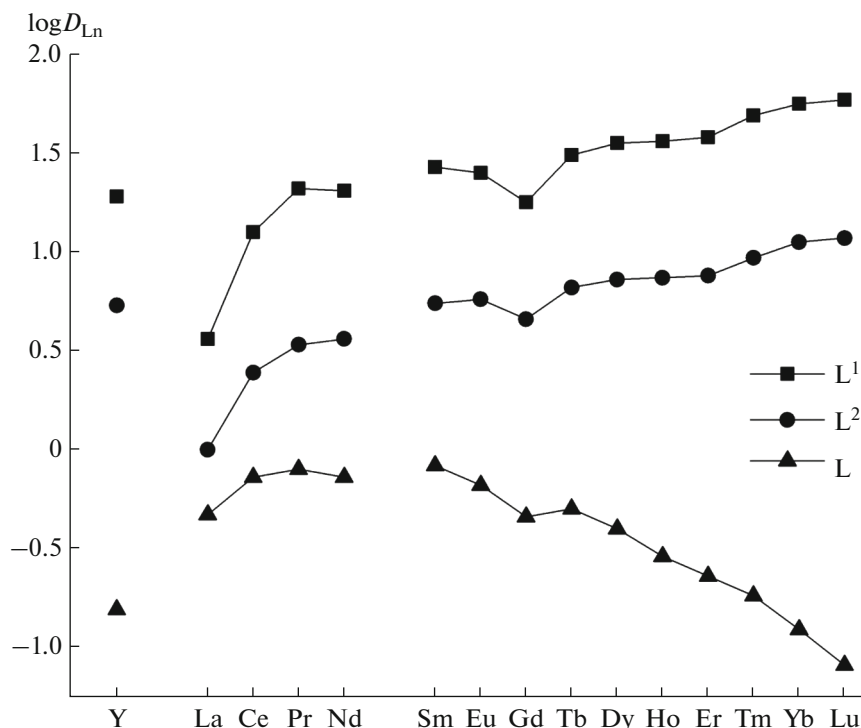
Fig. 1. Extraction of REE(III) and Y(III) from 4 M NH_4NO_3 solution with 0.05 M solutions of compounds L, L^1, and L^2 in dichloroethane.

compounds L^1 and L^2 do not extract REE(III) ($D_{Ln} <$ 10^{-2}) because they completely come into aqueous phase. The efficiency of REE(III) extraction with binary extractants decreases from La(III) to Lu(III) as Z rises. The position of Y(III) in the series of REE(III) between Ho(III) and Er(III) corresponds to the proximity of their ionic radii [34]. Similar character of $\log D_{Ln}$–Z dependence was observed on REE(III) extraction from nitric acid solutions with CMPO solutions [35, 36]. One can suppose that, in contrast to REE(III) extraction with compounds L^1 and L^2 from ammonium nitrate solutions, the extraction with binary extractants L^1HA and L^2HA from HNO_3 solution proceeds via complexation with Ln^{3+} ions of only bidentate complexing fragment $Ph_2P(O)CH_2C(O)NH-$ of the binary extractants. On formation of extractable REE(III) complexes, the cationic moiety of binary extractant provides coordination solvation of Ln^{3+} ions, while anionic moiety imparts them high hydrophobicity, which favors to efficient transfer of metal ions into organic phase. Binary extractants L^1HA and L^2HA exceeds considerably CMPO L in the extraction ability of REE(III) ions (Fig. 2).

The separation factor of La(III) and Lu(III) $\beta_{La/Lu} =$ D_{La}/D_{Lu} on extraction with binary extractant solutions in dichloroethane ($\beta_{La/Lu} = 32.3$ and 28.2 for L^1HA and L^2HA, respectively) exceeds that for DNNSA–dichloroethane system ($\beta_{La/Lu} = 0.64$). This fact indi-

cates the considerable enhancement for the selectivity of REE(III) extraction from nitric acid solutions with solutions of binary extractants.

At constant initial concentration of binary extractant in organic phase, increase in HNO_3 concentration in equilibrium aqueous phase is accompanied by decrease of D_{Ln} (Fig. S1). In the studied range of HNO_3 concentrations, the slope of $\log D_{Ln}$–$\log[HNO_3]$ dependence is close to -2 for all REE(III), which indicates the transition of two H^+ ions into aqueous phase during extraction.

The stoichiometric ratio REE(III) : binary extractant in extracted complexes was determined by equilibrium shift method. At constant HNO_3 concentration in aqueous phase, the slope of $\log D_{Ln}$–$\log[L^1HA]$ dependences is close to 2 (Fig. S2). Solutions of binary extractant L^2HA extract REE(III) ions as complexes of the same stoichiometry (Fig. S3).

The process of REE(III) extraction from nitric acid solutions with binary extractants can be described by the equation:

$$Ln^{3+}_{(aq)} + NO^-_{3(aq)} + 2LHA_{(org)}$$
$$\leftrightarrows LnL_2A_2NO_{3(org)} + 2H^+_{(aq)}, \qquad (3)$$
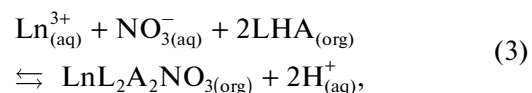
where symbols (aq) and (org) refer to the components of aqueous and organic phase, respectively
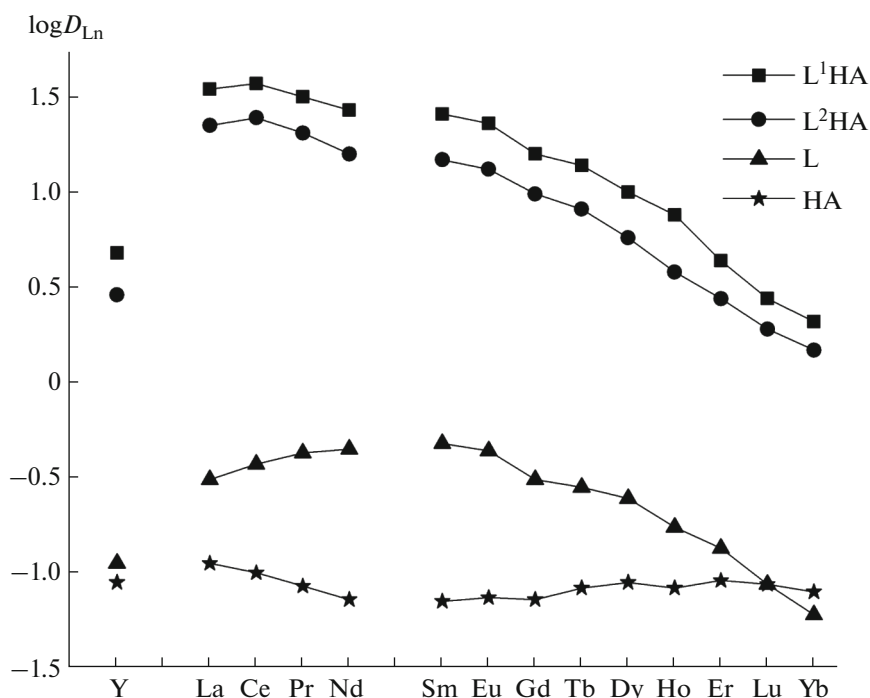
Fig. 2. Extraction of REE(III) and Y(III) from 3 M HNO_3 solutions with 0.05 M solutions of CMPO L, DNNSA, and binary extractants L^1HA and L^2HA in dichloroethane.

Organic solvent nature has considerable effect on REE(III) extraction with CMPO solutions [37, 38]. On extraction with 0.05 M L^2HA solutions in organic solvents from 1 M HNO_3 solution, D_{Ln} values increase in the series chloroform < o-xylene < 1,2-dichloroethane (Fig. 3). Let us note that the change in polarity and solvating ability of organic diluent in the system with binary extractant shows considerably lower effect on REE(III) extraction efficiency than in systems with neutral CMPO. In the system with L^2HA, the transition from o-xylene to dichloroethane is accompanied by the four-fold growth of D_{Eu}, whereas D_{Eu} rises by 50 times on extraction with neutral CMPO [39]. This effect may be caused by higher hydrophobicity of $LnL_2A_2NO_3$ complexes as compared with that for coordination-solvated REE(III) nitrates extracted with neutral CMPO. The suppression of extraction on the use of chloroform as solvent seems to result from the solvation of donor centers of extractant molecule due to hydrogen bonding between P=O and $HCCl_3$ to decrease activity of binary extractant in organic phase.

The presented data show that the binary extractants obtained from equimolar amounts of dialkylamino derivatives of carbamoylmethylphosphine oxides and dinonylnaphthalenesulfonic acid in organic solvents efficiently extract REE(III) ions from nitric acid solutions. On the formation of extractable REE(III) complexes, the cationic moiety of the binary extractant provides coordination solvation of Ln^{3+} ions, while anionic moiety imparts their high hydrophobicity, which favors efficient transition of metal ions into organic phase.

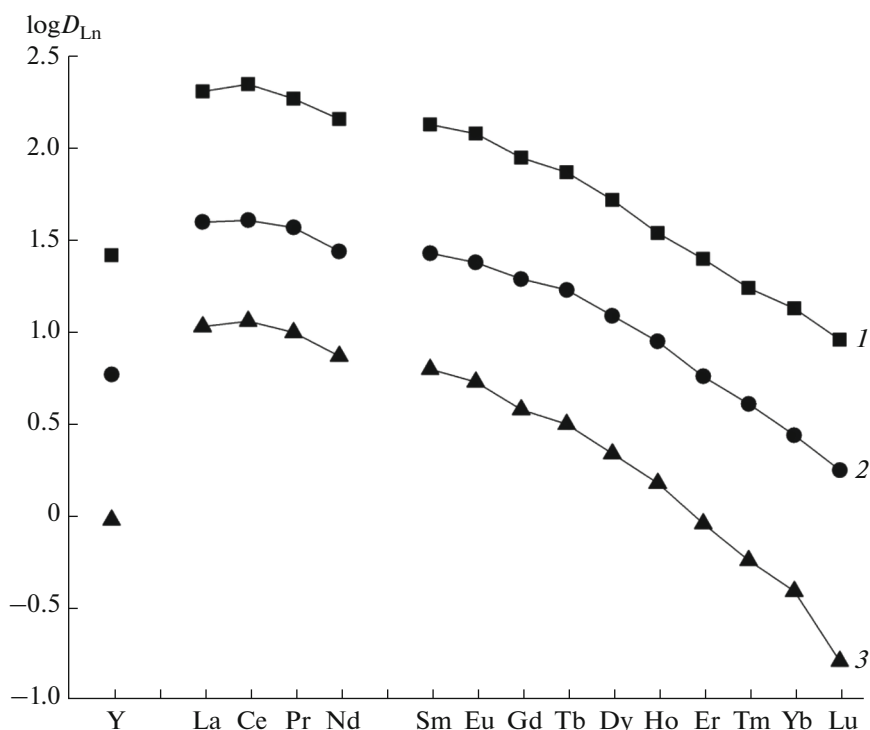## CONFLICT OF INTEREST

The authors declare no conflict of interest.

SUPPLEMENTARY MATERIALS

Supplementary information to this article is available for authorized users via https://doi.org/10.1134/S0036023620080185.

Fig. 3. Extraction of REE(III) and Y(III) from 1 M HNO_3 solutions with 0.05 M solutions of binary extractants L^1HA in (*1*) dichloroethane, (*2*) *o*-xylene, and (*3*) chloroform.

Fig. S1. The effect of HNO_3 concentration in aqueous phase on REE(III) extraction with 0.05 M L^1HA solutions in 1,2-dichloroethane.

Fig. S2. The effect of binary extractant L^1HA concentration in 1,2-dichloroethane on REE(III) extraction from 1 M HNO_3 solutions.

Fig. S3. The effect of binary extractant L^2HA concentration in 1,2-dichloroethane on REE(III) extraction from 1 M HNO_3 solutions.

REFERENCES

1. B. F. Myasoedov and S. N. Kalmykov, Mendeleev Commun. **25**, 319 (2015).
   https://doi.org/10.10016/j.mencom.2015.09.001

2. M. Yu. Alyapyshev, V. A. Babain, and Yu. A. Ustynyuk, Russ. Chem. Rev. **85**, 943 (2016).
   https://doi.org/10.1070/RCR4588

3. A. Leoncini, J. Huskens, and W. Verboom, Chem. Soc. Rev. **46**, 7229 (2017).
   https://doi.org/10.1039/C7CS00574A

4. A. M. Wilson, P. J. Bailey, and P. A. Tasker, Chem. Soc. Rev. **43**, 123 (2014).
   https://doi.org/10.1039/C3CS60275C

5. E. J. Werner and S. M. Biros, Org. Chem. Front. **6**, 2067 (2019).

6. M. G. Patterson, A. K. Mulville, E. K. Connor, et al., Dalton Trans. **47**, 14318 (2018).

7. K. M. Coburn, D. A. Hardy, M. G. Patterson, et al., Inorg. Chim. Acta **449**, 96 (2016).

8. H. T. Sartain, S. N. McGraw, and C. L. Lawrence, Inorg. Chim. Acta **426**, 126 (2015).

9. A. Bhattacharyya and P. K. Mohapatra, Radiochim. Acta **107**, 931 (2019).

10. L. Nigond, N. Condaamines, P. Y. Cordier, et al., Sep. Sci. Technol. **30**, 2075 (1995).

11. S. A. Ansari, P. Pathak, P. K. Mohapatra, and V. K. Manchanda, Chem. Rev. **112**, 1751 (2012).

12. M. Yu. Alyapyshev, V. A. Babain, L. I. Tkachenko, Radiokhimiya **56**, 481 (2014).

13. K. L. Nash, Solvent Extr. Ion Exch. **33**, 1 (2015).

14. S. I. Stepanov and A. M. Chekmarev, Rare Metal Extraction with Quaternary Ammonium Salts (IzdAT, Moscow, 2004).

15. A. I. Khol'kin and V. I. Kuz'min, Zh. Neorg. Khim. **27**, 2070 (1982).

16. A. I. Kholkin, G. L. Pashkov, I. Yu. Fleitlich, et al., Hydrometallurgy **36**, 109 (1994).

17. A. I. Kholkin, V. V. Belova, G. L. Pashkov, et al., J. Mol. Liq. **82**, (1999).

18. V. V. Belova, A. A. Voshkin, A. I. Kholkin, and A. K. Payrtman, Hydrometallurgy **97**, 198 (2009).

19. V. V. Belova, M. M. Martynova, Yu. V. Tsareva, et al., J. Mol. Liq. **293**, Article 111568 (2019).
    https://doi.org/10.1016/j.molliq.2019.111568

20. V. V. Belova, M. M. Martynova, V. E. Baulin, and D. V. Baulin, Russ. J. Inorg. Chem. **64**, 1059 (2019).
    https://doi.org/10.1134/S0036023619080023

21. A. M. Safiulina, D. V. Ivanets, E. M. Kudryavtsev, et al., Russ J. Inorg. Chem. **63**, 1679 (2018).

22. Z. Fei, T. J. Geldbach, D. Zhao, and P. J. Dyson, Chem.-Eur. J. **12**, 2122 (2006).

23. A. E. Visser, R. P. Swatloski, R. Mayton, et al., Environ. Sci. Technol. **36**, 2523 (2002).

24. H. Luo, S. Dai, P. V. Bonnesen, and A. C. Buchanan, J. Alloys Compd. **418**, 195 (2006).

25. A. Ouadi, O. Klimchuk, C. Gaillard, and I. Billard, Green Chem. **9**, 1160 (2007).

26. S. Miroshnichenko, D. Ternova, I. Billard, et al., Phosphorus, Sulfur Silicon Relat. Elem. **186**, 903 (2011).

27. M. Bonaffe-Moity, A. Ouadi, V. Mazan, et al., Dalton Trans. **41**, 7526 (2012).

28. P. K. Mohapatra, A. Sengupta, M. Iqbal, et al., Chem.-Eur. J. **19**, 3230 (2013).

29. I. L. Odinets, E. V. Sharova, O. I. Artyushin, et al., Dalton Trans. **39**, 4170 (2010).

30. P. K. Mohapatra, P. Kandwal, M. Iqbal, et al., Dalton Trans. **42**, 4343 (2013).

31. D. Ternova, A. Ouadi, V. Mazan, et al., J. Solution Chem. **47**, 1309 (2018).

32. O. I. Artyushin, E. V. Sharova, I. L. Odinets, et al., Russ. Chem. Bull. **53**, 2499 (2004).

33. P. R. Danesi, R. Chiarizia, and G. Scibona, J. Inorg. Nucl. Chem. **35**, 3926 (1973).

34. R. D. Shannon, Acta Crystallogr. A **32**, 751 (1976).

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