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N,S-containing soft ligands for extractive separation of *f*-metals: synthesis and unexpected inverse selectivity

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A number of heterocycle-based bis(phosphine sulfides) have been synthesized from the corresponding phosphine oxides using phosphorus(V) sulfide in good to excellent yields, for one representative compound the molecular structure has been determined by single crystal X-ray diffraction. The compounds obtained were tested as extractants for *f*-metals both in nitric acid and ammonium nitrate media, distribution coefficients and selectivity factors have been determined for an Am/Eu pair.

Nuclear power is an important energy source that does not produce carbon dioxide. The major disadvantage of this power production method is the formation of highly toxic spent nuclear fuel (SNF) and further, during the SNF reprocessing for the return of uranium and plutonium to the fuel cycle (plutonium and uranium extraction, PUREX-process), the generation of high-level liquid waste (HLLW).¹ The handling of HLLW is a complicated technological task due to its high radioactivity, presence of concentrated nitric acid and a variety of components including lanthanides and actinides, with long-lived isotopes of americium and neptunium making the main contribution to the radiotoxicity. The separation of the HLLW components is hampered by the close similarity of the chemical properties of americium and lanthanides. So far, the most effective approach to HLLW processing is the liquid-liquid extraction using appropriate organic ligands.^{2,3} The extractants with required selectivity between Am^{III} and Ln^{III} typically contain soft donor atoms, their successful examples include bis(1,2,4-triazinyl)-N-heterocycles,^{4,5} diaryldithiophosphinic acids^{6,7} and dipicolinamide derivatives.8

The aim of this work was a synthesis of the new class of ligands that combine the features of the above successful structural examples, namely the nitrogen heterocycle and the tertiary phosphine sulfides (Scheme 1), and investigation of their extraction properties. In the ligand design, we initially used the HSAB principle applied to the known difference between the ionic radii for the Am^{III} and Eu^{III} model pair, though this difference is small and is not actually valid for all the *f*-elements.⁹ We expected that the soft sulfur atoms could improve the organic ligand selectivity in favor to softer actinides compared with harder lanthanides.

In general, phosphine sulfides can be obtained from the corresponding phosphines or phosphine oxides as well as by the reaction of Grignard reagents or organolithium compounds with PSCl₃,¹⁰ from these known approaches we choose the sulfurization of tertiary phosphine oxides. The starting phosphine oxides were synthesized by the palladium-catalyzed cross-coupling of hetaryl chlorides and secondary phosphine oxides, which was developed in our laboratory.¹¹ From the known sulfurizing



reagents, namely P₄S₁₀,¹² Lawesson's reagent (LR),¹³ B₂S₃¹⁴ and sulfur,15 LR was tested at first due to its high reactivity and solubility in hot organic solvents to attain homogeneous reaction conditions. Unfortunately, the use of 1.2 or 2.4 equiv. LR in refluxing toluene or chlorobenzene led to poor yield of products 2a or 2e, along with the corresponding monosulfides and mainly the unchanged starting material, as evidenced by ³¹P NMR. An excess of LR and prolonged reaction time had no effect on the outcome, the plausible reason could be the decomposition of the reagent under the reaction conditions. Next, the use of two equivalents of P₂S₅ in chlorobenzene at 120 °C overnight allowed us to obtain the target disulfides in good yields. The conversion of the starting material was ~100% (³¹P NMR), so no attempts of optimization were made. Thus, the sulfurization of tertiary phosphine oxides provided us with new symmetrical and unsymmetrical phosphine sulfides 2a-i based on pyridine and 2,2'-bi-



Scheme 1 Reagents and conditions: i, P₄S₁₀, PhCl, 120 °C.

pyridine core with various substituents at phosphorus atom such as primary, secondary and tertiary alkyl as well as phenyl and alkylphenyl groups (Scheme 1).

The yields of compounds **2a–i** were not affected by the structure of substituents at phosphorus atom, thus phosphine sulfides with cyclohexyl and *tert*-butyl groups as well as less sterically hindered aryl-substituted analogues were successfully synthesized. Note that only one instance of bipyridine-based structure, namely compound **2a**, was synthesized due to its poor extraction efficiency (see further).

Single crystal of ligand 2a, obtained by slow evaporation of its acetonitrile solution at room temperature, was investigated by X-ray diffraction (Figure 1).[†] According to the data obtained, two pyridine rings of the 2,2'-bipyridine core are in the same plane and adopt anti-conformation, this arrangement was reported for the phosphine oxide counterpart 1a.¹⁶ The lengths of P-Ph bonds in compound 2a (1.811 and 1.815 Å) are similar to those for the reported analogue,¹⁶ while the P-HetAr bond is somewhat longer, namely 1.840 Å. These bond lengths are also consistent with the known data for pyridine-2,6-diylbis(diphenylphosphine sulfide) **2b**¹⁷ (1.806, 1.810 and 1.823 Å, respectively). The P–S bonds in ligand 2a have a length of 1.942 Å, which is very close to the published value (1.943 Å) for analogue 2b, and are distorted by 16.91° from the plane of the bipyridine core, whereas for disulfide 2b the distortion is unsymmetrical and reveals larger values of 21.26° and 27.99°. The C-P-C angles are in the range of 103.80°–107.21° for compound **2a**, while those for disulfide 2b are 101.31°-105.52°. The P-C-N angles for ligand 2a are wider than those for analogue 2b, namely 117.10° both vs. 113.12° and 114.30°, respectively.

All the synthesized ligands were tested for the separation of Am and Eu pair by liquid–liquid extraction. Note that despite the nature of nitric acid as strong oxidant, no decomposition of the ligands was observed under the extraction conditions, as confirmed by NMR spectroscopy. The resulting distribution coefficients *D* and separation factors SF are given in Table 1.

Phosphine sulfides **2a,b**, containing only phenyl groups as substituents at the phosphorus atom, demonstrated SF values of 1.0 and 1.9 as well as low distribution coefficients. Methyl substituents in phenyl groups of compounds **2c,d** did not affect



Figure 1 An ORTEP diagram for compound 2a. Thermal ellipsoids are given at the 50% probability level. Hydrogen atoms are omitted for clarity.

[†] Crystal data for **2a**. $C_{34}H_{34}N_2P_2S_2$, M = 596.72, monoclinic, space group $P2_1/n$, a = 8.6803(2), b = 12.8014(4) and c = 13.2818(3) Å, $\beta = 95.389(2)^\circ$, V = 1469.35(7) Å³, Z = 2, $d_{calc} = 1.330$ g cm⁻³, $\mu = 2.875$ mm⁻¹, F(000) = 612. Total of 12376 reflections were measured and 2462 independent reflections ($R_{int} = 0.074$) were used in a further refinement, which converged to $wR_2 = 0.0986$ for all independent reflections [$R_1 =$ = 0.0311 was calculated against F for 2299 observed reflections with $I > 2\sigma(I)$]. The data were collected on a STOE diffractometer with a Pilatus 100K detector, focusing mirror collimation with λ (CuK α) = = 1.54086 Å in rotation method mode at 293(2) K. The structure was solved and refined with SHELX program. The non-hydrogen atoms were refined using the anisotropic full matrix least-square procedure.

CCDC 1887405 contains 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.

Table 1 Distribution coefficients *D* and separation factors SF for the simultaneous extraction of Am^{II} and Eu^{II} by ligands **2a–i**.^{*a*}

| Ligand | 3 m HNO ₃ | | | 3 m NH ₄ NO ₃ | | |
|--------|----------------------|-------------------|---------------------|-------------------------------------|-------------------|---------------------|
| | D^{Am} | D^{Eu} | SF ^{Am/Eu} | D^{Am} | D^{Eu} | SF ^{Am/Eu} |
| 2a | 0.003 | 0.003 | 1.0 | 0.023 | 0.029 | 0.8 |
| 2b | 0.017 | 0.009 | 1.9 | 1.2 | 2.1 | 0.6 |
| 2c | 0.421 | 0.221 | 1.9 | 0.364 | 0.545 | 0.7 |
| 2d | 0.431 | 0.246 | 1.8 | 0.241 | 0.405 | 0.6 |
| 2e | 283 | 504 | 0.6 | 88 | 112 | 0.8 |
| 2f | 0.014 | 0.007 | 2.0 | 0.228 | 0.390 | 0.6 |
| 2g | 657 | 385 | 1.7 | 165 | 159 | 1.0 |
| 2h | 375 | 565 | 0.7 | 140 | 204 | 0.7 |
| 2i | 0.004 | 0.004 | 1.0 | 0.585 | 0.856 | 0.7 |

^{*a*} 0.01 M solutions of ligands **2a–i** in *m*-nitrobenzotrifluoride. An aqueous phase initially contained trace amounts of 241 Am and 152 Eu.

the selectivity of the separation, however, about two orders of magnitude increase in the distribution coefficients was achieved. With *n*-octyl groups as substituents in ligands 2e, 2g and 2h, the solubility of extractants improved greatly, resulting in four orders of magnitude increase in the distribution coefficients, namely up to 657. Unexpectedly, two of the three ligands with n-octyl groups demonstrated preferential extraction of europium over americium, *i.e.*, inverse selectivity in relation to the desired preferential binding of actinide, despite the similarity in the ligand structure. We also evaluated compounds with secondary and tertiary alkyl groups, namely 2f and 2i. The introduction of sterically hindered cyclohexyl and tert-butyl substituents resulted in low distribution coefficients, similarly to ligand 2b; moreover, the extraction selectivity completely disappeared for compound 2i. An additional investigation was carried out in NH₄NO₃ solution as less acidic medium compared with HNO3. This replacement resulted in an inverse selectivity for all the ligands, while n-octylcontaining ones had again the largest distribution coefficients. The range of SF values for all compounds was smaller than that for nitric acid solution, all D values were somewhat lower as well. The reason for the inverse selectivity is not evident, because the consideration of published data is complicated by the difference in experimental conditions. To the best of our knowledge, there are no examples of such behavior for ligands with similar structure.

Next, we investigated the extraction of rare earth elements by ligands **2b** and **2d** from 3 M NH_4NO_3 , as well as additionally from 3 M HNO₃ for ligand **2d** (Figure 2). Higher *D* values for heavier lanthanides have been observed, though according to the



Figure 2 Distribution coefficients for extraction of different rare earth elements by ligands **2b** and **2d**. *m*-Nitrobenzotrifluoride is an organic phase, 3 M HNO₃ or 3 M NH₄NO₃ solution is an aqueous phase.

HSAB principle the late lanthanides are harder than the early ones.

In summary, nine polydentate nitrogen heterocycle-based sulfurcontaining ligands have been obtained from the corresponding phosphine oxides using phosphorus pentasulfide in 72–90% yields. The ligand with bipyridine core has been investigated in the solid state by X-ray crystallography. All the compounds were tested in liquid–liquid extraction of *f*-element ions from an aqueous medium, selective binding of Am in the presence of Eu has been found for several ligands in nitric acid solution, the opposite selectivity occurred in less acidic ammonium nitrate solution. Distribution coefficients D and separation factors SF have been determined. D values for selected ligands have been determined for the lanthanides row, and in general, the late metal ions bind the ligands stronger than the early ones.

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Online Supplementary Materials

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References

- 1 B. F. Myasoedov and S. N. Kalmykov, *Mendeleev Commun.*, 2015, 25, 319.
- 2 A. Leoncini, J. Huskensa and W. Verboom, *Chem. Soc. Rev.*, 2017, **46**, 7229.
- 3 S. A. Ansari, P. Pathak, P. K. Mohapatra and V. K. Manchanda, *Chem. Rev.*, 2012, **112**, 1751.

- 4 M. J. Hudson, F. W. Lewis and L. M. Harwood, in *Strategies and Tactics in Organic Synthesis*, ed. M. Harmata, Elsevier, Amsterdam, 2013, vol. 9, pp. 177–202.
- 5 F. W. Lewis, L. M. Harwood, M. J. Hudson, M. G. B. Drew, J. F. Desreux, G. Vidick, N. Bouslimani, G. Modolo, A. Wilden, M. Sypula, T.-H. Vu and J.-P. Simonin, J. Am. Chem. Soc., 2011, 133, 13093.
- 6 S. R. Daly, J. M. Keith, E. R. Batista, K. S. Boland, D. L. Clark, S. A. Kozimor and R. L. Martin, J. Am. Chem. Soc., 2012, 134, 14408.
- 7 G. Modolo, P. Kluxen and A. Geist, Radiochim. Acta, 2010, 98, 193.
- 8 I. Lehman-Andino, J. Su, K. E. Papathanasiou, T. M. Eaton, J. Jian, D. Dan, T. E. Albrecht-Schmitt, C. J. Dares, E. R. Batista, P. Yang, J. K. Gibson and K. Kavallieratos, *Chem. Commun.*, 2019, 55, 2441.
- 9 CRC Handbook of Chemistry and Physics, ed. W. M. Haynes, 97th edn., CRC Press, Boca Raton, FL, 2016–2017, Sect. 12, p. 12.
- 10 A. K. Bhattacharya and N. K. Roy, in *The Chemistry of Organophosphorus Compounds: Phosphine Oxides, Sulphides, Selenides and Tellurides*, eds. F. R. Hartley and S. Patai, Wiley, Chichester, 1992, vol. 2, pp. 195–285.
- 11 G. G. Zakirova, D. Yu. Mladentsev and N. E. Borisova, *Tetrahedron Lett.*, 2017, 58, 3415.
- 12 F. Nief, C. Charrier, F. Mathey and M. Simalty, *Tetrahedron Lett.*, 1980, 21, 1441.
- 13 Y. Lin, D. Bernardi, E. Dori and F. Taran, Synlett, 2009, 1466.
- 14 B. E. Maryanoff, R. Tang and K. Mislow, J. Chem. Soc., Chem. Commun., 1973, 273.
- 15 N. P. Nesterova, T. Ya. Medved, Yu. M. Polikarpov and M. I. Kabachnik, Bull. Acad. Sci. USSR, Div. Chem. Sci., 1974, 23, 2210 (Izv. Akad. Nauk SSSR, Ser. Khim., 1974, 2295).
- 16 N. E. Borisova, A. V. Kharcheva, S. V. Patsaeva, L. A. Korotkov, S. Bakaev, M. D. Reshetova, K. A. Lyssenko, E. V. Belova and B. F. Myasoedov, *Dalton Trans.*, 2017, 46, 2238.
- 17 R. Sevcik, M. Necas and J. Novosad, Polyhedron, 2003, 22, 1585.

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