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Separation and complexation of palladium (II) with a new soft

N-donor ligand 6,6'-bis(5,6-dinonyl-1,2,4-triazin-3-yl)-2,2'

-bipyridine (C9-BTBP) in nitric acid medium

Anyun Zhang*, Lei Xu, Gaoming Lei

College of Chemical and Biological Engineering, Zhejiang University, No.38 Zheda Road, Hangzhou 310027, P. R. China

Abstract

Soft N-donor bis-triazine ligands developed for separation of minor actinides (MAs) from lanthanides have been intensively studied for recent two decades. However, the investigation on recovery and complexation of fission products Pd(II) with these ligands has rarely been reported to date. Herein, the synthesis, solvent extraction of Pd(II) and some typical metals from HNO₃ solutions as well as Pd(II) complexation by a new soft N-donor ligand C9-BTBP were presented. The C9-BTBP ligand exhibited high extraction capability and high selectivity for Pd(II) in HNO₃ solution._Both the 1:1 and 2:1 Pd(II) with C9-BTBP complexes were found in solution by a combination of ESI-MS and ¹H NMR titration experiments. The solid binuclear Pd(II) complex [Pd₂(NO₃)₄·(C9-BTBP)]·2.5H₂O was synthesized and characterized by elemental analysis, DSC-TGA and ¹H NMR. This is the first example that a binuclear Pd(II) complex with any N-donor bis-triazine ligands has been confirmed both in solution and in solid state.

Introduction

Nuclear power has been revived in recent years for its high energy density and low carbon dioxide emissions. However, how to make the best use of irradiated spent nuclear fuel and at the same times reduce its long-term radiotoxicity to the environment has been one of the most important issues nowadays. The well-known reprocessing process called PUREX (Plutonium Uranium Reduction Extraction) is developed to separate and recover the uranium, plutonium and neptunium from spent nuclear fuel.¹ The PUREX raffinate, so called the HLW (High Lever Waste) contains fission or non-fission products, such as the long-lived minor actinides Cm(III) and Am(III), rare earths, platinum group metals (PGMs), Fe(III), Zr(IV), Mo(VI), Tc(VII) and heat-emission elements Sr(II) and Cs(I). The removal of these radioactive nuclides, effective treatment and safe disposal of HLW has been one of the most challenging

works worldwide. The partitioning and transmutation strategy² was proposed to solve w Article Online DOI: 10.1039/C5NJ030823 these problems.

As is known, the key step of partitioning and transmutation (P&T) strategy is to separate the minor actinides (MAs) from lanthanides. This is because lanthanides have higher neutron capture cross sections compared with actinides which would significantly reduce the efficiency of the transmutation for actinides. After separation from lanthanides, MAs can be transmuted to short-lived or stable nuclides by neutron fission.³ However, this separation is very difficult given the very similar chemical properties between the trivalent Am(III) and Cm(III) and trivalent lanthanides. Recently, intensively research focused on the effective separation of the minor actinides (MAs) from lanthanides.⁴ Fortunately, it has been reported that the R-BTP, R-BTBP as well as R-BTPhen type ligands (Fig. 1) exhibit high extraction selectivity toward MAs over lanthanides in highly acidic media.⁵



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Fig. 1 N-donor ligands for minor actinides and palladium (II) separation

Unfortunately, when using these soft N-donor bis-triazine ligands to separate MAs from lanthanides by solvent extraction some other undesired metals are also co-extracted.⁶ For example, the ligand CyMe₄-BTBP has been developed for directly selective extracting radioactive minor actinides from PUREX raffinate in 1-cycle SANEX (Selective Actinide Extraction) process.⁷ However, not only Cm(III) and Am(III) but also some other fission or corrosion products such as Cu, Ni, Zr, Mo, Pd, Ag, and Cd are co-extracted by CyMe₄-BTBP. Of which, palladium is reported as one of the most abundant transition fission products in HLW. Especially the long-lived ¹⁰⁷Pd(II) has a half-life of about 6.5×10⁶ years and its abundance in spent fuel is about 0.17 ka/ton. If Pd(II) could also be removed from HLW by BTBP type ligands, it will be very helpful for developing a separation process based on BTBP type ligands that can be used to simultaneously partition the long-lived minor actinides as well as long-lived ¹⁰⁷Pd from HLW. Furthermore, the effective elimination of Pd can also make the vitrification as a long-term disposal of HLW easier.⁸ In our previous work, the R-BTP ligand had been designed and developed for the separation of the Pd(II) from HNO₃ solution.9 The two very successful examples are Non-BTP (2,6-Bis(5,6-dinonyl-1,2,4-

triazi-ne-3-yl)-pyridine) and BD-BTP (2,6-bis(5,6-dibutyl--1,2,-triazine-3-yl)pyridine)^{ww Article Online} which exhibit high separation factor of Pd(II) from other typical metals in HNO₃ solution. However, the investigation on recovery and complexation of fission products Pd(II) with BTBP type ligands has not been reported to date.

In order to investigate the separation and complexation behavior of palladium with RBTBP type ligands, a new ligand 6,6'-bis(5,6-dinonyl-1,2,4- triazin-3-yl)-2,2' -bipyridine (C9-BTBP, Fig. 2) was synthesized and characterized. Its extraction properties for Pd(II) over some typical metals in HNO₃ solution was studied. To strip the Pd(II) from loaded organic phases, thiourea was selected as the strippant and the stripping conditions were optimized. Importantly, the formation of complexes between Pd(II) and C9-BTBP both in solution and solid state were investigated.



Fig. 2 Synthesis route of C9-BTBP.

Results and discussion

Effect of contact time on extraction

The extraction capability and selectivity of an extractant towards target metals strongly relies on the strength of the chemical complexation ability between them. Based on the Pearson's HSAB (hard / soft acids and bases) principle¹⁰, the ligand C9-BTBP containing eight soft nitrogen atoms can be considered as a soft base. In contrast, the Pd(II) with the unoccupied *p* orbit, can therefore be considered as a typical soft Lewis acid. The HSAB principle tells us that the hard acids tend to form strong chemical bonds with hard bases and the soft acids tend to form strong bonds with soft bases.¹¹ Therefore, it is predicted that the stable complex can be formed between Pd(II) and the ligand C9-BTBP and it will have a strong extraction ability toward Pd(II).

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To investigate the extraction properties of C9-BTBP, the effect of contact time on the evaluation of Pd(II) and the other typical elements Na(I), K(I), Rb(I), Cs(I), Sr(II),Ba(II), Ru(III), and Fe(III) from 2.0 M HNO₃ solution by C9-BTBP in chloroform was studied. As shown in Fig. 3, C9-BTBP exhibited excellent extraction ability and high selectivity for Pd(II) over other tested metals. The *D* value of Pd(II) was larger than 45 even after 30 minutes of contact and higher than 1000 after the extraction equilibrium was reached. These results indirectly confirmed the above prediction that the soft base C9-BTBP would have a strong coordination ability with Pd(II).



Fig. 3 Distribution ratio as a function of contact time (Aqueous phase, Na(I), K(I), Rb(I), Cs(I), Sr(II),Ba(II), Ru(III), Fe(III) and Pd(II) (5.0×10^{-4} M each) in 2.0 M HNO₃. Organic phase, 1.0×10^{-3} M C9-BTBP dissolved in chloroform. T=298K, A/O=1.0).

Conversely, the ligand showed weak or no extraction efficiency for other tested elements such as Na(I), K(I), Rb(I), Cs(I), Sr(II), Ba(II), Ru(III) and Fe(III). Based on the HSAB principle, the metals such as Na(I), K(I), Fe(III) and Sr(II) are the hard acids which can only form the stable complexes with the hard bases. So they exhibited weak or no affinity with the soft base C9-BTBP. On the other hand, Ru(III), Ba(II), Rb(I), and Cs(I) are regarded as the borderline or the transition acids, so they are unmatched with the soft base C9-BTBP. Thus the *D* values of them were very smaller than that of Pd. Consequently, the presence of these metals in HLW solution will have no adverse impact on the removal of Pd(II) by C9-BTBP.

On the other hand, with contact time increasing, the extraction of Pd increased within the initial 80 minutes and then kept constant indicating that the extraction equilibrium was reached. Similar with CyMe₄-BTBP type ligands, which showed slow extraction rates for Am(III)¹², the ligand C9-BTBP also exhibited slow extraction kinetics for Pd(II). As is reported, one main reason may be responsible for this slow extraction rate. ^{4b} Prior to complexation with Pd(II), a conformation change of ligand C9-BTBP from its thermodynamically stable trans-conformation to its less-favored

cis-conformation was required (see Fig. 4). That is, the configure change of this warticle Online procedure slows the extraction rates for Pd(II) by C9-BTBP. This argument can be proven by the trans-conformation of the free RBTBP type ligands and the cis-conformation of their complexes with some metals that have been determined by X-ray crystallographic analysis in solid state.^{5c}



Fig.4 The conformation change of C9-BTBP.

Effect of HNO₃ concentration on extraction

As is well known, HLW is a highly nitric acid solution, which means that the selected ligands must have good extraction ability for Pd(II) even in 3-4 M HNO₃ solution.¹³ Therefore, the effect of HNO₃ concentration from 0.4 M to 6.0 M on the extraction of Na(I), K(I), Rb(I), Cs(I), Sr(II), Ba(II), Ru(III), Fe(III) and Pd(II) was investigated and the results were shown in Fig. 5.



Fig. 5 Distribution ratio as a function of HNO_3 concentration (Aqueous phase, Na(I), K(I), Rb(I), Cs(I), Sr(II),Ba(II), Ru(III), Fe(III) and Pd(II) (5.0×10⁻⁴ M each) in different HNO_3 concentration. Organic phase, 1.0×10^{-3} M C9-BTBP dissolved in chloroform, contact time: 120 min, T=298K, A/O=1.0.).

The largest *D* value for Pd(II) was observed (D_{Pd} >1100) in optimum 2.0 M HNO₃ solution. Indeed, when the HNO₃ concentration was higher than 3.0 M, the D_{Pd} was still larger than 450 indicating that an effective extraction could still be achieved even in 3.0 M HNO₃ solution if desired. Meanwhile, the amount of other tested metals extracted was very small, resulting in the separation factors between Pd(II) and other

metals larger than 10³. These results demonstrated that C9-BTBP was capable of the ward of the separation for Pd(II) over other tested metals with high selectivity.

Similar to R-BTP type ligands¹⁴, the extraction of Pd(II) by C9-BTBP (see Fig.5) underwent a quickly increase until the maximum was reached at 2.0 M HNO₃ and then a slowly decrease was observed from 2.0 M to 6.0 M HNO₃. This could be explained by competitive reaction of metal cations and HNO₃ for R-BTBP molecules. That is, except for complexation with Pd(II), the ligand C9-BTBP as a base will also be protonated in HNO₃ solution. The following two equations illustrated both the positive (Eq(a)) and negative (Eq(b)) effects on the extraction of Pd(II) by C9-BTBP. In other words, the positive effect was dominant when the concentration of HNO₃ was lower than 2.0 M. However, the decrease of Pd(II) extraction in excess of 2.0 M HNO₃ was probably due to the protonation of the ligand. Further studies are needed to investigate in terms of the co-extraction behavior of HNO₃ by R-BTBP ligands.

(a) $2NO_3^{-} + Pd^{2+} + C9$ -BTBP \leftrightarrow Pd(NO₃)₂·C9-BTBP

(b) $HNO_3 + C9-BTBP \leftrightarrow HNO_3 \cdot C9-BTBP$

Stripping behavior of Pd(II)

To recover the Pd(II) as well as make the ligands reusable in further extraction cycles, the back-extraction of Pd(II) from loaded organic phases was required. Thiourea was used for stripping of Pd in this work because it is widely used as an effective strippant for the back-extraction of Pd(II) from organic phase.^{14, 15} The loaded organic phases were brought into contact with thiourea solution of different concentrations (1.0~10 mM) in 0.1 M HNO₃ solutions and the results were presented in Fig. 6a. A Pd(II) stripping efficiency of more than 99.5% was achieved when the concentration of thiourea was 5 mM in 0.1 M HNO₃ solution. Further increasing the thiourea concentration in 0.1 M HNO₃ solution was determined as 5mM.



Fig.6 (a) Back-extraction of Pd(II) with thiourea of different concentrations in 0.1M HNO_3 ; (b) back-extraction of Pd(II) with 0.005 M thiourea in HNO_3 of different concentrations; contact time: 120 min, T=298K, A/O=1.0.

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Then the stripping behavior of Pd(II) by thiourea as a function of HNO concentration was investigated. As shown in Fig. 6b, the HNO₃ concentration had an significant effect on the recovery of Pd(II) by thiourea and the optimized HNO₃ concentration was 0.3 M, under which condition almost 100% Pd(II) was stripped from The extraction of Pd(II) and Na(I), K(I), Rb(I), Cs(I), Sr(II), Ba(II), Ru(III), Fe(III) from 2.0 M HNO₃ by C9-BTBP in chloroform under different temperatures was studied. As presented in Fig. 7, the extraction of Pd(II) decreased gradually with an increase of temperature from 298 K to 318 K, indicating that the extraction of Pd(II) from HNO_3 into CHCl₃ was an exothermic process. That is, increasing the temperature was unfavorable for the Pd(II) extraction, thus the best temperature in Pd(II) separation by C9-BTBP appeared to be at room temperature or at 298K. The extraction of other tested metals by C9-BTBP, however, exhibited small change with temperature



Fig. 7 Distribution ratios as a function of extraction temperature (Aqueous phase, Na(I), K(I), Rb(I), Cs(I), Sr(II), Ba(II), Ru(III), Fe(III) and Pd(II) (5.0×10⁻⁴ M each) in 2.0 M HNO₃. Organic phase, 1.0×10⁻³ M C9-BTBP dissolved in chloroform, contact time: 120 min, T=298K, A/O=1.0).

Extraction mechanism

the loaded organic phase.

Effect of temperature on extraction

increasing from 298 K to 318 K.

ESI-MS (electrospray ionization mass spectrometry) is considered as an effective technique to investigate the composition of the RBTBP complexes in solution¹⁶. The results of the ESI-MS of organic phases after extraction for Pd(II) were shown in Fig.8. L:M ratios stand for the relative molar concentration of the C9-BTBP in organic phases and that in aqueous phases (where L=C9-BTBP, M=Pd). In the case of L:M=0.5, the most abundant peak (m/z=923.6-926.6) corresponding to the 1:1 type Pd(II) complex $[L+Pd^{2+}-H^+]^+$ was found in Fig.8a and Fig.8b,. In addition, another peaker Article Online locating at m/z=986.5 was assigned to the 1:1 type complex of $[L+Pd^{2+}+NO_3]^+$. Similar 1:1 Pd(II)-BTBP complexes have also been reported in CyMe₄-BTBP type ligand.¹⁶ What's more, this type of complexes were also observed in cases of L:M= 1:1 and 1:2. As shown in Fig. 8c and 8d, the peak of m/z=1049.5 was ascribed to the formation of complexes of $[L+Pd^{2+}+2NO_3^-+H^+]^+$. It is worth mentioning that a peak at m/z=1270.9 were assigned to the 2:1 type Pd(II) complexes $[L+2Pd^{2+}+3NO_3^-+3H_2O]^+$, indicating that the binuclear complexes of Pd(II) with BTBP type molecules were formed in solution. Further investigations about this 2:1 Pd-BTBP complex were shown on the following solid state Pd complex study section.

In addition, the peaks locating at m/z=1660.7 corresponded to the complexes of $[2L+Na^+]^+$, indicating that some free C9-BTBP molecules were present as dimers in solution. Usually, the decomposition and rearrangement of the ligand molecular during the ionization were very common in the ESI-MS tests. A peak locating at m/z=1468.6 was assigned to the complex $[2L-C_{10}N_2H_{19}]^+$ and a possible fragmentation of C9-BTBP in complex $[2L-C_{10}N_2H_{19}]^+$ was shown in Fig 9.

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Fig. 8 Positive ESI-MS of loaded organic phases after extraction, contact time: 120 min, T=298K, A/O=1.0; Organic phase 1.0 mM C9-BTBP in chloroform; aqueous phase: 2.0 M HNO₃ containing Pd with different concentrations (a) 2.0 mM Pd, L/M= 0.5, (b) the enlargement of a in the range of m/z=800~1000, (c) 1.0 mM Pd, L/M= 1.0, (d) 0.5 mM Pd, L/M= 2.0; L/M = C9-BTBP equivalents.



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¹H NMR titrations of C9-BTBP with Pd(II) nitrate were carried out to elucidate the coordination chemistry of Pd(II) with BTBP type ligands in solution. A mixture of CDCl₃/CD₃CN (3/7, v/v) was used for ¹H NMR titration due to the poor solubility of Pd(NO₃)₂ in CDCl₃. The results of the ¹H NMR titrations were shown in Fig. 10 and Fig. 11 respectively and the selected protons and nitrogen atoms for illustrating the ¹H NMR titration spectra were presented in Fig. 12.



Fig. 10 ¹H NMR titration spectra (0-9.0 ppm) of 10.0 mM C9-BTBP with various equivalents of $Pd(NO_3)_2$ in $CDCI_3-CD_3CN$ (3/7, v/v), M/L=Pd equivalents.

The rate exchange of ligand C9-BTBP was not slow enough¹⁸ on the NMR time-scale to allow the observation of different ¹H NMR peaks for free C9-BTBP and the complex. Also the rate exchange of ligand was not high enough¹⁹ on the NMR time-scale that more than three broadening peaks were found for protons H1, H2 and H3 (Fig. 11, M/L = 0.4). That is, the moderate rate of ligand exchange led to the large broadening peaks in the ¹H NMR spectra (Fig. 11, 0 < M/L<1.0).

Further, in the ¹H NMR spectrum of free C9-BTBP, the H4 and H5 exhibited two independent triplets due to the different chemical environments of them. However, with an increase of Pd(II) amounts, these two triplets shifted downfield and overlapped. This change indicated that the two Pd-N bonds were most likely formed between two nitrogen atoms N2/N2` and Pd(II), which resulted in the much more similar chemical

environments of H4 and H5 in Pd complex than that in free ligand. Meanwhile, with evaluation of Pd(II) contents increasing, the chemical shifts of protons (H1, H2 and H3) of pyridine rings also significantly changed and the two peaks of H1 and H3 exhibited upfield. Conversely, the resonance peak related to proton H2 showed a big chemical downfield shift of 0.39 ppm upon addition of 1.0 equivalents of Pd(II). These changes provided evidence for the formation of two Pd-N bonds between two nitrogen atoms N4/N4` and Pd(II). Based on the above analysis, the four nitrogen atoms N2, N2`, N4 and N4` (see Fig.12) in C9-BTBP were confirmed to bound with Pd and a typical square-planar geometry Pd(II) complex was formed.



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Fig. 11 The enlargement of partial ¹H NMR titration spectra (2.8-9.0 ppm) of 10.0 mM C9-BTBP with various equivalents of Pd(II) in CDCl₃/CD₃CN (3/7, v/v).



Fig. 12 Structure of C9-BTBP molecular and the selected protons and nitrogen atoms.

Furthermore, the results of ¹H NMR titrations spectra indicated that the C9-BTBP initially formed only the 1:1 Pd-C9-BTBP complexes in solution, since transformation to a new single complex was complete after addition of 1.0 equivalents of Pd(II). The only 1:1 Pd-C9-BTBP complexes found in ESI-MS (M/L=0.5, 1.0) study demonstrated this argument. Subsequent formation of small amounts of 2:1 Pd-C9-BTBP complexes was proposed since the appearance of three new class peaks upon

addition of excess amount of Pd in solution (labeled red lines, Fig. 11). The existence of this type complex was supported by the peak of $[L+2Pd^{2+}+3NO_3^-+3H_2O]^+$ observed in ESI-MS study (Fig. 8c) and the formation of 2:1 solid complex $[Pd_2(NO_3)_4 \cdot (L)] \cdot 2.5H_2O$ which was characterized by elemental analysis and ¹H NMR in the following parts. Based on the typical square-planar geometries of Pd(II) complexes, four NO₃ were presumed to bound with Pd(II) in 2:1 Pd-C9-BTBP complex. Consequently, two structures of 1:1 and 2:1 Pd-C9-BTBP complexes were proposed and shown in Fig. 13, respectively.



Fig. 13 Possible structures of the 1:1 and 2:1 Pd(II)-C9-BTBP complexes, \prec stands for NO⁻₃.

It should be noted that the ESI-MS (Fig. 8d) tests were performed under the identical conditions with the liquid / liquid solvent extraction experiments, where L:M=2:1 (M:L=0.5). In this case, only 1:1 type Pd-C9-BTBP complexes were found both in ESI-MS and ¹H NMR titration studies. Therefore, the extraction mechanism of Pd(II) by C9-BTBP/CHCl₃ is illustrated in Fig. 14.



Fig. 14 The extraction mechanism of Pd(II) from HNO_3 solution by C9-BTBP in chloroform.

Solid Pd(II) complex study.

In order to elucidate the composition of the complexes in solid state, the solid Pd(II) with C9-BTBP complex was synthesized and characterized by elemental analysis,

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DSC-TGA, ¹H NMR. However, attempts to obtain the crystals of complex suitable for (C5NJ03082J) X-ray diffraction failed. Found: C, 47.63; H, 6.18; N, 12.19; requires C, 47.36; H, 6.57; N, 12.69. Formula of the complex: $[Pd_2(NO_3)_4 \cdot (L)] \cdot 2.5H_2O$, L stands for C9-BTBP. This results demonstrated that the complex was a binuclear structure in solid state.



Fig. 15 (a) TGA-DSC curves of 2:1 Pd-C9-BTBP complex under nitrogen atmosphere with a heating rate of 10 °C/ min; (b) the possible decomposition fragments and processes of the 2:1 bis-complex of Pd in nitrogen atmosphere.

The thermal decomposition processes of the complex were investigated by TGA analysis under nitrogen atmosphere. As shown in Fig.15a, the first stage occurred from 0 to 100°C with the mass loss of 3.7%, corresponding to the loss of water (calc. 3.5%). Subsequent mass loss of 23.8% occurred at 100–280°C, which was assigned to the loss of two $C_{10}N_2H_{19}$ (calc. 25.0%) fragments from the complex molecular. The same loss of $C_{10}N_2H_{19}$ moiety from the C9-BTBP molecular was also observed in ESI-MS study (Fig. 8). The last stage occurred from 280 to 700°C with the mass loss of 23.3% which was in agreement with the loss of two $C_{10}NH_{19}$ (calc. 23.3%). The final residues were palladium salts and carbides. Based on the above analysis, the thermal decomposition processes of $[Pd_2(NO_3)_4 \cdot (L)] \cdot 2.5H_2O$ were occurred in three steps which could be elucidated with the scheme as presented in Fig.15b.

In addition, the solid Pd-C9-BTBP complex was characterized by ¹H NMR in CDCl₃ solution (ESI, Fig. S4). A comparison of ¹H NMR spectra of ligand C9-BTBP, solid 2:1 Pd complex and C9-BTBP titration with 2.0 equivalents of Pd(II) in CDCl₃/CD₃CN (3/7, *v/v*) solution was shown in Fig.16. The relative strength of two class peaks corresponding to H2 and H3 (labeled red font) in spectrum of the solid Pd complex was much stronger than that of C9-BTBP (see Fig.16b and a). According to the above ¹H NMR titration analysis, these two sets of peaks were assigned to the protons in binuclear Pd(II) complexes. In addition, the overlapped peaks of H1 and H3 (black font) corresponding to 1:1 Pd-C9-BTBP complex were observed, which suggested that part of 2:1 type complex was transformed to 1:1 type in solution.



Fig. 16 (a) partial ¹H NMR spectra of 10.0 mM C9-BTBP with 2.0 equivalents of Pd(II) in CDCl₃/CD₃CN (3/7, v/v); (b) partial ¹H NMR spectrum (400 MHz, CDCl₃, 298K) of solid Pd(II) complex in $CDCI_3$ and (c) ligand C9-BTBP in $CDCI_3$.

The solid Pd(II) complex and ¹H NMR titration studies demonstrated the presence binuclear complex of Pd with C9-BTBP both in solid state and in solution. The specific structure of this type of complex deserves to be further determined in our laboratory.

Conclusions

The recovery and complexation of Pd(II) from some typical metals in highly nitric acid medium was achieved by a new ligand C9-BTBP. The C9-BTBP/CHCl₃ system exhibited high extraction capability and high selectivity for Pd(II) over other tested metals in HNO₃ solution whereas the extraction kinetics was relatively slow. Both the 1:1 and 2:1 Pd to C9-BTBP complexes were found in solution, while the Pd with C9-BTBP complex in solid state was 2:1 type. The thermal decomposition processes of the complex were proposed based on the results of TGA-DSC.

This is the first report on the binuclear Pd(II) complexes formed with BTBP type molecules. More comprehensive studies of structures of Pd(II) complexes with these multi-dentate N-donor ligands needs to be further investigated. To elucidate the coordination mechanism between these soft N-donor ligands and some fission products co-existent with MAs in HLW is very important for the partitioning of minor actinides. The outcome of this work is very valuable for understanding the mechanism of complexation of Pd(II) with RBTBP type ligands.

Experimental

General methods

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The ruthenium nitrosyl nitrate solution with 1.5% (w/v) of Ru(III) was from Alfa-Aeset^{View Article Online} Palladium(II) nitrate solution with 5.0% (w/w) of Pd(II) was from Shanxi Kaida Chemical Engineering Co.,Ltd. China. The Fe(NO₃)₃·9H₂0, $M^{II}(NO_3)_2$ (M^{II} =Ba and Sr) and alkali metals nitrates M^I(NO₃) (M^I=Na, K, Rb and Cs) tested were of analytical grade. All the nitric acid solutions used were made by diluting concentrated HNO₃ with deionized water. The concentrations of all the tested elements were about 0.5 mM. All the other reagents were of analytical grade and used without further purification except for anhydrous ether which was dried with P2O5 and zeolite. NMR spectra were performed with a Bruker Avance DMX 400 spectrophotometer or a Bruker Avance 500 spectrophotometer. FT-IR spectra were taken on a Bruker Vector 22 FT-IR spectrometer. The electrospray ionization mass spectra (ESI-MS) were collected on a Varian 500-ES Model instruments or a Bruker Esquire 3000 Plus spectrometer. Elemental analyses were performed with Thermo Finnigan Italia S.P.A EA 1112 CHNS elemental analyzer. The DSC-TGA curves were recorded on TA SDTQ600 thermal analyzer. The concentrations of all the tested elements in the aqueous phases were determined by the Atomic Absorption Spectrometer (AA 240).

Synthesis of 6,6'-bis(5,6-dinonyl-1,2,4-triazin-3-yl)-2,2'-bipyridine (C9-BTBP)

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To obtain the C9-BTBP two intermediates were synthesized in advance as shown in Figure 2. One was icosane-10,11-dione obtained by the reaction of decanoate ethyl with sodium, followed by acidification with H_2SO_4 (55%, *w/w*), and oxidation with copper(II) acetate. Treating the 2,2'-bipyridine with hydrogen peroxide (30%, *w/w*), the 2,2'-bipyridine dioxide²⁰ was obtained. Followed by the reaction of 2,2'- bipyridine dioxide with benzoyl chloride and trimethylsilyl cyanide, 6,6'-dicyano-2,2'- bipyridyl²¹ was synthesized. Then 6,6'-dicyano-2,2'-bipyridyl was reacted with hydrazine hydrate (98%, *w/w*) in ethanol solution and the mixture was stirred at room temperature for 17 days to get the compound 2,2'-Bipyridine-6,6'-dicarboxbisamidrazone.²²

A suspension of 2,2'-Bipyridine-6,6'-dicarboxbisami-drazone (2.60 g, 9.62 mmol) in a mixture of triethylamine (12.5 mL) and THF (450 mL) was added with icosane-10,11-dione (6.60 g, 21.3 mmol). The mixture was stirred and heated under reflux for 3 days. The heavy black oil was obtained after removing the solvent by the rotary evaporation and the mixture was purified by column chromatography (ethyl acetate-petroleum ether, 1:3, v/v). Then, the solid obtained was recrystallized with ethanol and allowed to dry in the vacuum oven to afford the C9-BTBP as a yellow solid (2.7g, 34 %). Mp 79.2°C; IR (neat) cm⁻¹ : 2923, 2853, 1575, 1517, 1462, 1384, 1270, 1079, 784, 634 cm⁻¹; ¹H NMR (400 MHz, CDCl₃): δ 8.99 (d, *J* = 7.8 Hz, 2H; -Ar*H*), 8.59 (d, *J* = 7.6 Hz, 2H; -Ar*H*), 8.08 (t, *J* = 7.8 Hz, 2H; -Ar*H*), 3.08 (t, *J* = 7.8 Hz, 2H; -Ar*H*), 0.88

(m, 12H, -C H_3) ppm; ESI-MS: m/z=841.7 [M + Na]⁺, 817.7 [M - H]⁻; elemental analysis we Article Online DOI:19.1039/C5NJ03082J calcd (%) for C₅₂H₈₂N₈ (M_r = 819.26): C, 76.23; H, 10.09; N, 13.68; found: C, 76.03; H, 10.19; N, 13.67.

Synthesis of the solid Pd(II) complex of C9-BTBP

C9-BTBP (0.12 mmol 100.0 mg) was dissolved in ethanol (10.0 mL). To this solution was added with the concentrated nitric acid (65%, w/w) to obtain the 2.0 M HNO₃ solution. Then palladium (II) nitrate (0.25 mmol 588.8 mg) in HNO₃ solution was added to the solution dropwise over 10 min. After stirring at room temperature for 2 hours, the insoluble orange solid was filtered, washed with ethanol and 2.0 M HNO₃ to obtain the complex as an orange solid (50.0 mg, 31%).

Liquid / liquid solvent extraction experiments

In extraction experiments performed, 1.0×10^{-3} M C9-BTBP in CHCl₃ was used as the organic phases. The aqueous phases were 5.0×10^{-4} M of Na(I), K(I), Rb(I), Cs(I), Sr(II), Ba(II), Ru(III), Fe(III) and Pd(II) in HNO₃ of different concentrations (0.4-6.0 M). Equal aqueous phases (5.0 mL each) were pre-equilibrated with the same volumes of CHCl₃ and the organic phases were pre-equilibrated with nitric acid (5.0 mL each) of the same concentration without adding any tested elements. Then equal amounts of organic phases (5.0 mL each) and aqueous phases were mixed by vigorous shaking (120 rpm) with TAITEC MM-10 model oscillation box in 25 mL glass flask for 120 min at 298 K. In preliminary experiments, it was found that a contacting time of 120 min was enough to reach the extraction equilibrium. After centrifugation, the concentrations of all the tested elements in the aqueous phases were determined by the Atomic Absorption Spectrometer. The distribution ratios (*D*) were calculated as the ratios of the concentrations of the tested metals in the organic to those in the aqueous phases. It should be noted that the solvent extraction experiments were repeated three times for each point we obtained.

Back extraction experiments

To optimize the stripping conditions, a solution of 1.0×10^{-3} M C9-BTBP in HCCl₃ (pre-equilibrated with 2.0 M nitric acid, A/O=1) was loaded with Pd(II) from 2.0 M HNO₃ aqueous phase. Then the loaded organic phases (1.0 mL each) were brought into contact with the equal volume of thiourea of different concentrations in HNO₃ solution.

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Separation and complexation of palladium (II) with a new soft N-donor ligand 6,6'-bis(5,6-dinonyl-1,2,4-triazin-3-yl)-2,2'-bipyridine (C9-BTBP) in nitric acid medium

Anyun Zhang^{*}, Lei Xu, Gaoming Lei

College of Chemical and Biological Engineering, Zhejiang University, No.38 Zheda Road, Hangzhou 310027, P. R. China

Graphical Abstract



Both the 1:1 and 2:1 Pd to C9-BTBP complexes were found in solution by 1 H NMR titration.