



# Quantitative solvent extraction from neutral aqueous nitrate media of silver(I) against lead(II) with a new calix[4]arene-based bipyridine podand

Jean-Bernard Regnouf-de-Vains,<sup>a,\*</sup> Jean-Olivier Dalbavie,<sup>b</sup> Roger Lamartine<sup>b</sup> and B. Fenet<sup>c</sup>

<sup>a</sup>GEVSM, UMR 7565 CNRS-UHP, Faculté de Pharmacie, 5 rue Albert Lebrun, F-54001 Nancy Cedex, France

<sup>b</sup>ROMB, ESA 5078 du CNRS, La Doua, F-69622 Villeurbanne Cedex, France

<sup>c</sup>Centre Commun de RMN, UCBL, La Doua, F-69622 Villeurbanne Cedex, France

Received 15 February 2001

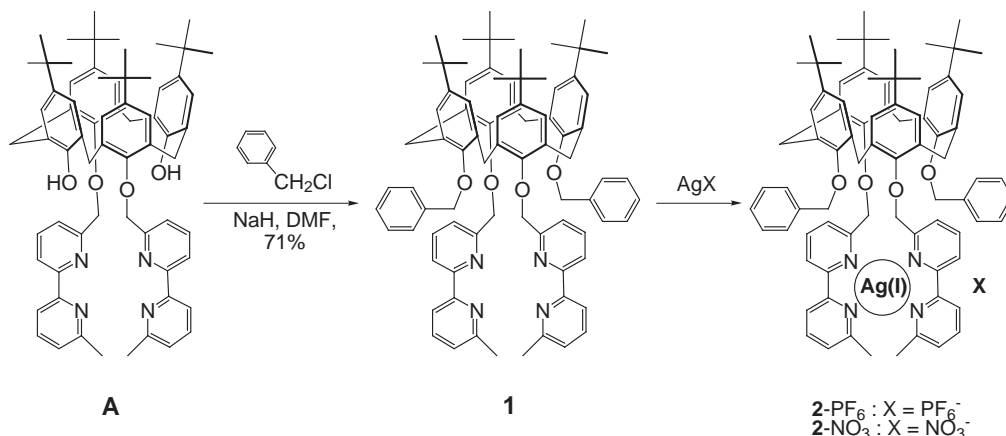
**Abstract**—A new calix[4]arene-based podand incorporating two 2,2'-bipyridine and two benzyl units in alternate positions at the lower rim was shown to quantitatively extract silver(I) from neutral aqueous solutions containing a mixture of lead and silver nitrates. The corresponding  $\text{AgPF}_6$  complex was synthesised and characterised. © 2001 Elsevier Science Ltd. All rights reserved.

The recovery of silver from ores and wastes is of interest only if the process is economically viable.<sup>1</sup> Therefore, it may be interesting to design ligands capable of selective binding and extraction of the  $\text{Ag}^+$  cation. However, a further step is needed, allowing by a decomplexation process, to regenerate the ligand on one hand, and to isolate the metal on the other hand. This may be achieved using chemical, hydrometallurgical or electrolytical processes.

Calixarenes have been widely used as spatial organisers for various chelating units,<sup>2</sup> e.g. ethers, esters, amides

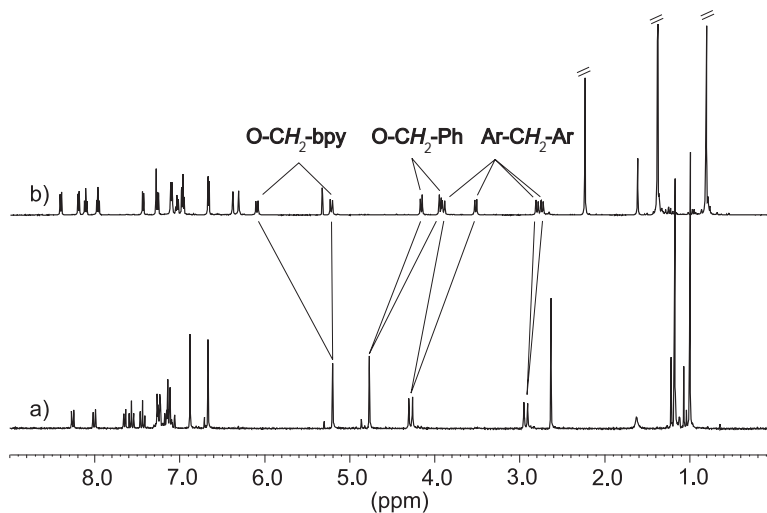
or their thio analogues, ketones, alkenes, ammoniums, amino acids, thiols, phosphine groups or heterocycles. Furthermore, the binding as well as the extraction ability of some of these ligands towards rare<sup>2b</sup> or toxic<sup>3</sup> metals have also been reported.

The liquid extraction of  $\text{Ag}^+$  by some of the above-mentioned calixarene derivatives<sup>4</sup> has been studied in the presence of alkaline ions and, in some rare cases, in the presence of transition metal cations.<sup>4b,4c</sup> However, to the best of our knowledge, the extraction ability of calixarenes bearing bis-heterocycles has not yet been



Scheme 1.

\* Corresponding author. Fax: (33) 3 83 17 90 57; e-mail: jean-bernard.regnouf@pharma.u-nancy.fr



**Figure 1.**  $^1\text{H}$  NMR spectra of **1** (a), **2-PF<sub>6</sub>** (b);  $\text{CDCl}_3$ , 500 MHz, rt.

investigated. Calix[4]arene podands incorporating at the lower rim two opposed 2,2'-bipyridine units give stable and hydrophobic mononuclear  $\text{Cu}^+$  complexes,<sup>5</sup> which, based on an X-ray crystal structure analysis,<sup>5c</sup> display a pro-helicoidal tetrahedral geometry. Since  $\text{Ag}^+$  adopts a pseudo-tetrahedral geometry with 2,2'-bipyridine and analogues,<sup>6</sup> we assumed that this geometry could also be obtained with such podands, allowing thus selective complexation of  $\text{Ag}^+$  with respect to other cations. Owing to the stability and lipophilicity of such complexes, one may expect an interesting extraction ability for these podands. Following these ideas, the ligand **1** described here with its silver complex **2-PF<sub>6</sub>**, was investigated for its extraction properties in the presence of  $\text{Ag}^+$  and  $\text{Pb}^{2+}$  cations.

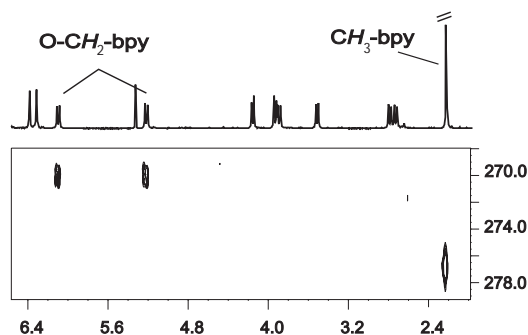
Ligand **1** was prepared in 71% yield by alkylation of the bis-bipyridyl podand **A<sup>5b</sup>** with benzyl chloride in the presence of NaH in dry DMF (Scheme 1). The pure air-stable white-silver complex **2-PF<sub>6</sub>** was obtained in 92% yield after chromatography ( $\text{Al}_2\text{O}_3$ ,  $\text{CH}_2\text{Cl}_2$ ) upon mixing stoichiometric amounts of ligand **1** with  $\text{AgPF}_6$  in  $\text{CH}_2\text{Cl}_2$ . Complex **2-PF<sub>6</sub>** was also prepared by extraction of silver nitrate from water using **1**, followed by anion metathesis with  $\text{KPF}_6$  and chromatography. The ML stoichiometry was confirmed by elemental analysis and by mass spectrometry (ES), which revealed a base peak at 1301.6 amu ( $[\text{I}+\text{Ag}]^+$ ).  $^{13}\text{C}$  NMR showed that **1** and **2-PF<sub>6</sub>** were both in the cone conformation<sup>7</sup> ( $\text{Ar-CH}_2\text{-Ar}$  signals at 31.40 ppm and 31.46, 32.42 ppm, respectively). Upon complexation, the  $^1\text{H}$  NMR spectrum of **1** was strongly modified (Fig. 1). Using COSY NMR experiment, it was observed that the  $\text{OCH}_2\text{-bipyridine}$  and the  $\text{OCH}_2\text{-C}_6\text{H}_5$  signals which respectively appear as singlets at 5.20 and 4.77 ppm for **1**, became two AB systems at 5.20, 6.08 ppm ( $J_{AB}=12.9$  Hz) and 3.92, 4.14 ppm ( $J_{AB}=11.8$  Hz) for **2-PF<sub>6</sub>**. This observation results from the chiral pro-helicoidal arrangement of the two bipyridine units around the metallic centre.

The natural abundance  $^1\text{H}\text{-}^{15}\text{N}$  HMBC experiment<sup>5d</sup> adapted to **2-PF<sub>6</sub>** (Fig. 2) showed two  $^{15}\text{N}$  signals at

276.7 ppm (N correlated to Me) and 269.9 ppm (N correlated to  $\text{O-CH}_2\text{-}$ ), versus internal  $^{15}\text{N}$  Bruker reference. With respect to the free ligand, the strong upfield shifts of ca. 40 and 42 ppm, similar to those obtained with parent copper(I) complexes, indicate that the bipyridines were indeed chelating the silver cation.

Upon reaction of **1** with  $\text{Pb}(\text{NO}_3)_2$ , no isolable complex could be obtained, suggesting the absence of competition between  $\text{Pb}^{2+}$  and  $\text{Ag}^+$  cations during the extraction process. The extraction experiments were carried out in solution;  $\text{AgNO}_3$  and  $\text{Pb}(\text{NO}_3)_2$  were dissolved in various ratios in water, and treated with a solution of **1** in  $\text{CHCl}_3$  or  $\text{CH}_2\text{Cl}_2$ .

For the first series of experiments, the Ag/Pb molar ratio varied from 1 to 1:10000, and the extraction was performed with a default of **1** versus  $\text{Ag}^+$ . The mixture was stirred at rt during 2 h, then the organic phase was separated and evaporated to dryness. The residue was dissolved in  $\text{CH}_2\text{Cl}_2$  and treated with an excess of  $\text{KPF}_6$ . The resulting complex **2-PF<sub>6</sub>** was isolated by chromatography over alumina and checked by  $^1\text{H}$  NMR. The results given in Table 1 show that the extraction of  $\text{Ag}^+$  was quantitative, with an average yield of 95%. The concentration of **1** in  $\text{CHCl}_3$  as well as the concentrations of  $\text{Ag}^+$  and  $\text{Pb}^{2+}$  cations in the aqueous phase did not affect the extraction results.



**Figure 2.** Natural abundance  $^1\text{H}\text{-}^{15}\text{N}$  HMBC spectrum of **1**.

**Table 1.** Extraction operating data—first series of experiments

Ag/Pb	Pb(NO <sub>3</sub> ) <sub>2</sub> mg (mol)	AgNO <sub>3</sub> mg (10 <sup>-5</sup> mol)	H <sub>2</sub> O (ml)	[Pb]; [Ag] (10 <sup>-3</sup> M)	1 mg (10 <sup>-5</sup> mol)	CHCl <sub>3</sub> (ml)	[1] (10 <sup>-3</sup> M)	Ag/1	2-PF <sub>6</sub> (mg) (10 <sup>-5</sup> mol)	Yield (%)
1	28.90 (8.7 × 10 <sup>-5</sup> )	15.00 (8.8)	10	8.7; 8.8	50 (4.2)	25	1.70	2.1	56 (3.9)	93
1/10	28.70 (8.66 × 10 <sup>-5</sup> )	1.80 (1.06)	10	8.7; 1.06	10 (0.84)	10	0.84	1.3	11.2 (0.78)	93
1/100	2790 (8.4 × 10 <sup>-3</sup> )	15.70 (9.24)	50	168; 1.85	100 (8.4)	30	2.80	1.1	115 (8.0)	95
1/1000	27750 (8.35 × 10 <sup>-2</sup> )	14.90 (8.77)	100	835; 0.88	100 (8.4)	20	4.20	1.0	114 (7.9)	94
1/10000	27750 (8.35 × 10 <sup>-2</sup> )	1.80 (1.06)	100	838; 0.10	10 (0.84)	10	0.84	1.3	12 (0.83)	98

A second set of experiments<sup>8</sup> was carried out in order to develop a continuous extraction process. It was performed in a decantation funnel containing an aqueous solution of Pb(NO<sub>3</sub>)<sub>2</sub> at 600 g.l<sup>-1</sup>, at the limit of saturation at rt, charged before extraction with AgNO<sub>3</sub>. The initial Ag<sup>+</sup>/Pb<sup>2+</sup> molar ratio of ca. 1:30000 was maintained at each addition of AgNO<sub>3</sub>, assuming that the extraction was complete. The organic phase (CH<sub>2</sub>Cl<sub>2</sub>) was charged with 15 equivalents of **1** versus silver, in order to perform 15 successive extractions; thus, the ligand was in excess during all experiments, except for the last one. The mixture was shaken for 30 seconds, then allowed to equilibrate for 15 minutes. TLC monitoring (Al<sub>2</sub>O<sub>3</sub>, CH<sub>2</sub>Cl<sub>2</sub>) showed a regular loss of **1** to the benefit of the AgNO<sub>3</sub> complex. All the ligand was complexed with the last aliquot of metal. The aqueous phase was washed with CH<sub>2</sub>Cl<sub>2</sub>, and the combined organic phases were concentrated, treated with KPF<sub>6</sub> then purified by chromatography to give 2-PF<sub>6</sub> in ca. 90% yield. The ligand was quantitatively recycled in CH<sub>2</sub>Cl<sub>2</sub> by treatment with NH<sub>4</sub>OH.

## Conclusion

The binding ability of the new podand **1**<sup>9</sup> towards Ag<sup>+</sup> was studied, affording the stable mononuclear complex 2-PF<sub>6</sub>.<sup>10</sup> We suggested that the tetrahedral mode of binding could be a driving force in the selective extraction of Ag<sup>+</sup> in the presence of Pb<sup>2+</sup>. The experimental results showed that the extraction was selective, quantitative and rapid, authorising a continuous process; this last point, the improvement of silver and ligand recovering processes, as well as competitive extractions of Ag<sup>+</sup> in the presence of other metal cations are currently under investigation.

## Acknowledgements

We are grateful to the MRES for financial support, especially J.-O.D. for a Ph.D. fellowship; to SAFAS (Monaco) and Bruker S.A. for UV spectroscopy and WinNMR facilities, respectively.

## References

- Guerlet, J.-P.; Pianelli, F., *Traité de Métallurgie*, M 2388, Techniques de l'Ingénieur Ed., Paris, 1992.
- (a) Wieser, C.; Dieleman, D. B.; Matt, D. *Coord. Chem. Rev.* **1997**, *165*, 93; (b) Yordanov, A. T.; Roundhill, D. M. *Coord. Chem. Rev.* **1998**, *170*, 93–124.
- Rao, P.; Enger, O.; Graf, E.; Hosseini, M. W.; De Cian, A.; Fischer, J. *Eur. J. Inorg. Chem.* **2000**, *7*, 1503–1508.
- For example: (a) Roundhill, D. M. In *Prog. Inorg. Chem.*; K. D. Karlin, Ed.; John Wiley and Sons, 1995; *43*, 533–592; (b) Yordanov, A. T.; Falana, O. M.; Koch, A. F.; Roundhill, D. M. *Inorg. Chem.* **1997**, *36*, 6468–6471; (c) Yordanov, A. T.; Whittlesey, B. R.; Roundhill, D. M. *Inorg. Chem.* **1998**, *37*, 3526–3531.
- For example: (a) Beer, P. D.; Martin, J. P.; Drew, M. G. B. *Tetrahedron*, **1992**, *48*, 9917–9928; (b) Regnouf-de-Vains, J.-B.; Lamartine, R. *Helv. Chim. Acta* **1994**, *77*, 1817–1825; (c) Regnouf-de-Vains, J.-B.; Lamartine, R.; Fenet, B.; Bavoux, C.; Thozet, A.; Perrin, M. *Helv. Chim. Acta* **1995**, *78*, 1607–1619; (d) Pellet-Rostaing, S.; Regnouf-de-Vains, J.-B.; Lamartine, R.; Fenet, B. *Inorg. Chem. Commun.* **1999**, *2*, 4–7.
- Ward, M. D.; Couchman, S. M.; Jeffrey, J. C. *Acta Crystallogr., Sect. C* **1998**, *54*, 1820–1823.
- Jaime, C.; de Mendoza, J.; Prados, P.; Nieto, P. M.; Sanchez, C. *J. Org. Chem.* **1991**, *56*, 3372–3376.
- Aqueous phase: 100 ml H<sub>2</sub>O; Pb(NO<sub>3</sub>)<sub>2</sub>: 60 g (1.8 mol l<sup>-1</sup>); AgNO<sub>3</sub>: 1.0 mg (5.9 × 10<sup>-5</sup> mol l<sup>-1</sup>); [Ag]/[Pb]: 1/30500; organic phase: 20 ml of CH<sub>2</sub>Cl<sub>2</sub>; initial mass of **1**: 105 mg (8.8 × 10<sup>-5</sup> mol)
- Compound **1**: White powder. Mp: 157°C. IR: 1570 cm<sup>-1</sup> (C–N), 2960 (C–H). UV–vis (CH<sub>2</sub>Cl<sub>2</sub>): 290 (31300). <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>): 1.00 (s, 18H, Me<sub>3</sub>C); 1.18 (s, 18H, Me<sub>3</sub>C); 2.63 (s, 6 H, Mebpy); 2.93, 4.28 (q, AB, J<sub>AB</sub> = 12.9, 8H, Ar-CH<sub>2</sub>-Ar); 4.77 (s, 4H, -OCH<sub>2</sub>C<sub>6</sub>H<sub>5</sub>); 5.20 (s, 4 H, -OCH<sub>2</sub>bpy); 6.67 (s, 4H, ArH); 6.88 (s, 4H, ArH); 7.06–7.29 (m, 12H, C<sub>6</sub>H<sub>5</sub><sup>2+</sup> H of bpy); 7.44 (t, J = 7.7, 2H, bpy); 7.57 (t, J = 7.7, 2H, bpy); 7.65 (d, J = 6.5, 2H, bpy); 8.00 (d, J = 8.1, 2H, bpy); 8.26 (d, J = 7.7, 2H, bpy). <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>): 24.66 (Mebpy); 31.35, 31.57 (Me<sub>3</sub>C); 31.40 (Ar-CH<sub>2</sub>-Ar); 33.76, 33.89 (Me<sub>3</sub>C); 77.05, 77.49 (OCH<sub>2</sub>C<sub>6</sub>H<sub>5</sub>, OCH<sub>2</sub>bpy); 118.33, 119.48, 122.99, 123.47, 124.92, 125.24, 127.51, 127.95, 129.26, 136.91, 137.04 (C(1), C(2), C(3), C(4), C(5) of C<sub>6</sub>H<sub>5</sub>; C<sub>m</sub> of Ar; C(3), C(4), C(5), C(3'), C(4'), C(5') of bpy); 133.34, 134.30, 138.06, 144.47, 144.58, 152.37, 153.37, 155.21, 155.90, 157.62, 157.88 (C(6) of C<sub>6</sub>H<sub>5</sub>, C<sub>ortho</sub> of Ar, C(2), C(2'), C(6), C(6') of bpy). ES-MS (pos. mode): 1193.7 ([I+H]<sup>+</sup>), 1215.7 ([I+Na]<sup>+</sup>), 597.7 ([I+2 H]<sup>2+</sup>/2). Anal. calcd for C<sub>82</sub>H<sub>88</sub>N<sub>4</sub>O<sub>4</sub> (1193.64): C, 82.51; H, 7.43; N, 4.69; O, 5.36. Found: C, 82.47; H, 7.24; N, 4.77; O, 5.68.
- Compound 2-PF<sub>6</sub>: White powder. Mp: 275°C; IR: 1576 (C–N), 2955 (CH), 843 (PF<sub>6</sub><sup>-</sup>). UV–vis (CH<sub>2</sub>Cl<sub>2</sub>): 291

(36100).  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ ): 0.78 (s, 18H, *t*-Bu); 1.35 (s, 18H, *t*-Bu); 2.22 (s, 6H,  $\text{CH}_3\text{bpy}$ ); 2.74, 3.90 ('q', AB,  $J_{AB}=13.2$ , 4H, Ar- $\text{CH}_2$ -Ar); 2.80, 3.52 ('q', AB,  $J_{AB}=12.5$ , 4H, Ar- $\text{CH}_2$ -Ar); 3.94, 4.15 ('q', AB,  $J_{AB}=11.8$ , 4H,  $\text{OCH}_2\text{C}_6\text{H}_5$ ); 5.22, 6.10 ('q', AB,  $J_{AB}=12.9$ , 4H,  $\text{OCH}_2\text{bpy}$ ); 6.32 (s, 2H, ArH); 6.39 (s, 2H, ArH); 6.67 (d,  $J=8.0$ , 4H,  $\text{C}_6\text{H}_5$ ); 6.97 (t,  $J=8.0$ , 4H,  $\text{C}_6\text{H}_5$ ); 7.03 (t,  $J=8.0$ , 2H,  $\text{C}_6\text{H}_5$ ); 7.10 (d,  $J=3.0$ , 4H, ArH); 7.26 (d,  $J=7.7$ , 2H,  $\text{Hpy}_{\text{CH}_2}$ ); 7.44 (d,  $J=7.7$ , 2H,  $\text{Hpy}_{\text{Me}}$ ); 7.97 (t,  $J=7.7$ , 2H,  $\text{Hpy}_{\text{Me}}$ ); 8.12 (t,  $J=7.7$ , 2H,  $\text{Hpy}_{\text{CH}_2}$ ); 8.19 (d,  $J=8.1$ , 2H,  $\text{Hpy}_{\text{Me}}$ ); 8.40 (d,  $J=8.1$ , 2H,  $\text{Hpy}_{\text{CH}_2}$ ).  $^{13}\text{C}$  NMR (75 MHz,  $\text{CDCl}_3$ ): 25.56

(*Me*bpy); 31.08, 31.73 ( $\text{Me}_3\text{C}$ ); 31.46, 32.42 (Ar- $\text{CH}_2$ -Ar); 33.60, 34.21 ( $\text{Me}_3\text{C}$ ); 77.49 ( $\text{OCH}_2\text{C}_6\text{H}_5$ ); 81.21 ( $\text{OCH}_2\text{bpy}$ ); 120.37, 122.56, 122.60, 124.21, 124.87, 125.62, 125.98, 126.01, 126.93, 127.77, 127.93, 128.91, 139.64, 139.79 (C(1), C(2), C(3), C(4), C(5) of  $\text{C}_6\text{H}_5$ ;  $\text{C}_m$  of Ar; C(3), C(4), C(5), C(3'), C(4'), C(5') of bpy); 131.20, 131.49, 134.58, 136.14, 137.13, 144.56, 146.02, 151.41, 151.45, 151.56, 151.59, 152.01, 153.43, 158.27, 158.28, 158.30 (C(6) of  $\text{C}_6\text{H}_5$ ,  $\text{C}_{\text{ortho}}$  of Ar, C(2), C(2'), C(6), C(6') of bpy). ES-MS (pos. mode): 1301.6 ( $[\text{I}+\text{Ag}(\text{I})]^+$ ). Anal. calcd for  $\text{C}_{82}\text{H}_{88}\text{AgF}_6\text{N}_4\text{O}_4\text{P}$  (1446.46): C, 68.09; H, 6.13; N, 3.87; found: C 68.26, H, 6.15; N 4.27.