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PHOSPHORYLATED THIALIX[6]ARENE: SYNTHESIS AND CHARACTERIZATION OF HOST-GUEST COMPLEX OF SELECTIVE Pd²⁺ ION EXTRACTION

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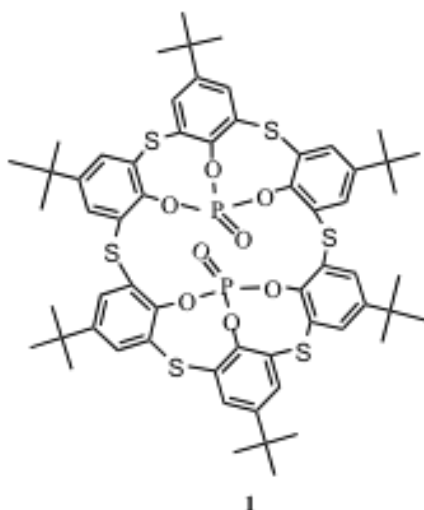
Abstract – New phosphorylated thiacalix[6]arene was synthesized and its metal extraction ability was examined by using automotive catalyst residue solution. The new host molecule showed high affinity towards Pd²⁺ ion and reasonable affinity towards other metals. Then we studied the effect of concentration and time on the Pd²⁺ ion extraction using Pd²⁺ ion standard solution. In addition to this, we successfully characterized the host-guest complex formed during Pd²⁺ ion extraction by using Job's method, ³¹P & ¹H NMR, IR and elemental analysis.

INTRODUCTION

In chemical science, reusability by recovering of chemical substances from the industrial waste gained high priority in recent years, because this will give benefits in different aspects such as recovering of less abundant species, financially effective and most importantly saving the environment from pollution due to hazardous waste chemical species. In particular selective recovery of precious metals from the secondary resources using supramolecular host is gaining importance due to their less abundance in nature.

Platinum-group metals (PGM) belonged in precious metals are important in many industrial fields such as solar cell, fuel cell and automotive catalyst. Platinum, palladium and rhodium composed of PGMs, which are the essential metals in the preparation of three-way catalyst (TWC). TWC can convert the emission of auto exhaust such as hydrocarbons, CO, NO_x to environment benign species by simultaneous oxidation and reduction. Among the PGMs, Pd is the highly demand metal in automobile industries.¹ Since its natural occurrence from the earth crust along with other PGMs is very low, it is necessary to extract from the secondary sources. Although leaching of PGMs from the industrial waste was well studied,² selective extraction of Pd metal from the PGMs remains challenge to the researchers.³ Some of the commercially available reagents are using currently for selective Pd extraction⁴ but none of these satisfactory. Hence, there is still need to search for better extractants with regards to their economic viability.

In recent years, supramolecular chemistry has been drawn to the calix[n]arenes (CnAs) due to their ability to act as pre-organizing complexing agents, carriers and potential biomimics as well as being able to undergo multiple functionalization.⁵ Since phosphine shows high affinity for metal ions, insertion of phosphorus containing moieties into CnAs allows extension of the possibilities for engineering of supermolecular systems. A number of phosphine modified CnAs have already been synthesized and tested their extraction ability.⁶ But very few contributions on phosphine modified thiacalixarenes (TCnAs), were reported.⁷ TCnAs are structural analogues of CnAs linked by sulfur bridges with basket shaped well-defined upper and lower bridges. High affinity of sulfur towards metal ions increases the importance of TCnAs in host-guest chemistry.⁸ Therefore TCnAs and their derivatives with additional donor atoms like phosphorus have higher metal-binding ability. Antipin and co-workers reported the first synthesis and structural analysis of phosphorylated TC₄As in the solution and crystalline state.^{7c} The reaction of TC₄A with PCl₃ followed by HNEt₂ gives the phosphorus diesteramide.^{7b} Even though the metal-binding ability of TCnAs and their derivatives with various metals was reported in recent years,⁹ but there is no report on



the phosphorylated TCnAs to the best of our knowledge. In this paper we synthesized phosphorylated thiocalix[6]arene (**1**) and evaluated its extraction properties towards Pd²⁺ ions from PGM solution of automotive catalyst residue and Pd²⁺ standard solution. We also attempt the characterization of host-guest complex formed during selective Pd²⁺ ion extraction by Job's method, IR, ¹H NMR, ³¹P NMR techniques and elemental analyses.

RESULTS AND DISCUSSION

Liquid-Liquid Extraction of Metals from PGM solution

We studied the metal extraction ability of **1** through liquid-liquid extraction from PGM solution. **Figure 1** shows the extractability of compound **1** towards PGM solution. Compound **1** extracted Pd²⁺ ions significantly (95.8%) along with reasonable extractability of other metals (Zr: 70.4%, Y: 67%, Pt: 38.8%). It is expected that the structural arrangements of PdCl₄²⁻ allows the direct interaction of P=O group with Pd²⁺ ion. Due to this interaction compound **1** showed high affinity towards Pd²⁺ ion.

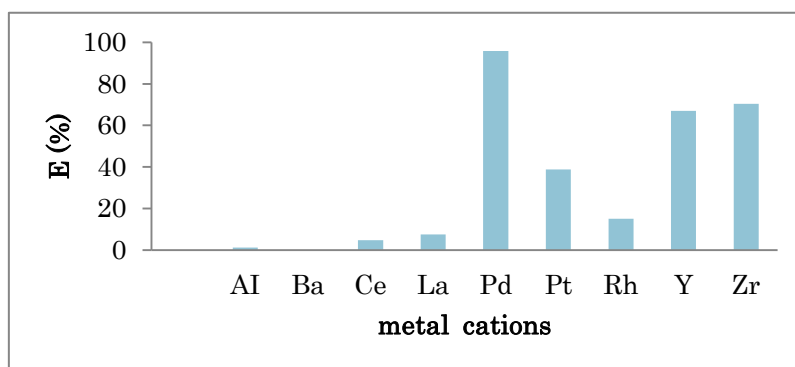


Figure 1. Extraction ability of **1** with PGM solution containing nine metal ions

Conditions: [extractant] = 0.292 mM, time = 0.5 h, pH = 3.68

Effect of Contact Time:

The effect of extraction time on the extractability (E%) was analyzed by varying the extraction time from 30 min. to 24 h at pH 1.64. Equal molar concentrations (0.1879 mM) of **1** and Pd²⁺ ion solution were shaken thoroughly using mechanical shaker. The aqueous and organic layers were separated using separating funnel. The concentration of Pd²⁺ ions in the aqueous phase was measured using ICP-AES. The maximum extraction was observed at 24 h (**Figure 2**). Hence the extraction time of **1** for the further studies was fixed as 24 h.

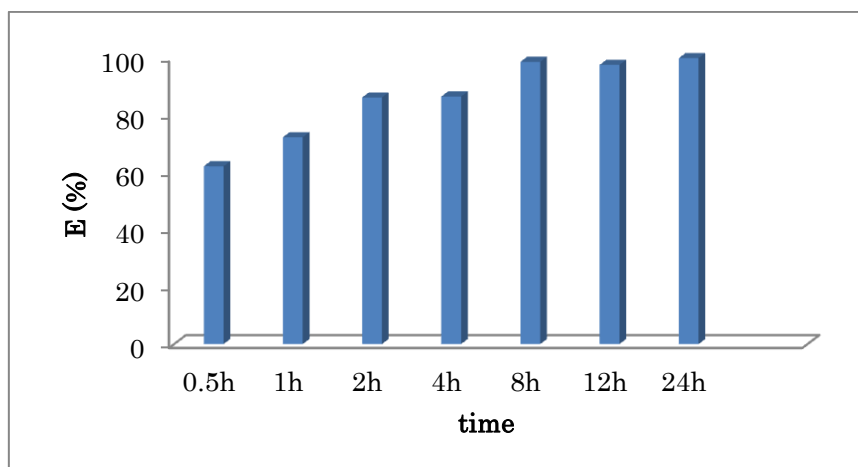


Figure 2. Effect of time on the extraction of Pd²⁺ ions with **1**

Conditions: [extractant] = 0.1879 mM, [Pd(II)] = 0.1879 mM, time = 0.5 h~24 h, pH = 1.64

Effect of Pd²⁺ ion concentration:

The E% of Pd²⁺ ion at different concentrations of **1** ranging from 0.0093 mM ~ 0.5639 mM was studied at fixed extraction time of 24 h. **1** showed higher E% (80.56%) even at low concentration (0.0093 mM (1:0.05)) and 99.86% extraction was observed at 0.1879 mM (1:1 ratio) (**Figure 3**).

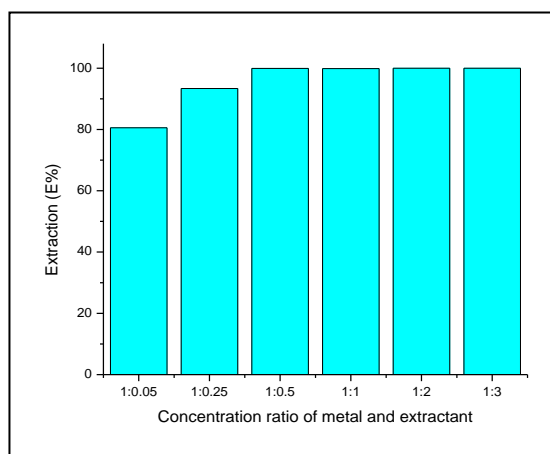


Figure 3. Effect of concentration of **1** on the extraction of Pd²⁺ ions

Conditions: [extractant] = 0.0093 mM~ 0.5639 mM, [Pd(II)] = 0.1879 mM, time = 24 h, pH = 1.64

Characterization of host-guest complex (1-Pd²⁺ complex):

Job's continuous variation method:

The formation of complex between **1** and Pd²⁺ ions was determined by Job's continuous variation method.

Same concentrations of aqueous solution of Pd^{2+} ions (0.1879 mM) and chloroform solution of **1** (0.1879 mM) were mixed in different ratios. After the contents had been shaken for 24 h, the layers were separated and the absorbance of the organic phase was measured using UV-visible spectroscopy at 419 nm. The results were plotted as absorbance versus mole fraction of **1**. The **1**- Pd^{2+} complex exhibited a maximum absorbance at 0.2 mole fraction, which indicates that one molecule of **1** coordinates with four Pd^{2+} ions (**Figure 4**). This result is also in good agreement with **Figure 3**, where 1:0.25 ratio of **1** and Pd^{2+} showed 93.37% of extractability.

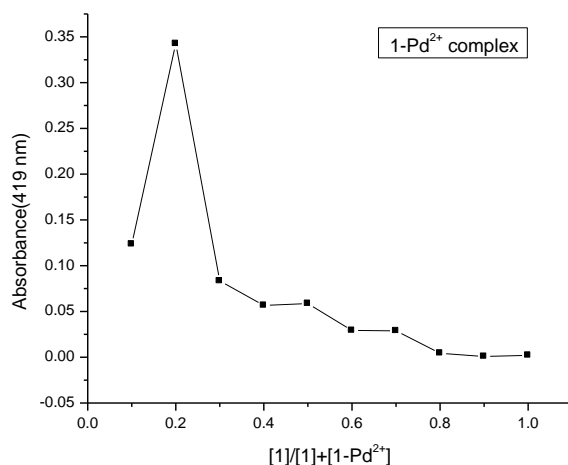


Figure 4. Job's continuous variation results for extraction Pd^{2+} ions with **1**

Spectral and analytical data:

^{31}P & ^1H NMR, FT-IR and CH Analyses of **1** and **1**- Pd^{2+} complex were recorded. The data of the complex were significantly different from **1** indicating complex formation between **1** and the Pd^{2+} ions. The ^{31}P NMR of **1** & **1**- Pd^{2+} complex showed two peaks at 106.4, 107.8 and four peaks at -23.4, 72.6, 105.9, 124.8 respectively. The shifting of peaks clearly suggests the coordination between PdCl_4^{2-} and P=O group of **1**. But one of the P=O shifted much higher region (-23.4) is may be due to the interaction of bridged sulfur of **1**. In addition to this, shifting of aromatic and aliphatic protons in ^1H NMR was also observed. In the ^1H NMR of **1**, the aromatic protons and aliphatic protons were resonated between 6.89-7.76 and 1.05-1.30 respectively and in **1**- Pd^{2+} complex the same protons resonated between 7.50-7.52 and 1.20-1.30. In FT-IR spectra, the peak corresponds to P=O in **1** shifted from 1139 to 1082 cm^{-1} . Elemental analysis of **1** revealed a composition of 60.63% C and 5.91% H. After complexation with PdCl_4^{2-} , the composition became 51.41% C and 5.61% H. The percentages of C and H decreased after extraction corresponds to complex formation between host and guest molecules.

CONCLUSION

We synthesized phosphorus modified thiacalix[6]arene and studied its extractability towards metals ions using automotive catalyst residue solution and concluded that the host molecule was efficient towards Pd²⁺ ion extraction. Further we studied the effect extraction time and concentration on Pd²⁺ extraction using Pd²⁺ standard solution and the results indicated that the compound was efficient even at low concentrations and times. We also characterized the resultant host-guest complex formed during extraction by using spectral and analytical techniques.

EXPERIMENTAL

Materials and Methods:

p-*tert*-Butylthiacalix[6]arene was synthesized according to literature methods.¹⁰ PCl₃, *p*-bromotoluene, chloroform, 1000 ppm Pd Standard solution were purchased from commercial sources and used without further purification. ¹H & ³¹P NMR data were recorded on JEOL600SSS ECA-600 instrument. Fourier transform infrared (FT-IR) spectra were measured using Thermo Fisher Scientific Nicolet iS5 spectrophotometer (attenuated total reflection (ATR) method). Electronic absorption spectra were recorded on a Shimadzu UV 3600 double-beam spectrophotometer using 1-cm matched quartz cells. Mass spectra were recorded on matrix-assisted laser desorption-ionization time-of-flight mass spectrometry (MALDI-TOF MS, Bruker autoflex speed- AK1). Elemental analysis was performed on CE-440 Elemental Analyzer.

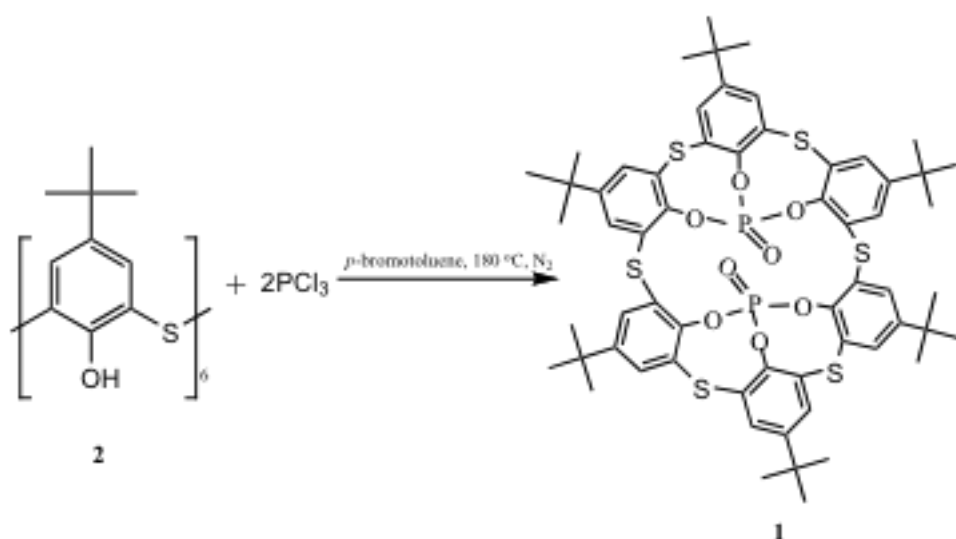
Typical Procedure for the Synthesis of 1:

A mixture of *p*-*tert*-butylthiacalix[6]arene (**2**) (0.5 g, 0.462 mmol), and PCl₃ (0.16 mL, 1.85 mmol), in 15 mL of *p*-bromotoluene was stirred at 80 °C for 1 h in N₂ atmosphere. The stirred mixture was then heated gradually to 180 °C over a period of 3 h and kept at this temperature for a further 2 h. The progress of the reaction was monitored by Thin Layer Chromatography (TLC) using hexane: EtOAc in 3:1 ratio. After completion of the reaction as indicated by TLC, the contents were cooled to room temperature, *p*-bromotoluene and excess of PCl₃ were removed *in vacuo*. Then the reaction mixture was diluted with hexane, white precipitate was formed after 12 h (0.265 g, 53%). ¹H, ³¹P, IR, MALDI-TOF MS, and elemental analysis characterized the structure of the new compound.

Spectral data:

White solid, IR 1139 (P=O); ¹H NMR (CDCl₃): 1.055 (9H, s), 1.16 (27H, s), 1.30 (18H, s), 6.89 (s, 1H), 7.0 (d, 2H, *J* = 3 Hz), 7.36 (d, 1H, *J* = 2.4 Hz), 7.39 (s, 2H), 7.58 (s, 1H), 7.76 (d, 5H, *J* = 1.8 Hz); ³¹P NMR (CDCl₃): 106.44, 107.87; MALDI-TOF MS: 1169 (M⁺). Anal. Calcd for C₆₀H₆₆O₈P₂S₆: C, 61.62; H,

5.69. Found: C, 60.63; H, 5.91.



Scheme 1. Synthesis of phosphorylated thiacalix[6]arene (**1**)

Liquid-Liquid Extraction of Pd²⁺ ions from PGM solution:

PGM solution was prepared according to literature methods.¹¹ The pH of the diluted PGM solution was 3.68. The concentration of nine metal ions at this pH was determined by inductively coupled plasma atomic emission spectrometry (ICP-AES) and listed in **ESI Table S1**. In a 50 mL vial, 20 mL of **1** (0.292 mM) in CHCl₃ was mixed with the diluted PGM solution (20 mL). The mixture was then shaken at 300 stokes/min for 30 min. The concentrations of metal ions remaining in the aqueous phase [M]_{aq} were determined by ICP-AES.

Liquid-Liquid Extraction of Pd²⁺ ions from standard solution:

Liquid liquid extraction experiments were performed triplicate at ambient temperature with equal molar concentrations of Pd standard solution (0.1879 mM, 20 mL) and extractant (0.1879 mM, 20 mL) in glass bottles. The mixture was shaken at 300 stokes/min for 24 h. The concentration of Pd²⁺ ions in the aqueous phase was measured using ICP-AES. The extractability, (E%) was calculated by using the following equation.

$$E\% = \frac{C1 - C2}{C2}$$

Where C1 and C2 are initial and final concentration (mM) of metal ion in aqueous layer, respectively.

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