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SYNTHESIS, X-RAY STRUCTURE AND METAL EXTRACTON ABILITIES OF NEW DIETHYL PHOSPHATE MODIFIED THIACALIX[4]ARENE

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Abstract – New lower rim modified phosphorylated thiacalix[4]arene (TC4A) derivatives such as TC4A-phosphate (**2a**) and de-t-Bu-TC4A-phosphate (**2b**) were synthesized. IR, ^{1}H & ^{31}P-NMR and mass spectral and elemental analysis characterized the structures of the synthesized compounds. Single crystal X-ray diffraction measurement reveals that, both the compounds (**2a** & **2b**) stabilized in pinched cone conformation. We also investigated the metal extraction ability of the newly synthesized compounds through solvent extraction technique and these compounds selectively extracted Pd (II) ions from automotive catalyst residue solution containing nine metals.

INTRODUCTION

The chemistry of thiacalixarenes play significant role in all fields of chemical science due to its vast number of applications.[1] Hence researchers around the world were attracted and applied serious attention since their first appearance in 1997.[2] The presence of sulfur bridges in these compounds is the responsible for its peculiar properties over the calixarenes.[3] In particular, complexation abilities with alkali, transition and lanthanide metals make them interesting host molecules in supramolecular chemistry.[4] This exclusive property is due to chemical modifications at upper and lower rims. Even though similar reactions conditions, as used in calixarenes, were applied for these modifications, different selectivity in the reaction pattern was observed due to steric and electronic factors. For example, palladium catalyzed Sonogashira coupling reaction of 1,3-bitriflate of calix[4]arene yields lower rim modified mono- and diiodo-*p*-*tert*-butylcalix[4]arene.[5] But the same reaction condition was inapplicable to 1,3-bitriflate of TC4A.[6]

Habicher *et al*. introduced phosphorus at lower rim of TC4A using PCl_3 yields phosphorus diester chloride derivative, which was stabilized by 1,2-alternate conformation, further gives phosphorus diester derivative by the reaction of diethylamine.[7] Pyrophosphate derivative was obtained when TC4A reacts with ethylene chlorophosphite.[8] Since organophosphorus compounds have wide range of applications in various sectors such as industry, medicinal and agriculture,[9] significant number phosphorus derivatives based on thiacalixarenes will strengthen its applications. In our previous study, we reported the synthesis and rare metal extraction ability of phosphorylated TC6A.[10]

Rare metal extraction is one of the important applications in supramolecular chemistry. Extraction of rare metals from secondary resources is challenging objective because of limited natural resources and economic viability.[11] In particular selective extraction of metals from automotive residue solution containing nine metals such as Al, Ba, Ce, Pd, Pt, Rh, La, Zr and Y (Platinum group metals (PGM)) using thiacalixarene derivatives gain considerable attention recently. Use of PGM metals in the automobile catalytic converters to reduce the harmful gas emissions was started in 1970s onwards.[12] Since then, the demand of these metals was highly increased due to their less abundance in nature.[11] Hence, extraction of PGMs from the secondary sources is an important objective to reduce their demand. The recovery of PGMs from secondary sources has been reported.[13] Extensive studies have been done on the metal extraction abilities of thiacalixarene derivatives from recovered PGM solution. *p*-Diethylaminomethyl TC4A shows remarkably high selectivity for Pt (IV) ions from precious metal solution.[14] Dimethylthiacarbomyl modified thiacalix[n]arenes can selectively extract Pd (II) ions from PGM solution.[15] TC6A derivatives have high affinity towards Pd (II) and Zr (II) ions.[16] *O*-Thiocarbonyl TC6A extracted Pd (II) ions selectively in chloride media.[17] But only one contribution was published on the metal extraction ability of phosphine modified TC6A from PGM solution.[10] Since phosphorus and sulfur have high affinity towards various metal ions,[18] extensive studies is required for metal extraction abilities of phosphine modified thiacalix[*n*]arenes.

In the present study, we synthesized TC4A-phosphate (**2a**) and *de-t-Bu*-TC4A-phosphate (**2b**). The structure of the new compounds was characterized by crystallographically along with spectral and analytical techniques. We also investigated the extraction ability of new compounds from PGM solution and Pd (II) standard solution, both the compounds showed high affinity and selectivity towards Pd (II) ions.

RESULTS AND DISCUSSION

Chemistry:

The reaction of TC4A derivatives (**1a** & **1b**) with diethyl chlorophosphate in the presence of K_2CO_3 in acetone under reflux temperature yielded corresponding phosphate derivatives (**2a** & **2b**) (**Scheme 1**). Under these conditions, **1a** & **1b** forms tetraphosphorylated derivatives. But when we applied similar conditions to calix[4]arene derivatives (**ESI 3a** & **3b**), diphosphorylated products (**4a** & **4b**) were yielded (**Scheme S1**).[19] Literature survey reveals that, tetraphosphorylation of **3a** & **3b** occurred under phase transfer catalysis conditions (CCl_4-H_2O, 50% NaOH, tetrabutylammonium chloride).[20] This change of reactivity pattern in thacalixarenes compared to calixarenes was due to the effect of steric and electronic factors, which were significantly changed by the substitution of methylene bridges with sulfide.

*X-Ray structures of **2a** & **2b**:*

Crystals of **2a** & **2b** were grown through slow evaporation of crude product in a mixed solution of n-hexane and chloroform (3:1 ratio). Compound **2a** crystallizes in triclinic space group such as P-1 with asymmetric unit composed of one TC4A molecule and 0.5 H_2O as guest where as **2b** in monoclinic space group i.e. $P2_1/c$ with asymmetric unit of one TC4A molecule and one $CHCl_3$ as guest (see supporting information for atomic numbering of **2a** & **2b**). Both **2a** & **2b** stabilized in pinched cone conformation with the following inward and out ward phenyl ring centroid distances 5.578Å (centroid B---centroid D), 7.508Å (centroid A---centroid C) for **2a**, 4.389 Å (centroid F---centroid H), 8.160Å (centroid E---centroid G) for **2b**. Intramolecular S---O interactions between divalent sulfur and phosphoryl oxygen further stabilized the conformations of **2a** & **2b**. The corresponding distances are 3.223Å (S4---O2), 3.222Å (S2---O10) in **2a** (**ESI Figure S1**) and 3.416Å (S---O2), 3.128Å (S3---O6), 3.321Å (S4---O4) in **2b (ESI Figure S1)**. In addition to S---O interactions **2b** also maintained the intramolecular CH---π interactions with distances 3.128Å (centroid F---H20B), 3.555Å (centroid H---H40) (**ESI Figure S2**).

The symmetry expansion of **2a** & **2b** reveals that the outward phenyl rings in the pinched cone TC4A molecules held together by intermolecular CH---π interactions. In both **2a** & **2b**, CH---π interactions were observed between aromatic rings and hydrogen atoms of the ethyl groups of neighboring TC4A molecules. The corresponding CH---centroid distances are 3.215Å (centroid A---H28C), 3.223Å (centroid C---H56A) for **2a** (**Figure 1**), 3.698Å (centroid F---H20A) for **2b** (**Figure 2**).

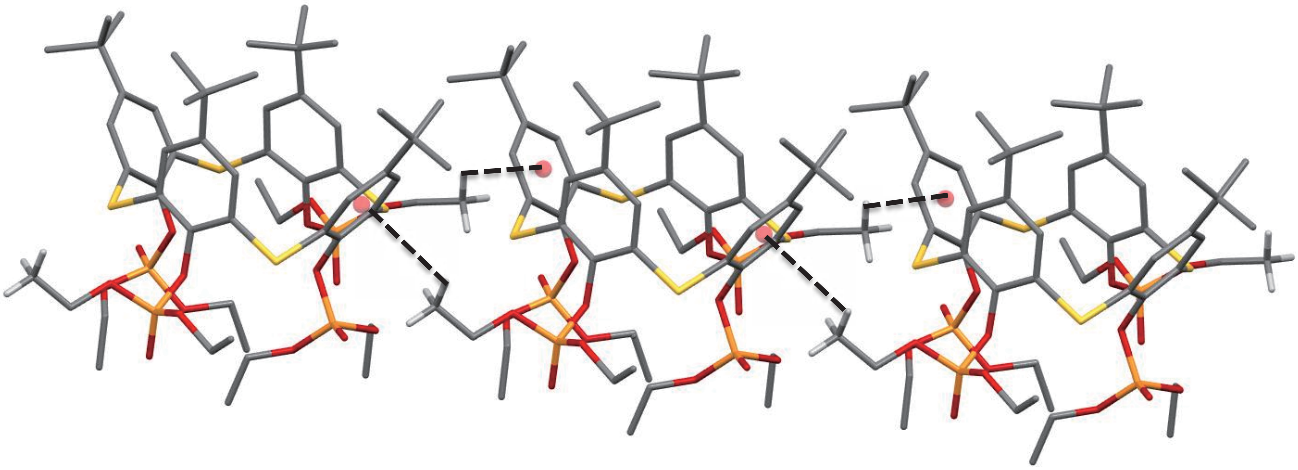


Figure 1. Expanded structure of 2a showing intermolecular CH---π interactions, except O8, O16A methyl groups, all hydrogens were omitted for clarity. Each element was depicted as follows: S=yellow, O=red, P=brown, C=grey, H=white

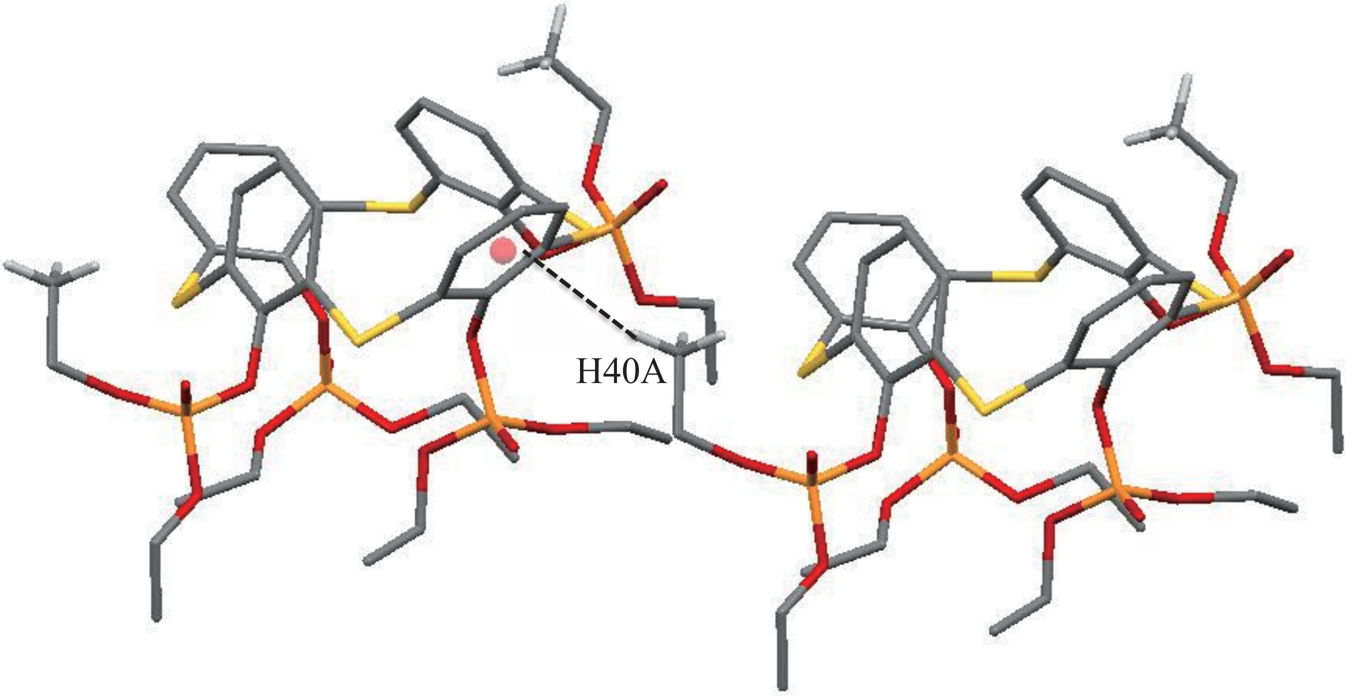


Figure 2. Expanded structure of 2b showing intermolecular CH---π interactions. Except C40 hydrogens, all hydrogens were omitted for clarity. Each element was depicted as follows: S=yellow, O=red, P=brown, C=grey, H=white

In addition to CH---π interactions, phosphoryl oxygens are actively participating in making the structures of **2a** & **2b** as three-dimensional supramolecular assemblies via hydrogen bonding. In the case of **2a**, all phosphoryl oxygens showed hydrogen bonding with ethyl groups of neighboring TC4A molecules and the corresponding distances are 3.138Å (O2---C25A^{a}), 2.580Å (O2---H25B^{a}) (**ESI Figure S3**), 3.298Å

(O6---C27A^{b}), 2.678Å (O6---H27B^{b}) (**ESI Figure S4**), 3.216Å (O10---C56A^{c}), 2.537Å (O10---H56C^{c}) (**ESI Figure S5**), 3.381Å (O14---C55A^{d}), 2.442Å (O14---H55B^{d}) (**ESI Figure S6**). Symmetry elements are ^{a}–x, 1-y, 1-z, ^{b}1-x, 1-y, 1-z, ^{c}1+x, y, z, ^{d}-x, 1-y,-z. In the case of **2b**, phosphoryl oxygens O2, O10 showed hydrogen bonding with ethyl groups and O6 showed hydrogen bonding with aromatic carbon atoms of neighboring TC4A molecules. The corresponding distances are 3.466 Å (O2---C38$^{a'}$), 2.615 Å (O2---H38A$^{a'}$) (**ESI Figure S7**), 3.221Å (O6---C4$^{b'}$), 2.577 (O6---H4$^{b'}$), 3.290 Å (O6---C3$^{b'}$), 2.737 Å (O6---H3$^{b'}$), 3.932 Å (O6---C14$^{c'}$), 3.027 Å (O6---H14$^{c'}$), 3.401Å (O6---C34$^{c'}$), 2.480 Å (O6---H34$^{c'}$) (**ESI Figure S8**), 3.522 Å (O10---C19$^{d'}$), 2.589 Å (O10---H19$^{d'}$), 3.569 Å (O10---C39$^{b'}$), 2.627 Å (O10---H39A$^{b'}$) (**ESI Figure S9**). The symmetry elements are $^{a'}$x, 1/2-y, -1/2+z, $^{b'}$x, 1+y, z, $^{c'}$-x, 1/2+y, 1/2-z, $^{d'}$x, 1.5-y, 1/2+z.

Further the $CHCl_3$ guest located between the TC4A molecules in the crystal structure of **2b** gives additional stability for its supramolecular assembly. Each $CHCl_3$ molecule interacts with four neighboring TC4A molecules through host-guest interactions such as halogen bonding and hydrogen bonding. There is three such types of interactions observed between host and guest molecules viz, (1) aliphatic-H---Cl interactions between Cl atoms of the guest and hydrogens of ethyl moiety of the host and the corresponding distances are 2.998Å (Cl1B---H8A$^{e'}$), 3.400Å (Cl1B---H37$^{e'}$) (**ESI Figure S10**), 2.888Å (Cl1B---H29$^{f'}$) (**ESI Figure S11**), 2.888Å (Cl3B---H38A$^{g'}$) (**ESI Figure S12**). (2) Interaction between the Cl and oxygen of phosphoryl group and the corresponding distance and angles are 3.006 Å (Cl3B---O2$^{b'}$), $\alpha = 176.43^{o}$ (C41B---Cl3B---O2$^{b'}$) (**ESI Figure S13**) (3) hydrogen bonding between carbon atom of the guest and oxygen of the phosphoryl group of host and the corresponding distances are 3.309Å (C41B---O10$^{f'}$), 2.382Å (H41B---O10$^{f'}$) (**ESI Figure S10**). The symmetry elements are $^{e'}$1-x, 1-y, 1-z, $^{f'}$1-x, 2-y, 1-z, $^{g'}$x, 1.5-y, -1/2+z.

*Liquid-Liquid extraction of **2a** & **2b** using PGM solutions:*

We studied liquid-liquid extraction of metals from PGM solution using **2a** & **2b**. Compounds **2a** & **2b** were most selective and efficient towards Pd (II) ions in PGM solution. Compound **2a** extracted 87.6% of Pd (II) along with 18.6% of Zr. 100% Selectivity was observed in the case of compound **2b**, it extracted 83.2% of Pd (II) selectivity from PGM solution. No other metal was extracted in the PGM solution (**Figure 3**). Phosphate group and bridged sulfur atom present in the macrocyclic structure of **2a** & **2b** may be the responsible for high selectivity towards Pd (II) ions in the PGM solution.[21] It is expected that, affinity of lower rim modified *tert*-Bu-TCnA derivatives towards Zr ions allowed the small amount of Zr ions along with Pd (II) ions in the case of **2a.**[10, 15, 22]

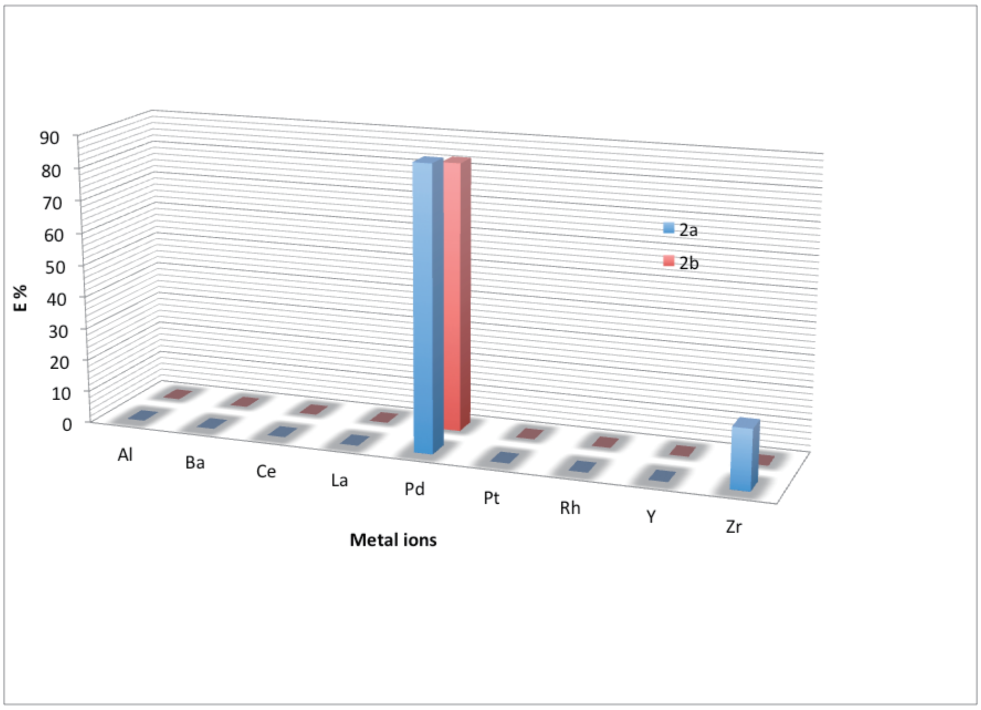


Figure 3. Extractability of Pd (II) ions from PGM solution containing nine metal ions by 2a and 2b. pH of PGM solution: 0.65.

Effect of pH:

The extraction of Pd (II) ions from aqueous solution is moderately depends on the pH of the solution. The extractability (E%) of **2a** was determined at six different pH levels in the range of 0-5 with 24 h contact time. The maximum E% was observed at pH >3. Reasonable E% values were observed at pH 0-2. 20.9% of extraction was observed at pH 0, and the E% value increased from pH 1 (**Figure 4**). As the pH increases from 0 - 3, the anionic species such as $PdCl_4^{2-}$ ions were predominant and favorable species[15] for the complexation with phosphorus and sulfur[21], which results increase in the extractability of **2a**. Hence 100% extractability was observed at pH 3. Similar results were observed with compound **2b**.

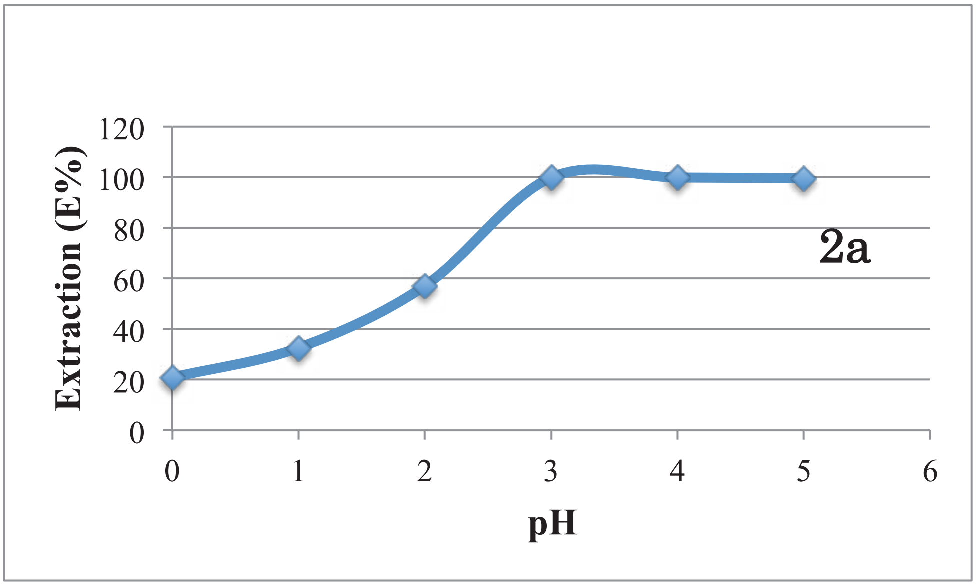


Figure 4. Effect of pH on Pd (II) extraction. Conditions: [extractant] = 1.0 mM, [Pd(II)] = 1.0 mM, time = 24 h.

Effect of contact time:

The effect of contact time on the E% values of **2a** & **2b** were determined by varying the contact time in the range of 1 h to 42 h (**Figure 5**). The E% values were highly depends on the contact time. As the contact time increases, the E% also increased and 100% extraction was observed at 24 h. hence the contact time of extractants used in the further studies was fixed as 24 h. Similar behavior was observed in the case of compound **2b**.

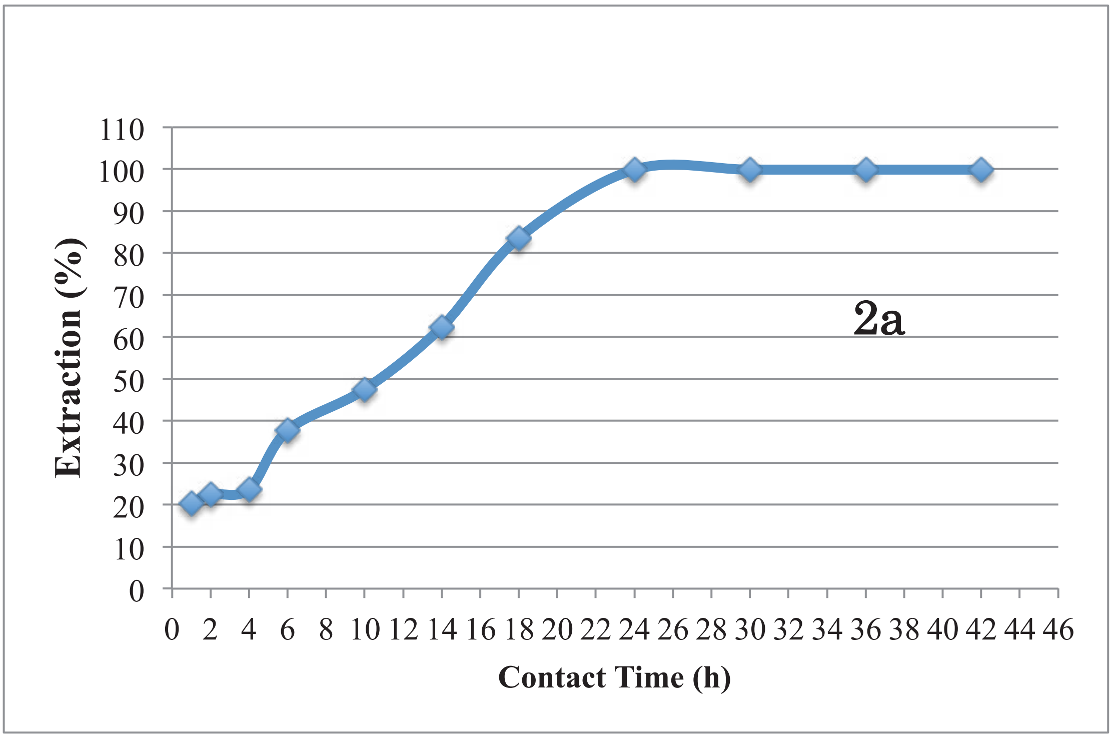


Figure 5. Effect of contact time on Pd (II) extraction. Conditions: [extrcactant] = 1.0 mM, [Pd (II)] = 1.0 mM, pH = 3.

Jobs Continuous Variation Method:

The favorable complexation formed between **2a** and Pd (II) ions were determined using Jobs continuous variation method. Same concentrations of **2a** in chloroform (1 mM) and Pd (II) (1 mM, pH 3) in HCl were mixed in different ratios. The solutions were shaken for 24 h and 300 strokes/min, then the layers were separated and the absorbance of the organic phase was determined using UV-visible spectrophotometry at 438 nm. The results were plotted as absorbance (A) versus mole fraction of **2a** (**Figure 6**). The **2a**-Pd(II) complex exhibited maximum absorbance at 0.5mol fraction, which indicates that the each molecule of **2a** coordinates one Pd (II) ion. Similar complexation behavior was observed with **2b** (**ESI Figure 14**)

^{31}P and FT-IR data of **2a** and **2a**-Pd (II) complex were recorded. The spectral data of the complex were significantly different from **2a** indicating complex formation between **2a** and Pd (II) ions. The ^{31}P NMR spectra of **2a** showed peak at -6.72 ppm where as **2a**-Pd (II) complex showed two peaks at -5.14 ppm and

-12.77ppm. The additional peak in ^{31}P NMR of **2a**-Pd (II) was due complex formation between Pd (II) ions and **2a**. In FT-IR spectra the peak corresponds P=O shifted from 1282 cm^{-1} to 1274 cm^{-1} also represents the complex formation between **2a** and Pd (II) ions.

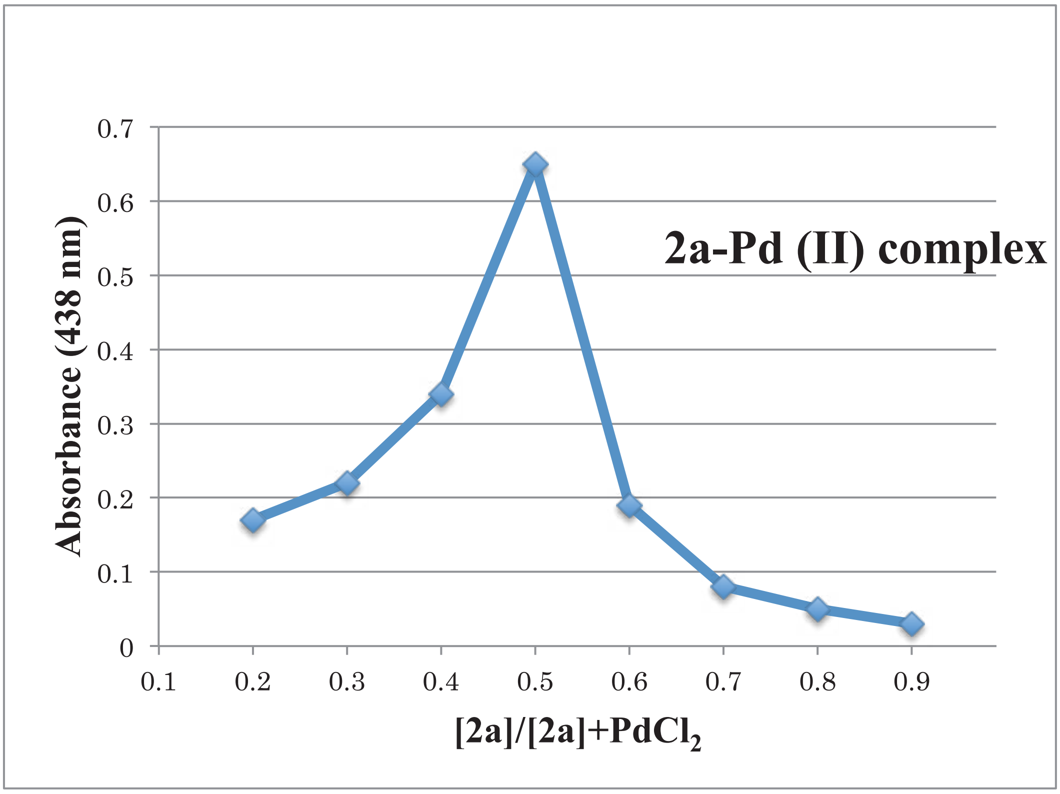


Figure 6. Jobs continuous variation results for extraction of Pd (II) using compound 2a

CONCLUSIONS

In conclusion, we synthesized two new lower rim phosphate modified TC4A derivatives and their crystal structure and extractability towards rare metal ions from PGM solution was investigated. CH---π interactions and hydrogen bonding are the building blocks in the construction of three dimensionalsupramolecular assemblies of **2a** & **2b**. In addition, both the compounds showed high affinity and selectivity towards Pd (II) ion in PGM solution.

EXPERIMENTAL

*Experimental procedure for the synthesis of **2a** & **2b***:

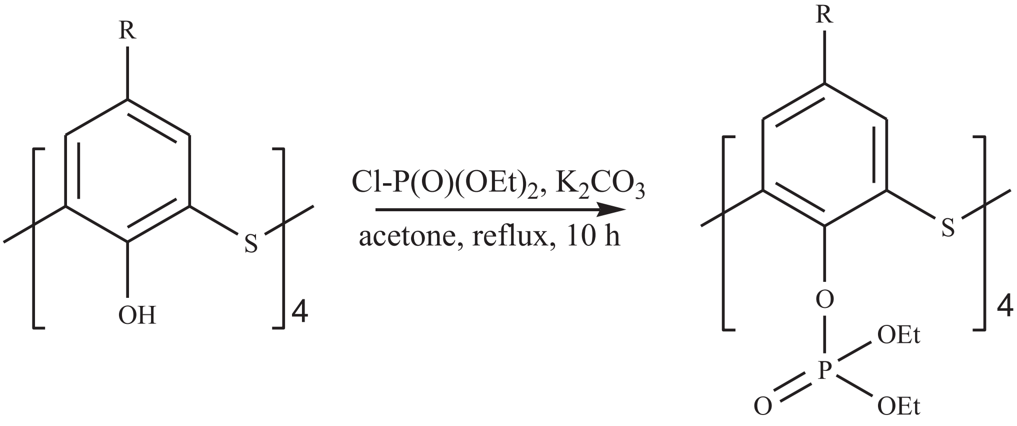
To a suspension of **1a** / **1b** (0.0005 mol) in acetone (20 mL), K_2CO_3 (0.004 mol) was added. Then, diethyl chlorophosphate (0.008 mol) in 10 mL of acetone was added drop wise. The mixture was refluxed for 10 h. The progress of the reaction was monitored using thin layer chromatography (TLC). After cooling down to room temperature, the solvent was removed under reduced pressure. The resultant material added $CHCl_3$, and then washed with 1N HCl solution. The solvent was removed under reduced pressure. The crude product was obtained, which was recrystallized from 3:1 n-hexane and $CHCl_3$ to give pure product **2a** / **2b**.

*Spectral data of **2a***:

Yield: 88.8%; ^{1}H NMR (600 MHz, $CDCl_3$): 7.43 (s, 2H, Ar), 4.39-4.48 (m, 6H, $P(O)CH_2C\underline{H_3}$), 1.39 (t, 6H, *J*=7.2 Hz, $P(O)CH_2C\underline{H_3}$), 1.12 (s, 9H, *tert*-Bu.); ^{31}P NMR (600 MHz, $CDCl_3$): -6.72; FT-IR: 1282 (P=O); MALDI-TOF MS: 1264 (M^+), 1287 (M+Na). Anal. Calcd for $C_{56}H_{84}O_{16}P_4S_4$ (%): C, 53.14; H, 6.69. Found: C, 52.99; H, 6.56.

*Spectral data of **2b***:

Yield: 74.4%; ^{1}H NMR (600 MHz, $CDCl_3$): 6.98 (s, 2H, Ar), 6.80 (d, 1H, *J*=6.6 Hz, Ar), 4.35-4.41 (m, 4H, $P(O)C\underline{H_2}CH_3$), 1.38 (t, 6H, *J*=6.6 Hz, $P(O)CH_2C\underline{H_3}$); ^{31}P NMR (600 MHz, $CDCl_3$): -4.69; FT-IR: 1266 (P=O); MALDI-TOF MS: 1040 (M^+), 1063 (M+Na). Anal. Calcd for $C_{40}H_{52}O_{16}P_4S_4$ (%): C, 46.15; H, 5.03. Found: C, 45.90; H, 4.82.



1a: R = *tert*-Bu
1b: R = H

2a: R = *tert*-Bu
2b: R = H

Scheme 1. Synthesis of TC4A-Phosphates (2a & 2b)

X-Ray crystallography:

The crystals in mother liquid were picked up with pipette, and dropped in Paraton. The single crystals coated with oil were isolated on Micromounts TM, and the crystals were placed in a cold nitrogen steam at 120 K. X-Ray diffraction data were collected on a Rigaku Saturn CCD diffractometer equipped with graphite-monochromated MoKα radiation. The structures were solved by direct methods using SHELXS-97[23] and refined using full-matrix least-squares method on F2 with the SHELXL-97 program.[24]

*Crystal data for **2a***:

$C_{56}H_{84}O_{16}P_4S_4$ 0.5(H_2O), Fw = 1274.35, crystal dimensions = 0.2 × 0.2 × 0.2 mm, colorless block, triclinic, space group P-1, a = 11.585 (2), b = 13.777 (3), c = 21.038 (5) Å, α = 88.757 (6)°, β = 80.115 (4)°, γ = 77.381 (5)°, V = 3227.6 (12) Å3, Z = 2, MoKα radiation (λ= 0.71075 Å), Å), T = 120K, μ(Mo Kα)=0.310 mm^{-1}, 44243 measured reflections, 14621 unique reflections (Rint = 0.0969), 12426 observed reflections, 855 parameters, R = 0.0315 (I>2.00 σ(I)), wR = 0.0770 (all data), refined against [F], GOF = 1.051. Several carbons and oxygens of diethyl phosphate moiety showed disorder and the disorder atoms were refined isotropically. The parts containing C14A and C14B, C25A and C25B, C26A and C26B, C27A and C27B, C28A and C28B, C55A and C55B, O7A and O7B, O16A and O16B were refined as parts of disordered carbon and oxygen atoms respectively.

Crystal data for ***2b***:

$C_{40}H_{52}O_{16}P_4S_4$ $CHCl_3$, Fw = 1160.31, crystal dimensions = 0.3 × 0.25 × 0.25 mm, colorless block, monoclinic, space group $P2_1/c$, a = 18.964 (4), b = 11.944 (2), c = 24.254 (5) Å, α = 90°, β = 109.415 (2)°, γ = 90°, V = 5181.3 (18) Å3, Z = 4, MoKα radiation (λ= 0.71075 Å), T = 120K, μ(Mo Kα)=0.310 mm^{-1}, 68866 measured reflections, 11766 unique reflections (Rint = 0.0380), 11244 observed reflections, 855 parameters, R = 0.0487 (I>2.00 σ(I)), wR = 0.1216 (all data), refined against [F], GOF = 1.104. Several carbons s of diethyl phosphate moiety showed disorder and the disorder atoms were refined isotropically. The parts containing C10A and C10B, C17A and C17B, C18A and C18B were refined as parts of disordered carbon atoms.

Crystallographic data of the crystals have been deposited at the Cambridge Crystallographic Data Center in CIF format CCDC no. 1049894, 1049895. Copies of the data can be obtained free of charge on application to CCDC (deposit@ccdc.cam.ac.uk).

Liquid – Liquid extraction of Pd (II) ions from a PGM solution:

Platinum group metal (PGM) solution containing nine metal ions, namely, Al, Ba, Ce, Pd, Pt, Rh, La, Zr and Y was diluted 10 times with water and used for the liquid liquid extraction study. The pH of the diluted PGM solution was 0.65. The concentrations of metal cations in the diluted solution were determined by inductively coupled plasma atomic emission spectrometry(ICP-AES) and listed in **ESI Table 1**.

In a 50 mL of tube, 10 mL of **2a** or **2b** (1 mM) in $CHCl_3$ was mixed with the diluted PGM solution (10 mL). The mixture was then shaken at 300 strokes/min for 24 h. The concentrations metal ions remaining in the aqueous phase, [M]aq, were determined by ICP-AES. Compounds**2a** and **2b** were highly selective and efficient towards Pd (II) ions in PGM solutions. Compound **2a** extracts 87.6% Pd along with 18.6% of Zr and compound **2b** extracts 83.2% Pd from PGM solution (**ESI Table 2**). Any other metal ions were not extracted in the PGM solution.

Liquid-Liquid extraction of Pd(II) ions:

Liquid-Liquid extraction studies were performed in triplicate at room temperature with 1 mM of **2a** (10 mL) in $CHCl_3$ and 1 mM $PdCl_2$ in HCl (10 mL) in glass bottles. The mixture was shaken at 300 strokes/min for desired time. The concentration of Pd(II) ions in the aqeous phase was measured using ICP-AES.

The extractability (E%) was calculated 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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