



Macrocyclic cyclodiphosphazane $[\{P(\mu\text{-}^t\text{BuN})\}_2(\text{O} - m - \text{C}_6\text{H}_4\text{CHNCH}_2)_2]_2$: synthesis of chalcogen derivatives and gold(I) complex

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Abstract. The synthesis of a Schiff base-appended macrocycle $[\{P(\mu\text{-}^t\text{BuN})\}_2(\text{O} - m - \text{C}_6\text{H}_4\text{CHNCH}_2)_2]_2$ (**1**) containing cyclodiphosphazane moieties is described. Reactions of **1** with H_2O_2 and elemental selenium yielded derivatives tetrakis(oxide) $[\{P(\text{O})(\mu\text{-}^t\text{BuN})\}_2(\text{O} - m - \text{C}_6\text{H}_4\text{CHNCH}_2)_2]_2$ (**2**) and tetrakis(selenide) $[\{P(\text{Se})(\mu\text{-}^t\text{BuN})\}_2(\text{O} - m - \text{C}_6\text{H}_4\text{CHNCH}_2)_2]_2$ (**3**), in ~80% yield. Tetragold complex $[\text{Au}_4\text{Cl}_4\{P(\mu\text{-}^t\text{BuN})\}_2(\text{O} - m - \text{C}_6\text{H}_4\text{CHNCH}_2)_2]_2$ (**4**) was prepared by reacting **1** with $[\text{AuCl}(\text{SMe}_2)]$ in 1:4 molar ratio. All the compounds have been characterized by various spectroscopic techniques. The molecular structure of **3** was confirmed by single crystal X-ray analysis.

Keywords. Cyclodiphosphazanes; chalcogen; selenide; macrocycle; gold(I).

1. Introduction

Cyclodiphosphazanes are the major class of saturated four-membered inorganic heterocycles containing phosphorus and nitrogen atoms arranged alternately with phosphorus in trivalent state.^{1–3} The dichlorocyclodiphosphazanes, *cis*- $[\text{CIP}(\mu\text{-NR})_2]$ are used as building blocks in the synthesis of a wide range of phosphorus-nitrogen macrocycles.^{4–10} Both main group and transition metal chemistry of cyclodiphosphazanes have been extensively studied in the last two decades.^{11–16} Many of these derivatives find applications in organometallic chemistry, macrocyclic chemistry, antitumor studies,^{17,18} chemical sensors,¹⁹ luminescence²⁰ and homogeneous catalysis.^{21–25} Recently cyclodiphosphazanes have been utilized in designing metal-organic frameworks with sodalite²⁶ and diamondoid²⁷ topologies and also in biradical based small molecule activations.^{28–33}

Cyclodiphosphazanes can exist as *cis* and *trans* isomers with respect to the exocyclic phosphorus substituents with a small energy difference in solution

as well as in the solid state.³⁴ *Cis-trans* isomerization in solution is very facile and leads to kinetically stable *cis*-isomers.³⁵ Our group has extensively studied the transition metal chemistry and various applications of cyclodiphosphazanes.^{36–44} Herein, we report the synthesis of a macrocyclic Schiff base appended cyclodiphosphazane $[\{P(\mu\text{-}^t\text{BuN})\}_2(\text{O} - m - \text{C}_6\text{H}_4\text{CHNCH}_2)_2]_2$ (**1**) and its tetrakis(oxide), tetrakis(selenide) derivatives and a tetragold complex.

2. Experimental

2.1 General procedures

All manipulations were performed using standard vacuum-line and Schlenk techniques under nitrogen atmosphere unless otherwise stated. All the solvents were purified by conventional methods⁴⁵ and distilled prior to use. The compounds, *cis*- $[\text{CIP}(\mu - \text{N}^t\text{Bu})_2]$ ⁴⁶ and $[\text{AuCl}(\text{SMe}_2)]$ ⁴⁷ were prepared according to the published procedures. H_2O_2 (30% aq.) and elemental selenium were from Merck Life Science Pvt. Ltd, Mumbai, India and used as received. All other chemicals were obtained from commercial sources and purified prior to use.

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2.2 Instrumentation

The NMR spectra were recorded at the following frequencies: 500 MHz (^1H), 202 MHz (^{31}P) and 125 MHz (^{13}C) using Bruker Avance-500 MHz spectrometer. The $^{13}\text{C}\{^1\text{H}\}$ and $^{31}\text{P}\{^1\text{H}\}$ NMR spectra were acquired using broad band proton decoupling. The spectra were recorded in CDCl_3 solutions with CDCl_3 as an internal lock; chemical shifts of ^1H and $^{13}\text{C}\{^1\text{H}\}$ NMR spectra are reported in ppm downfield from TMS, which was used as internal standard. The chemical shifts of $^{31}\text{P}\{^1\text{H}\}$ NMR spectra are referred to 85% H_3PO_4 (in D_2O) used as external standard. The microanalyses were performed using a Carlo Erba Model 1112 elemental analyzer. Mass spectra were recorded on BRUKER mass spectrometer using Electro-spray ionization mass spectrometry (ESI-MS) method. The melting points were observed in capillary tubes and are uncorrected.

2.3 Synthesis of $\{[P(\mu\text{-}^t\text{BuN})]_2(\text{O} - m - \text{C}_6\text{H}_4\text{CHNCH}_2)_2\}_2$ (**1**)

To a well stirred mixture of $[\text{HO} - m - \text{C}_6\text{H}_4\text{CHNCH}_2]_2$ (1 g, 3.72 mmol) and triethylamine (1.04 mL, 7.45 mmol) in toluene (50 mL), a solution of $[\text{BuNPCl}]_2$ (1.02 g, 3.72 mmol) also in toluene (25 mL) was added dropwise at 0°C and the reaction mixture was allowed to warm to room temperature and then refluxed for 12 h. The reaction mixture was filtered through celite and the solvent was evaporated under reduced pressure to give compound **1** as off-white solid. Recrystallization from a mixture of dichloromethane (5 mL) and petroleum ether (3 mL) at 10°C afforded analytically pure samples of **1** as colorless crystals. Yield 63% (1.10 g). M.p.: $207\text{--}210^\circ\text{C}$ (dec). Anal. Calcd. for $\text{C}_{48}\text{H}_{66}\text{O}_4\text{N}_8\text{P}_4 \cdot \text{CH}_2\text{Cl}_2$: C, 61.43; H, 6.93; N, 11.91%. Found: C, 61.29; H, 6.83; N, 11.64%. HRMS (ESI): m/z Calc. for $\text{C}_{48}\text{H}_{66}\text{O}_4\text{N}_8\text{P}_4(\text{M} + \text{H})$: 943.4230, Found: 943.4156. FT-IR (KBr disc) cm^{-1} : ν_{CH} : 2961, 2930, 2863, $\nu_{\text{C}=\text{N}}$: 2360, 1641, 1583, 1458, 1365, 1238 s^1 . ^1H NMR (400 MHz, CDCl_3): δ 8.19 (s, 4H, HC=N), 7.52–7.05 (m, 16H, Ar-H), 3.86 (s, 8H, H_2CN), 1.32 (s, 36H, $^t\text{CH}_3$) ppm. $^{13}\text{C}\{^1\text{H}\}$ NMR (125 MHz, CDCl_3): 162.1 (HC=N), 153.7 (Ar-C), 137.6 (Ar-C), 129.5 (Ar-C), 129.3 (Ar-C), 123.1 (Ar-C), 122.9 (Ar-C), 120.8 (Ar-C), 61.8 (N- CH_2), 31.4 ($^t\text{C}(\text{CH}_3)_3$) ppm. $^{31}\text{P}\{^1\text{H}\}$ NMR (202 MHz, CDCl_3): δ 138.3 ppm.

2.4 Synthesis of $\{[P(\text{O})(\mu\text{-}^t\text{BuN})]_2(\text{O} - m - \text{C}_6\text{H}_4\text{CHNCH}_2)_2\}_2$ (**2**)

To a solution of **1** (0.05 g, 0.053 mmol) in tetrahydrofuran (15 mL), H_2O_2 (30% aq.) (0.0144 g, 0.424 mmol) was added and the reaction mixture was stirred for 3 h at room temperature. After the volatiles were evaporated under reduced pressure, solid residue obtained was recrystallized from diethyl ether to give the analytically pure product of **2** as colorless crystalline solid. Yield 80% (0.042 g). M.p.: $182\text{--}185^\circ\text{C}$ (dec). Anal. Calcd. for $\text{C}_{48}\text{H}_{66}\text{O}_4\text{N}_8\text{P}_4\text{O}_4 \cdot \text{CH}_2\text{Cl}_2$:

C, 54.00; H, 6.10; N, 11.74%. Found: C, 54.37; H, 6.52; N, 11.48%. FT-IR (KBr disc) cm^{-1} : ν_{CHN} : 2965 s, 1698 m, $\nu_{\text{C}=\text{C}}$: 1585 m, 1482 m, 1448 m, $\nu_{\text{C}-\text{H}}$: 1372 m, $\nu_{\text{P}=\text{O}}$: 1262 vs, 1091 vs, 922 s, 800 vs cm^{-1} . ^1H NMR (500 MHz, CDCl_3): δ 7.86 (s, 4H, HC=N), 7.76–7.38 (m, 16H, Ar-H), 3.75 (s, 8H, H_2CN), 1.47 (s, 36H, $^t\text{CH}_3$) ppm. $^{31}\text{P}\{^1\text{H}\}$ NMR (202 MHz, CDCl_3): δ -7.81(s) ppm.

2.5 Synthesis of $\{[P(\text{Se})(\mu\text{-}^t\text{BuN})]_2(\text{O} - m - \text{C}_6\text{H}_4\text{CHNCH}_2)_2\}_2$ (**3**)

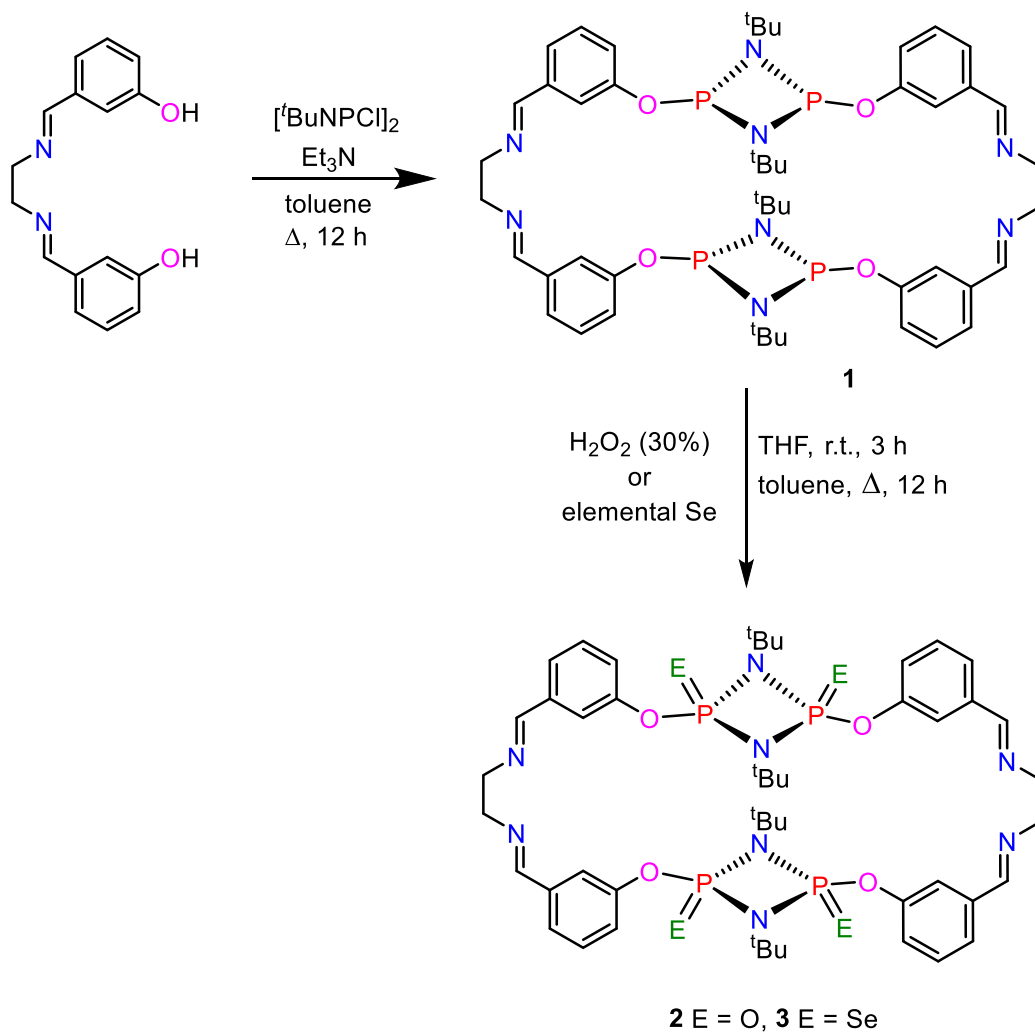
This was synthesized by reacting **1** (0.03 g, 0.031 mmol) with elemental selenium (0.0195 g, 0.248 mmol) in toluene (15 mL) under refluxing condition for 12 h. After completion of the reaction, the reaction mixture was filtered through celite. The solvent was removed under reduced pressure to afford **3** as off-white solid. Recrystallization from toluene/petroleum ether gave colorless crystals. Yield 78% (0.03 g). M.p.: $207\text{--}209^\circ\text{C}$ (dec). Anal. Calcd. for $\text{C}_{48}\text{H}_{66}\text{O}_4\text{N}_8\text{P}_4\text{Se}_4 \cdot \text{toluene}$: C, 48.81; H, 5.36; N, 8.28%. Found: C, 48.53; H, 4.93; N, 8.21%. MS (ESI): m/z Calc. for $\text{C}_{48}\text{H}_{64}\text{N}_8\text{O}_4\text{P}_4\text{Se}_4(\text{M} + \text{H})$: 1260.0661, Found: 1261.0614. FT-IR (KBr disc) cm^{-1} : ν_{CHN} : 2967 s, 1943 m, 1867 m, $\nu_{\text{C}=\text{N}}$: 1703 $\nu_{\text{C}=\text{C}}$: 1646 s, 1581 s, 1443 s, $\nu_{\text{C}-\text{H}}$: 1372 m, $\nu_{\text{P}=\text{Se}}$: 1259–1234 (br) vs, 1049 s, 922 s, 894 s cm^{-1} . ^1H NMR (400 MHz, CDCl_3): δ 8.19 (s, 4H, HC=N), 7.52–7.05 (m, 16H, Ar-H), 3.86 (s, 8H, H_2CN), 1.32 (s, 36H, $^t\text{CH}_3$) ppm. $^{31}\text{P}\{^1\text{H}\}$ NMR (202 MHz, CDCl_3): δ 37.5 (s, $^1J_{\text{SeP}} = 982$ Hz) ppm.

2.6 Synthesis of $[\text{Au}_4\text{Cl}_4\{[P(\mu\text{-}^t\text{BuN})]_2(\text{O} - m - \text{C}_6\text{H}_4\text{CHNCH}_2)_2\}_2]$ (**4**)

A solution of $\text{AuCl}(\text{SMe}_2)$ (0.037 g, 0.127 mmol) in dichloromethane (5 mL) was added to a solution of **1** (0.03 g, 0.032 mmol) in the same solvent (15 mL) and the reaction mixture was stirred at room temperature for 6 h under dark. After the volatiles were removed under reduced pressure, the resulting off-white solid was crystallized from dichloromethane/petroleum ether. Yield 77% (0.046 g). M.p.: $180\text{--}183^\circ\text{C}$ (dec). Anal. Calcd. for $\text{C}_{48}\text{H}_{66}\text{O}_4\text{N}_8\text{P}_4\text{Au}_4\text{Cl}_4$: C, 30.82; H, 3.45; N, 5.99%. Found: C, 31.37; H, 3.83; N, 6.24%. MS (ESI): m/z Calc. for $\text{C}_{48}\text{H}_{64}\text{Au}_4\text{Cl}_4\text{N}_8\text{O}_4\text{P}_4$ $[\text{M} - 2\text{AuCl} + \text{Na}]^+$: 1427.2607, Found: 1427.7053. FT-IR (KBr disc) cm^{-1} : ν_{CHN} : 2972 s, 2586 m, 2487 m, 2034 m, 1642br, s, $\nu_{\text{C}=\text{C}}$: 1376 m, 1217br, s, 1103 m, 917 m cm^{-1} . ^1H NMR (500 MHz, CDCl_3): δ 8.24 (s, 4H, HC=N), 7.86–7.17 (m, 16H, Ar-H), 3.86 (s, 8H, $\text{H}_2\text{C}=\text{N}$), 1.71 (s, 36H, $^t\text{CH}_3$) ppm. $^{31}\text{P}\{^1\text{H}\}$ NMR (202 MHz, CDCl_3) δ 101.2 ppm.

2.7 X-ray crystallography

A crystal of tetrakis(selenide) **3** suitable for single crystal X-ray analysis was mounted on a Cryoloop with a drop of Paratone oil and placed in the cold nitrogen stream of the



Scheme 1. Synthesis of **1** and its tetrakis(chalcogenides).

Kryoflex attachment of the Bruker APEX CCD diffractometer. A full sphere of data was collected using different sets of frames using the APEX2⁴⁸ program suite. For **3**, the raw data were reduced to F^2 values using the SAINT software.⁴⁸ Multiple measurements of equivalent reflections provided the basis for an empirical absorption correction as well as a correction for any crystal deterioration during the data collection (SADABS⁴⁸). The structure was solved by direct method (SHELXS⁴⁹) and refined by full-matrix least-squares procedures on F^2 using SHELXL⁴⁹ (SHELXTL program package⁴⁹). Hydrogen atoms attached to carbon were placed in the calculated positions and included as riding contributions with isotropic displacement parameters tied to those of the attached non-hydrogen atoms. Those attached to nitrogens were placed in locations derived from a difference map and also included as riding contributions as for the others. Crystallographic data (including structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC No. 1560989 (Compound **3**).

3. Results and Discussion

3.1 Synthesis of **1** and its tetrakis(chalcogenides)

The reaction of dichlorocyclodiphosphazane ($[t\text{BuNPCl}_2]_2$) with an equimolar amount of $[\text{HO} - m - \text{C}_6\text{H}_4\text{CHNCH}_2]_2$ (**3**, 3'-((1E,1'E)-(ethane-1,2-diylbis(azanylylidene))bis-(methanylylidene))diphenol) in the presence of triethylamine in toluene under refluxing condition yielded a macrocyclic compound $[\{\text{P}(\mu\text{-}^t\text{BuN})\}_2(\text{O} - m - \text{C}_6\text{H}_4\text{CHNCH}_2)_2]_2$ (**1**) as shown in Scheme 1. The $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum of **1** showed a single resonance at 138.3 ppm and the mass spectrum showed m/z ion peak for $[\text{M} + \text{H}]^+$ at 943.4156 depicting a dimeric structure.

Treatment of **1** with H_2O_2 (30%) or elemental selenium resulted in the formation of tetrachalcogenides, $[\{\text{P}(\text{O})(\mu\text{-}^t\text{BuN})_2\}_2(\text{O} - m - \text{C}_6\text{H}_4\text{CHNCH}_2)_2]_2$ (**2**) and $[\{\text{P}(\text{Se})(\mu\text{-}^t\text{BuN})_2\}_2(\text{O} - m - \text{C}_6\text{H}_4\text{CHNCH}_2)_2]_2$

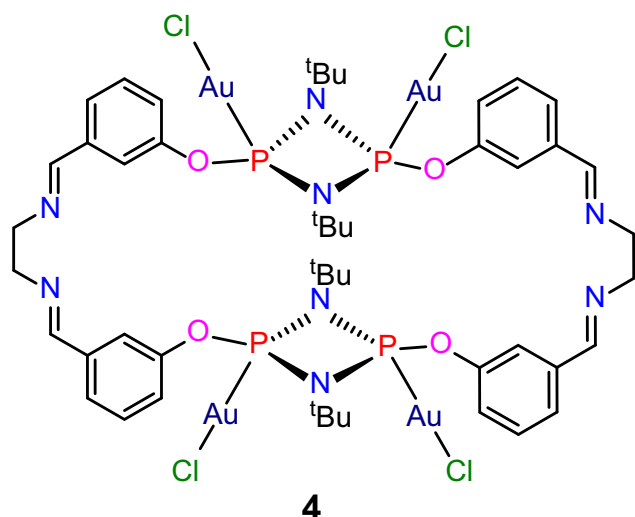


Figure 1. Tetragold complex **4**.

(**3**), respectively. The $^{31}\text{P}\{^1\text{H}\}$ NMR spectra of **2** and **3** showed single resonances at -7.8 and 37.5 ppm, respectively. The tetrakis(selenide) showed characteristic ^{77}Se satellites with a large $^1J_{\text{PSe}}$ coupling of 982 Hz. The phosphorus chemical shifts indicate the symmetric nature of the molecule with all phosphorus atoms being magnetically equivalent. ^1H NMR data is consistent with the structures proposed for **1-3**. Attempts to grow crystals of **1** suitable for single crystal X-ray analysis have been unsuccessful. However, the structure of tetrakis(selenide) **3** was confirmed by single crystal X-ray analysis.

The reaction of **1** with four equivalents of $[\text{AuCl}(\text{SMe}_2)]$ in dichloromethane afforded a tetragold derivative $[(\text{Au}_4\text{Cl}_4)\{\{\text{P}(\mu\text{-}^t\text{BuN})\}_2(\text{O}-m-\text{C}_6\text{H}_4\text{CHNCH}_2)_2\}]_2$ (**4**) in 77% yield (Figure 1). The $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum of complex **4** showed a single resonance at

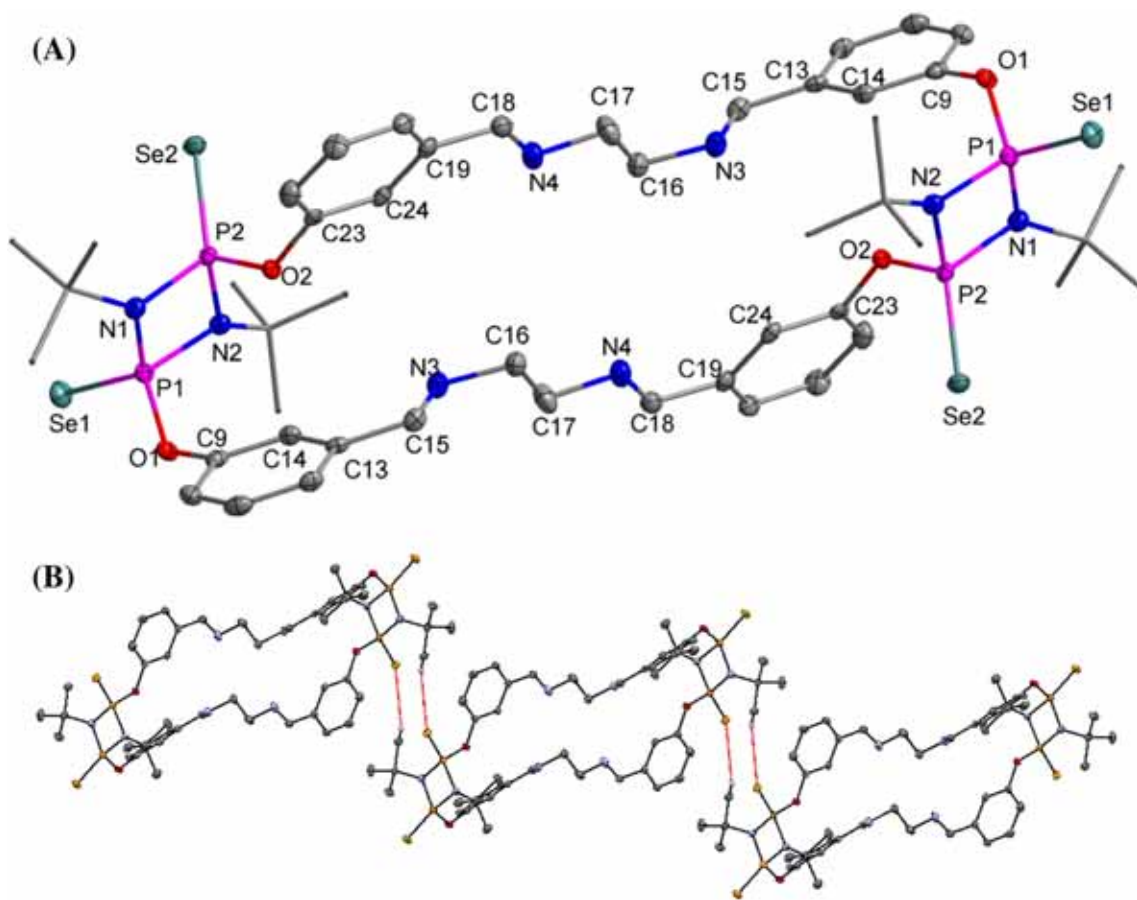


Figure 2. (A) Molecular structure of $[\{\text{P}(\text{Se})(\mu\text{-}^t\text{BuN})\}_2(\text{O}-m-\text{C}_6\text{H}_4\text{CHNCH}_2)_2]_2$ (**3**). (B) The core of 1D polymeric structure of **3** showing Se-H-C interactions. All hydrogen atoms have been omitted for clarity. Thermal ellipsoids are drawn at the 50% probability level. Selected bond distances (\AA) and bond angles ($^\circ$): Se1-P1 = $2.067(2)$, P1-O1 = $1.600(5)$, P1-N1 = $1.673(6)$, P1-P2 = 2.488 O1-P1-N1 = $108.9(3)$, O1-P1-N2 = $110.2(3)$, N2-P1-N1 = $84.4(3)$, N1-P1-Se1 = $122.5(2)$.

101.2 ppm and the mass spectrum showed m/z ion peak for $[M-2AuCl + Na]^+$ at 1427.7053.

3.2 Molecular structure of **3**

The molecular structure of **3** was confirmed by single crystal X-ray analysis. The slow evaporation of petroleum ether into the saturated solution of **3** in dichloromethane afforded crystals suitable for single crystal X-ray study. The cyclodiphosphazane moieties adopted *cis*-conformation, whereas the Schiff's base linker adopted *trans*-conformation with respect to the ethylenediamine linkers. All four selenium atoms are projected exterior to the molecule. The macrocyclic compound **3** is centrosymmetric with puckered conformation as shown in Figure 2. The molecule exhibits one dimensional polymeric structure due to the intermolecular interaction between selenium atoms and C-H of one of the tertiary butyl groups of N_2P_2 ring on both sides with Se-H-C angle of 139.9° .

4. Conclusions

A new Schiff base appended dimeric cyclodiphosphazane derivative $[\{P(\mu\text{-}^t\text{BuN})\}_2(O\text{-}m\text{-}C_6H_4CHNCH_2)_2]_2$ (**1**) was synthesized by reacting dichlorocyclodiphosphazane with 3, 3'-((1E,1'E)-(ethane-1,2-diylbis(azanylylidene))bis-(methanylylidene))diphenol. Compound **1** readily reacts with H_2O_2 and Se_8 to give the corresponding tetrachalcogenides. The tetragold complex **4** was obtained by reacting **1** with four equivalents of $[AuCl(SMe_2)]$. The molecular structure of tetraselenide was established by single crystal X-ray analysis. Four selenium atoms are projected exterior from the macrocyclic unit making it an ideal ligand for moderately soft transition elements as well as lanthanides. Presently we are exploring the utility of compound **1** and its tetrachalcogenides to synthesize 2D- and 3D-coordination polymers and metal organic frameworks.

Supplementary Information (SI)

NMR and IR spectra for compounds **1–4** and crystallographic data for **3** are provided at www.ias.ac.in/chemsci. Crystallographic data for compound **3** has been deposited at the Cambridge Crystallographic Data Centre with CCDC no. 1560989 (Compound **3**). These data can be obtained free of charge at www.ccdc.cam.ac.uk/conts/retrieving.html [or from the Cambridge Crystallographic Data Centre (CCDC), 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44(0)1223-336033; E-mail: deposit@ccdc.cam.ac.uk].

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