

# Contrasting coordination behaviour of 22-membered chalcogenaaza (Se, Te) macrocycles towards Pd(II) and Pt(II): Isolation and structural characterization of the first metallamacrocycle with a C–Pt–Se linkage†

Snigdha Panda,<sup>a</sup> Harkesh B. Singh<sup>\*a</sup> and Ray J. Butcher<sup>b</sup>

<sup>a</sup> Department of Chemistry, Indian Institute of Technology, Bombay, Powai, Mumbai 400076, India.

E-mail: chhsia@chem.iitb.ac.in

<sup>b</sup> Department of Chemistry, Howard University, Washington D.C. 20059, USA

Received (in Cambridge, UK) 6th October 2003, Accepted 24th November 2003

First published as an Advance Article on the web 8th January 2004

Interaction of the 22-membered selenaza macrocycle **3** with Pt(II) leads to the formation of the novel cationic Pt(IV) metallamacrocyclic complex **5** via the oxidative addition of a C–Se bond to Pt(II), whereas corresponding reactions of **3** and **4** with Pd(II) afford cationic complexes **6** and **7** with differing ligating properties.

The coordination chemistry of chalcogen (Se/Te) containing macrocycles is a subject of growing interest.<sup>1</sup> As a part of our research on the ligating properties of mixed donor macrocycles, we have recently reported novel Schiff base chalcogenaaza macrocycles **1** and **2** and characterized their Ni(II), Pd(II) Pt(II), Hg(II) complexes.<sup>2–5</sup> Attempted complexation reaction of **1** with Pd(II) led to partial hydrolysis of the macrocycle<sup>5</sup> whereas treatment of **2** with Pt(II) and Hg(II) afforded transmetallated products.<sup>2,3</sup> We are now interested in the ligating property of the reduced Schiff base chalcogenaaza macrocycles which would be more robust and flexible to give stable complexes. Herein we report complexation reactions of macrocycles **3** and **4** with Pd(II) and Pt(II).

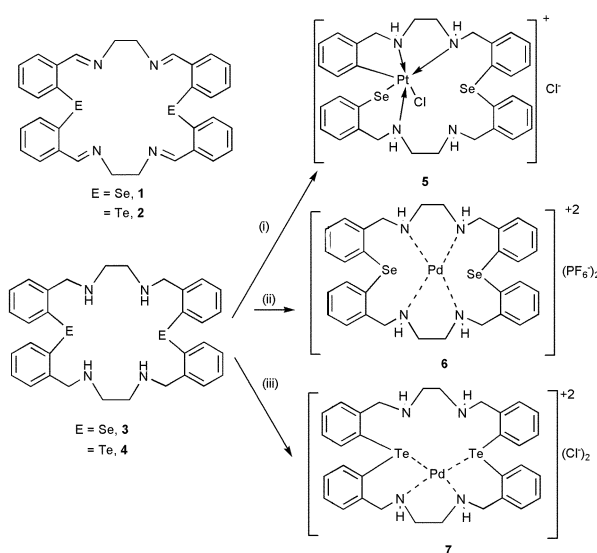
Refluxing equimolar amounts of **3** and PtCl<sub>2</sub> in MeOH for 15 minutes yielded a clear solution of the complex **5** which was crystallized by slow diffusion of ether into the reaction mixture at room temperature as brick red colored crystals (Scheme 1). The complex formed was poorly soluble in most of the organic solvents and only partially soluble in MeOH. The elemental analysis data suggested the formation of a 1:1 (ligand : metal) complex. The molecular ion peak was not observed in ESI-MS, however, the peak at *m/z* 863 corresponding to M<sup>+</sup>–Cl<sup>–</sup>+2H<sub>2</sub>O was observed. The <sup>1</sup>H

and <sup>13</sup>C NMR spectra of complex are too complicated for complete analysis. Due to the partial solubility of the complex in MeOH, no satisfactory <sup>77</sup>Se NMR could be recorded even after over night data acquisition.‡

The X-ray crystal structure (Fig. 1) shows the formation of an unexpected complex **5** with a C–Pt–Se linkage.§ Complex **5** is presumably formed by oxidative addition of one of the C–Se bonds of the macrocycle **3** to Pt(II) forming a 23-membered cationic metallamacrocycle. The structure exhibits a typical octahedral geometry around Pt(IV) center.

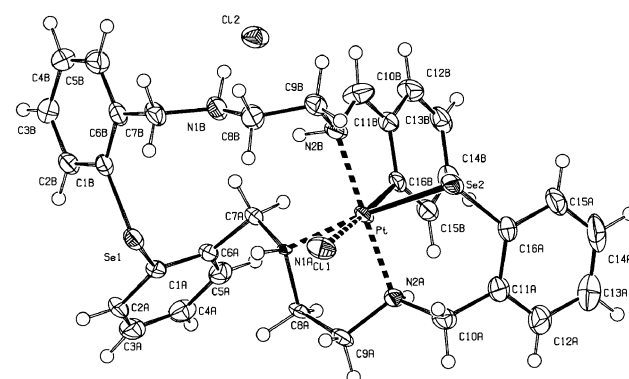
The behaviour of the macrocycle to form the cationic Pt(IV) complex by oxidative addition of C–Se bond to Pt(II) center is in contrast to the reported stable Pt(II) and Pt(IV) complexes with homodonor and mixed donor cyclic selenoether ligands.<sup>6,7</sup> The facile oxidative addition in this case may be facilitated by the more polar nature of C–Se bond which results from the N→Se intramolecular interaction present in parent macrocycle.<sup>8</sup> Though the oxidative addition of halogens and the alkyl halides to the Pt(II) center are common,<sup>9</sup> there is only one example of oxidative addition of C–Se bond to Pt(II).<sup>10</sup> Another novel feature of the metallamacrocycle **5** is the stability of the cationic Pt(IV) species with a selenolate linkage in the macrocyclic ring. Puddephatt *et al.* have reported the synthesis of the first cationic Pt(IV) selenolate which was formed by oxidative addition of much polar Hg(II)–Se bond of an adamantanoid compound,<sup>11</sup> compound **5** is the first example of a metallamacrocycle with a cationic Pt(IV) selenolate which has been isolated by the oxidative addition of C–Se bond.

The Pd(II) complexes **6** and **7** were prepared by refluxing **3** with Pd(C<sub>6</sub>H<sub>5</sub>CN)<sub>2</sub>Cl<sub>2</sub> followed by addition of NH<sub>4</sub>PF<sub>6</sub> and **4** with PdCl<sub>2</sub> respectively. The elemental analysis data and ESI-MS suggested the formation of 1:1 complexes. The <sup>77</sup>Se NMR spectrum for complex **6** exhibited a single signal at 869 ppm, which is considerably downfield shifted compared to the free ligand value (329 ppm), and indicates metal coordination to selenium in solution state which is in contrast to the solid state structure (*vide infra*).



**Scheme 1** Reagents and conditions: (i) PtCl<sub>2</sub>, MeOH (ii) Pd(C<sub>6</sub>H<sub>5</sub>CN)<sub>2</sub>Cl<sub>2</sub>, NH<sub>4</sub>PF<sub>6</sub>, MeOH (iii) PdCl<sub>2</sub>, MeOH

† Electronic supplementary information (ESI) available: synthesis and characterization of ligands **1** and **3**, structure refinement details for **7**. See <http://www.rsc.org/suppdata/cc/b3/b312358h/>

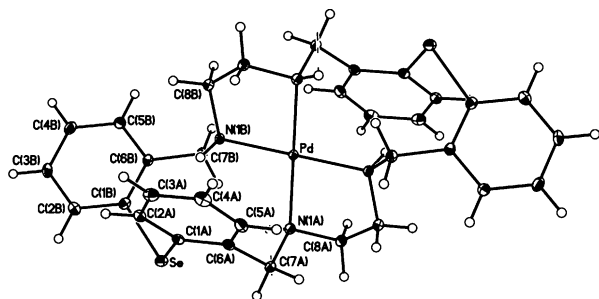


**Fig. 1** An ORTEP diagram of Pt complex **5**. Selected bond lengths (Å) and bond angles (°): Pt–C(16B) 2.009(5), Pt–Se(2) 2.4165(7), Pt–N(2B) 2.0384(4), Pt–N(2A) 2.050(4), Pt–N(1A) 2.180(3), Pt–Cl(1) 2.4292(13), C(16B)–Pt–N(2B) 81.52(19), C(16B)–Pt–Se(2) 88.54(12), N(2A)–Pt–Se(2) 93.88(11), N(2A)–Pt–N(1A) 82.35(14), N(2B)–Pt–N(1A) 97.27(15).

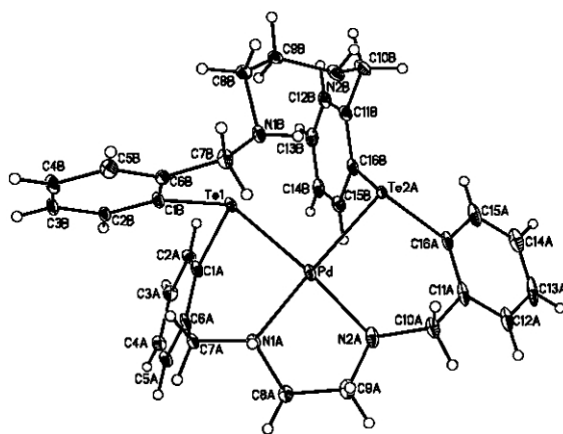
Whereas the  $^{125}\text{Te}$  NMR spectrum in  $\text{DMSO-d}_6$  of complex **7** showed a peak at 710 ppm, which disappeared after half an hour due to decomposition of the complex. The molecular structures of Pd(II) complexes **6** and **7** show contrasting coordination behavior of Pd(II) towards ligands. The structure of complex **6** (Fig. 2) shows coordination of Pd(II) to only hard N donor atoms. This is in contrast to isolation of Pd(II) complexes of mixed donor Se/Te macrocycles containing O or P where Pd(II) coordinates to soft donor centers Se/Te.<sup>7</sup> This anomalous behaviour may be due to the formation of stable 5-membered chelate rings rather than the formation of 6-membered chelate rings which would result on coordination to Se. Interestingly, the molecular structure (Fig. 3) of complex **7** shows coordination to two nitrogen and two tellurium atoms which is similar to the parent Schiff base macrocycle Pd(II) complex.<sup>5</sup> The coordination of Te in **7** may be due to the greater  $\sigma$ -donor property of the Te over Se leading to soft–soft interaction and stabilization of the 6-membered chelate ring.

There are several examples of metallamacrocycles containing Pt(II) formed by metal–ligand interactions;<sup>12</sup> complex **5** is the first example of a metallamacrocycle formed by oxidative addition of a C–Se bond to Pt(II) center. Further investigation on coordination behavior of these mixed donor chalcogenaza macrocycles is in progress.

We are grateful to the Department of Science and Technology (DST), New Delhi for funding this work.



**Fig. 2** An ORTEP diagram of Pd complex **6**. Selected bond lengths (Å) and bond angles (°): Pd–N(1B) 2.063(2), Pd–N(1A), 2.066(3), N(1B)–Pd–N(1A)#1 180.000(1), N(1B)–Pd–N(1A)#1 83.73(10).



**Fig. 3** An ORTEP diagram of Pd complex **7**. Selected bond lengths (Å) and bond angles (°): Te(1)–Pd 2.5611(11), Te(2B)–Pd 2.422(3), Pd–N(1A) 2.112(5), Pd–N(2A) 2.117(6), Te(1)–Pd–Te(2A) 89.94(3), N(1A)–Pd–Te(1) 93.98(14), N(1A)–Pd–N(2A) 84.0(2), N(2A)–Pd–Te(2A) 94.02(17).

## Notes and references

‡ *Analytical data*: **5** Yield, 0.074 g, 52%, mp 252 °C (d); Elemental analysis calcd (%) for  $\text{C}_{32}\text{H}_{40}\text{N}_4\text{O}_2\text{Se}_2\text{PtCl}_2$ : C 41.05, H 4.30, N 5.99; found: C 41.93, H 3.46, N 6.41. **6** Yield 0.087 g, 56%, mp. 247–249 °C (d), Elemental analysis calcd (%) for  $\text{C}_{32}\text{H}_{36}\text{N}_4\text{Se}_2\text{PdP}_2\text{F}_{12}$ : C 37.28, H 3.52, N 5.43; found: C 36.88, H 3.68, N 5.02. **7** Yield: 0.2 gm (78%); mp 196(d); Analysis calcd (%) for  $\text{C}_{32}\text{H}_{36}\text{N}_4\text{Te}_2\text{PdCl}_2$ : C 41.46, H 3.88, N 6.04; found C 40.88, H 4.22, N 5.77.

§ *Crystal data for 5*:  $\text{C}_{32}\text{H}_{39}\text{Cl}_2\text{N}_4\text{O}_2\text{PtSe}_2$ ,  $M = 935.58$ ; triclinic, space group  $P\bar{1}$ ,  $a = 9.9635(19)$ ,  $b = 10.210(2)$ ,  $c = 17.427(3)$  Å,  $\alpha = 94.196(3)$ ,  $\beta = 105.466(3)$ ,  $\gamma = 106.808(4)^\circ$   $V = 1613.7(7)$  Å<sup>3</sup>,  $Z = 2$ , 16279 reflections collected, 7802 independent reflections ( $R_{\text{int}} = 0.049$ ),  $R(R_w) = 0.0352(0.0801)$ . For **6**:  $\text{C}_{32}\text{H}_{36}\text{F}_{12}\text{N}_4\text{P}_2\text{PdSe}_2$ ,  $M = 1030.91$ ; triclinic, space group  $P\bar{1}$ ,  $a = 9.9501(14)$ ,  $b = 10.5010(15)$ ,  $c = 10.6403(16)$  Å,  $\alpha = 103.622(2)$ ,  $\beta = 117.296(2)$ ,  $\gamma = 103.042(3)^\circ$   $V = 885.6(2)$  Å<sup>3</sup>,  $Z = 1$ , 5787 reflections collected, 4045 independent reflections ( $R_{\text{int}} = 0.0277$ ),  $R(R_w) = 0.0330(0.0760)$ . For **7**:  $\text{C}_{32}\text{H}_{30}\text{Cl}_2\text{N}_4\text{O}_2\text{PdTe}_2$ ,  $M = 1035.26$ ; triclinic, space group  $P\bar{1}$ ,  $a = 12.072(6)$ ,  $b = 13.264(6)$ ,  $c = 14.527(7)$  Å,  $\alpha = 104.235(8)$ ,  $\beta = 107.668(9)$ ,  $\gamma = 110.244(8)^\circ$   $V = 1912.6(16)$  Å<sup>3</sup>,  $Z = 2$ , 13450 reflections collected, 8797 independent reflections ( $R_{\text{int}} = 0.0674$ ),  $R(R_w) = 0.0782(0.1844)$ . CCDC 221526–221528. See <http://www.rsc.org/suppdata/cc/b3/b312358h/> for crystallographic data in .cif or other electronic format.

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