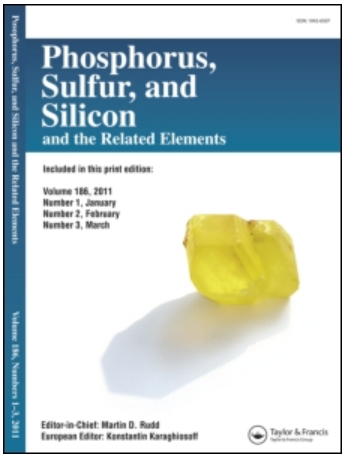


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# Design and Synthesis of Heteroatom Bearing Organoselenium Donor and its Reactivity towards Platinum (II) Metal

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Potentially tridentate ligand, phenylselenoethylaminopent-3-en-2-one [PhSe$(CH_2)_2$NH-C$(CH_3)$CHC(=O)$(CH_3)$], having (N,O,Se) donors set has been synthesized from the condensation of 2,4 pentanedione with Phenylselenoethylamine and its reactivity towards Pt(II) has been evaluated for extended reach structures.

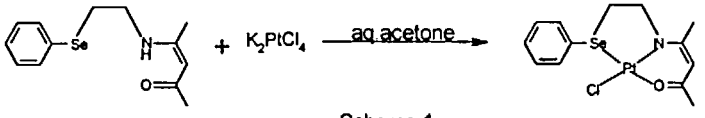
*Keywords:* Design; synthesis; tridentate (N, O, Se) donors; Pt(II) complexes; characterization; intermolecular interactions

## INTRODUCTION

Non-bonded interactions due to heavier chalcogens at *intramolecular level* in organochalcogens play an important role and were found responsible for their unusual structures and novel physical, optical, biological and catalytic properties[1,2]. Work in our laboratory has been directed towards the design and understanding of synthetic methods of new organoselenium donors[3,4], in a view to develop a rational assembly of individual components to achieve extended-reach structures.

## RESULTS AND DISCUSSION

The synthesis of the ligand $[PhSe(CH_2)_2NH\text{-}C(CH_3)CHC(=O)(CH_3)]$, is straightforward and can be prepared by the condensation of phenylselenoethylamine, $PhSe(CH_2)_2NH_2$ and 2,4-petanedione in refluxing methanol. The higher denticity of the ligand, contrasting hard/soft character, orientation of heterofunctional donor groups and non-bonded interactions due to selenium are the important factors that may have significant influence on the structure of the resulting metal complexes. The ligand is existing mainly in 'keto-form' in solution and as expected may undergo 'keto-enol' tautomerism in solution and various possible coordination modes are possible depending on the choice of the metal. A room temperature reaction between the ligand and $K_2PtCl_4$ in (1:1) molar ratio in aqueous acetone was sufficient to deprotonate the ligand and produce $[ClPtOC(CH_3)CH(CH_3)CN(CH_2)_2SeC_6H_5]$ as yellow solid (Refer to Scheme 1). Crystals suitable for X-ray analysis were grown from




Scheme 1

$CHCl_3$-$CH_3OH$ solution of the complex . The X-ray diffraction study revealed that the ligand with unusual steric demands prefers to coordinate platinum through all its heteroatom donor sites and adopts a square planar geometry around platinum. It is interesting to note that the ligand interacts with the metal center without any 'hard-soft' discrimination. This is mainly due to its 'designing' in such a way that it allows tuning of steric and electronic properties of metal center leading to new types of reactivity at the metal center. The complex prefers to form 'loose dimer' through weak non-covalent intermolecular (Pt...Pt) and (Pt...Se) interactions in

solid state (see Figure 1).

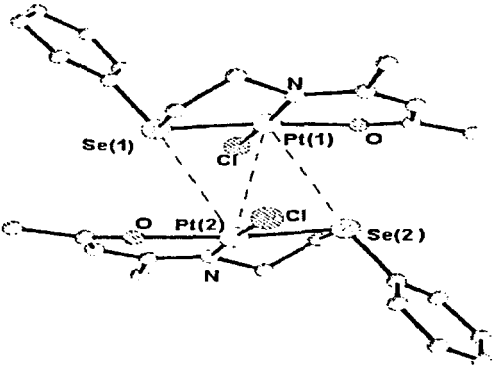



FIGURE 1 [PhSe$(CH_2)_2$N=C$(CH_3)$CHC$(CH_3)$OPtCl]; a loose dimer Pt...Pt=3.8375Å, Pt...Se=3.6955 Å

**Selected Bond Lengths and Angles:** distance(Å) Pt(1)-Se(1) 2.3563(3), Pt(1)-Cl 2.3350(6), Pt(1)-O 2.0033(1), Pt(1)-N 1.9939(1) ; angle(°) O-Pt(1)-N 92.91 , Cl-Pt(1)-O 87.04, Se(1)-Pt(1)-N 89.23, Se(1)-Pt(1)-Cl 91.37.

We are currently involved in design and synthesis of analogous organochalcogen donors which could give extended-reach structures.

## EXPERIMENTAL

All the solvents were dried and distilled before use. Potassiumtetrachloroplatinate(II) (Aldrich) was used as such.

Synthesis of Ligand

A methanolic solution of 2,4-pentanedione (1.0012g, 10 mmol) was added dropwise to a solution of phenylselenoethylamine (2g, 10mmol) in methanol (20ml) .The reaction mixture was then refluxed for 3h. The solvent was removed by evaporation giving yellowish-brown viscous mass. This residue was triturated with hexane several times giving yellow colored solid product in 85% yield .$^1$H NMR (300MHz, $CDCl_3$): δ10.96(1H,s, N*H*), δ7.57(2H) and δ7.31(3H)(*multiplets,* phenyl), δ4.98(1H,s, C*H*), δ3.52(2H,t, NC$H_2$), δ3.04(2H,t, SeC$H_2$), δ1.93(3H, s, OC$H_3$), δ1.86(3H,s, NC$H_3$)

Synthesis of [PhSe$(CH_2)_2$N.C$(CH_3)$CHC$(CH_3)$OPtCl]

To a solution of the ligand (0.3396g, 1.2mmol) in acetone (9 $cm^3$) an aqueous solution of $K_2PtCl_4$ (0.5g, 1.2mmol) was added dropwise. A yellow precipitate started appearing immediately .The reaction mixture was stirred for 2h at room temperature. The solid product was filtered and dried under vacuum. The product was recrystallized from $CH_2Cl_2$-$CH_3OH$ mixture giving yellow colored crystals of X-ray quality.$^1$H NMR (300MHz,$CDCl_3$): δ8.09(2H) δ7.42(3H)(*multiplets* Phenyl protons), δ5.02(1H,s, -C*H*-), δ4.12(1H,double triplet, C$H_2$), δ3.37(1H,t, C$H_2$), δ2.91(1H,t,C$H_2$),. δ2.53(1H,double triplet, C$H_2$), δ2.03(3H,s, C$H_3$), δ1.94(3H,s, C$H_3$)



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