Synthesis of Chalcogenolate Complexes of Platinum Group Metals as Molecular Precursor

Sandip Dey
Novel Materials & Structural Chemistry Division
Bhabha Atomic Research Centre

Abstract

Several complexes of palladium(II) and platinum(II) containing benzylselenolate of the types \( [M(\text{SeBz})_2]_n \), \([M(\text{SeBz})_2(P\text{P})]_n\), \([M_2\text{X}_2(\mu-\text{SeBz})_2(\text{PR}_3)_2] (X = \text{Cl} \text{ or Me}) \) and \([M_2\text{Cl}_2(\mu-Y)(\mu-\text{SeBz})(\text{PR}_3)_2] (Y = \text{Cl} \text{, } p_2 \text{, } \text{Bu}_3\text{S}) \) have been prepared. Similarly, a variety of products such as \([\text{PdCl}(\text{Se}^-\text{N})]_n\), \([\text{MCl}(\text{Se}^-\text{N})(\text{PR}_3)_2]\), \([\text{PtCl}(\text{Se}^-\text{N})]_n\) and \([\text{PtCl}(\mu-\text{Se}^-\text{N})_2(P\text{P})]_n\) have been synthesized using the ligand \(2-(\text{dimethylamino})\text{ethylselenolate (Me}_2\text{NCH}_2\text{CH}_2\text{Se} = \text{Se}^-\text{N})\). All these complexes were characterized by elemental analyses, IR, NMR ('\(\text{H}\), \(\text{C}\), \(\text{P}\), \(\text{Se}^{77}\), \(\text{Pt}^{195}\)) and UV/Vis spectroscopy. Structures of \([\text{PtCl}_2(\mu-\text{SeBz})_2(\text{PPR}_3)_2]\) and \([\text{PdCl}(\text{SeCH}_2\text{CH}_2\text{NMe}_2)_2]\) were established by X-ray diffraction analyses. The thermal behaviour of a few complexes has been investigated.

Introduction

Materials growth techniques like MOCVD, plasma CVD, etc. employ molecular precursors rather than the elements to synthesize low temperature solid state inorganic materials for electronic devices [1]. During the last decades platinum group metal chalcogenolates have attracted considerable attention as molecular precursors for the synthesis of metal chalcogenides for electronic devices [2]. The area of metal chalcogenolates has been dominated by thiolo complexes which in most cases have been isolated as non-volatile, insoluble (sparingly soluble) and polymeric complexes thus making them inconvenient as precursor for the preparation of metal chalcogenide [3]. To suppress polymerization several strategies have been explored such as, (a) strongly coordinating ligand such as tertiary phosphines, (b) sterically demanding chalcogenolate ion, (c) internally functionallised ligands containing both soft chalcogen and hard N donors [4-6]. The latter class of ligands not only yield low nuclearity complexes but also enhance complex stability. With the current interest in selenium containing inorganic materials and in pursuance of our program on the design and development of molecular precursors in NM&SCD, BARC, dibenzyl diselenide (Bz\(_2\text{Se}_2\)) and 2-dimethylaminoethyl diselenide (Me\(_2\text{NCH}_2\text{CH}_2\text{Se})_2\) were prepared and their palladium and platinum chemistry was explored.

Discussion

1 (i) Synthesis and characterization of benzylselenolate complexes

Sodium benzylselenolate has been prepared by the reductive cleavage of the Se-Se bond in Bz\(_2\text{Se}_2\) (due to slow photo-decomposition it was recrystallised every month from petroleum ether) with NaBH\(_4\) and the following Pd(II)/Pt(II) complexes have been prepared (scheme 1) [7]. The compound is a sparingly soluble polymeric complex. Strong neutral donor ligands like tertiary phosphines can easily cleave the selenolate bridge of 1 with the formation of monomeric cis isomer 2. In the case of binuclear complexes (4-6) three isomers, viz. one trans and two cis isomers are possible.

On the basis of NMR spectroscopy, except in few cases, binuclear complexes (4-6) were formed exclusively as a cis isomer.

The \(^{77}\text{Se} \) NMR spectrum of \([\text{PtCl}_2(\mu-\text{SeBz})_2(\text{PPR}_3)_2]\) (Fig 1) shows that two Se
atoms are magnetically in-equivalent, one is trans to P atoms and other is trans to chlorides. The X-ray structure of this complex (Fig 2) revealed that it consists of two distorted square planar platinum atoms Pt(1) and Pt(2) which show deviation of 0.046 and 0.032 Å, respectively from the mean planes defined by P(1)Cl(1)Se(1)Se(2) and P(2)Cl(2)Se(1)Se(2). This suggests pyramidization of platinum atoms. The molecule has a sym-cis configuration with a non planar four-membered "Pt₂Se₂" ring (hinge angle 131.1°).

1 (ii) Thermal studies
The TG trace of [Pd(SeBz)₂]₃ showed two stage of decomposition. The product forms after the first stage of decomposition (in the temperature range 210 to 500°C) has been identified as a mixture of products PdSe₂ and Pd₁₅Se₁₅ contaminated with carbon (typical analysis of a sample heated at 300°C : C, 7.7; H, 0.6; Se, 49.1; Pd, 40.4%, XRD pattern showed peaks due to PdSe₂ and Pd₁₅Se₁₅). In the second of decomposition (above 600°C) selenium is eliminated leading to the formation of Pd₁₅Se₁₅ as indicated by
The weight loss and XRD pattern. The carbon contents (C 5.7%) in this product has been reduced slightly.

2. (i) Synthesis and characterization of 2-(dimethylamino)ethaneselenolate complexes

Using this ligand and its sodium salt i.e. NaSeCH₂CH₂NMe₂ several Pd(II)/Pt(II) complexes have been prepared (scheme 2).

The molecule contains three distorted square planar palladium centers held together by three bridging selenium atoms of the chelating dimethylaminotheane selenolate ligand. The resulting six-membered Pd₃Se₃ ring adopts a twist conformation. The dimethylaminoethyl selenolate ligands form "exocyclic" five-membered PdSeC,N chelate ring, with envelope conformations.

Tertiary phosphines react with 7 and results pink to violet coloured Pd complexes 8. According to NMR spectroscopy and X-ray structural analysis these complexes are monomeric with Se cis to phosphorus ligand.

The series [M₂Cl₂(SeCH₂CH₂NMe₂)(PR₃)] (9) showed two major ³¹P signals the one at lower frequency is attributed to the phosphine attached to the metal atom containing the chelating Se-N ligand. The second signal is due to the phosphine attached to MCI₂ fragment. The series [Pt₂(µ-SeCH₂CH₂NMe₂)(P'Pr)] (11) show two sets of ³¹P{'H} and ¹⁹⁵Pt{'H} (Fig 4) NMR peaks indicate that the non-equivalence of phosphorus nuclei of P'Pr ligand. In case of Se bridged binuclear complexes the Pt-Se bond distances are not equal (diff. ≈ 0.065 Å) thus making the Pt₂Se₂ fragment an asymmetric ring (Fig 5) in contrast to symmetric Pt₂Se₂ ring [8].

The absorption spectra of the series [MCI(SeCH₂CH₂NMe₂)(PR₃)] 8 showed week (ε = 100 M⁻¹cm⁻¹) long wavelength band at about 514 nm for Pd complexes, at ca. 400-430 nm for Pt derivatives. The band is hypsochromically shifted on replacing the phenyl substituents on the PR₃ group by donating alkyl groups. This absorption is due to a HOMO (Se) - to - LUMO (PR₃), i.e., ligand - to - ligand charge transfer (LLCT) transition and is responsible for the unusual colour of the complexes. This is further
confirmed by electrochemical data and TD-DFT calculations [9, 10].

2 (ii) Thermal studies

Thermogravimetric analyses of [Pd(SeCH₂CH₂NMe₂)Cl₂] (7) and [PdCl(SeCH₂CH₂NMe₂)(PPh₃)] have been carried out under flowing argon atmosphere. The TG curve of 7 shows closely spaced two-step decomposition (284°C), leading to the formation of Pd₁₇Se₁₅ as inferred from the calculated mass loss. The XRD patterns of the product and the elemental analyses [Found: Pd 59.0, Se 41.0 (±2%), C 3.9, H and N not detected (detection limit 0.2%); calc for Pd₁₇Se₁₅: Pd, 60.9; Se, 39.6%] are in agreement with the Pd₁₇Se₁₅ formulation. The complex [PdCl(SeCH₂CH₂NMe₂)(PPh₃)] also decomposes via two steps resulting in Pd₁₇Se₁₅ at 350°C (from calculated mass loss), as confirmed by the XRD pattern.

To prepare large quantities of palladium selenide, a substantial amount of precursors (7, [PdCl(SeCH₂CH₂NMe₂)(PPh₃)]) (100-500 mg) have been heated in a furnace under a dry flowing argon atmosphere and then annealed at 400°C (7), 450°C ([PdCl(SeCH₂CH₂NMe₂)(PPh₃)]). The Pd₁₇Se₁₅ thus obtained shows a similar XRD pattern as the samples obtained from TG, indicating formation of the same product in each case. The XRD pattern of these products have been interpreted in terms of a cubic structure with the lattice parameter 10.584 Å. The surface morphology of these products has been studied by the SEM technique. The scanning electron micrographs taken at different resolutions of Pd₁₇Se₁₅ shows large aggregates of microcrystals (Fig 6) [6].

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References


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About the author...

Mr Sandip Dey passed out from the 41st batch of BARC Training School and is working in Novel Materials & Structural Chemistry Division, BARC, on the design and development of molecular precursors of platinum group metals for the synthesis of advanced materials.