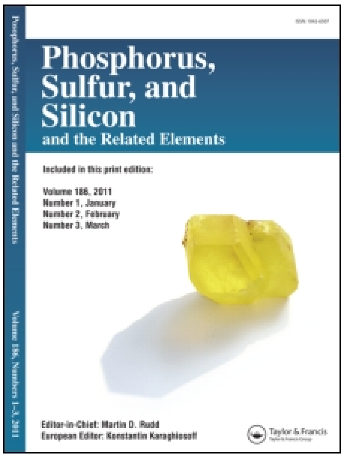

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Design, Synthesis and Structural Aspects of Terdentate (N,O,Se/Te) Donors and their Competitive Coordination Behavior towards Pt(II)

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Design, Synthesis and Structural Aspects of Terdentate (N,O,Se/Te) Donors and their Competitive Coordination Behavior towards Pt(II)

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Design and synthesis of new potentially terdentate donors, $[PhE(CH_2)_2NH\text{-}C(CH_3)CHC(CH_3)(=O)]$ (E = Se or Te) having (N, O, Se/Te) donors sets, and their structure and reactivity towards d^8 platinum metal ion have been evaluated.

Keywords: (N, O, Se/Te) donors; Pt(II) complexes; (Pt-Se) and (Pt-Te) bond; Intermolecular interactions; X-ray structure

INTRODUCTION

Non-bonded interactions due to heavier chalcogens (Se and Te) at intramolecular level were found to be an important factor that quite often dictates the structure and reactivity of organochalcogen compounds[1-3].

Various physical and chemical properties of molecular solids depend directly upon their crystal structure. Thus the ability to design particular structures is of great importance when one contemplates applications of molecular solids. Our recent research interest has been in understanding the fundamentals of designing organochalcogen donors as building blocks for 'extended-reach' structures with specific involvement of non-bonded interactions at intermolecular level in desired molecular species[4,5]. The relevance of such studies is based upon the chemical, electrical, optical, and materials properties of chalcogenide species, each of these properties being structure dependent. Although, various organochalcogen donors of varying coordination abilities, including mixed donors, macrocycles and their metal complexes are well documented in the literature[6-8], a working methodology for creating extended-reach structures have seldom been addressed. The supramolecular[9] polymeric structure of $Te_2(S_2PPh_2)_2$, serendipitously obtained in the reaction of TeO_2 with $Ph_2P(S)SH$ and extended reach supramolecular structures in silver complexes with bidentate organoselenium[10] can be accounted for specific structures. As in the former case intermolecular Te...Te interactions have spectacular effect in the structure and was not strong enough to survive in solution whereas in the latter the role of selenium relied mainly upon coordination to saturate the coordination sphere. In the course of our systematic studies on the design and synthesis of new organochalcogen bearing ligands, we paid attention to design a tridentate heterofunctional ligand framework in order to be able to promote the formation of a defined structure. It should be noted that the ligand should not use up all of its coordination sites in binding to a metal center and structurally rigid tridentate ligands appeared as a judicious choice to achieve this objective. It was taken into account that most of the metal (II) ions, when interact with tridentate ligands will preferentially bind two of the chelating units to form a tetracoordinated species leaving the remaining coordination site for further coordination. Thus it can be considered a new metal containing ligands which can be induced to self assemble with the same metal or with other metal ions or unsaturated metal complexes through its free coordination site, and thus an extended-reach structure may be generated. We also reasoned that the synthesis of Pd(II) and Pt(II) metal ion complexes with these heterofunctional tridentate ligands will preferentially form a square planar arrangement leaving one of the sites for further coordination.

Our present work specifically involves coordination complexes of platinum metals in the oxidation state +2, where ligands have been carefully designed to control chemical reactivity. Tridentate ligands are prepared which incorporate O, N and/or Se or Te donor atoms in their structural framework. The Schiff base ligands $[PhE(CH_2)_2N{=}C(CH_3)CHC(CH_3)({=}O)]$ (E= Se or Te) (keto-enol tautomerism, fig. 1) are accessible in good yields(> 85%) *via* standard imine condensation from phenylchalcogenoethylamine and acetylacetone.

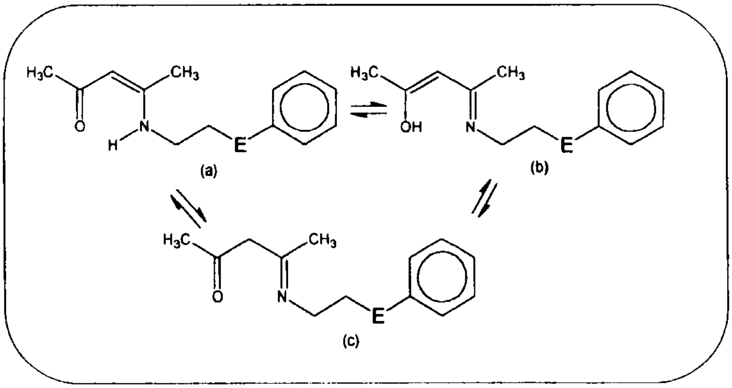
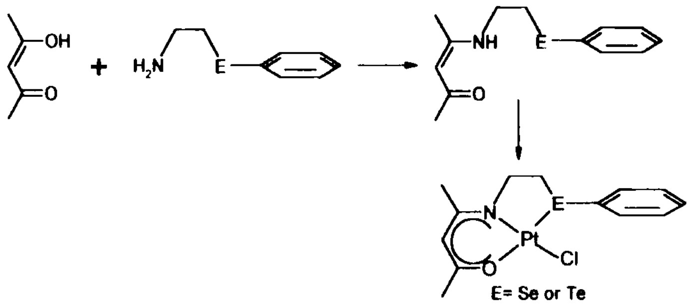


FIGURE 1

The higher denticity of the ligands, variation in ring size, contrasting hard/soft character, orientation of heterofunctional donor groups and non-bonded interactions involving chalcogens, are the important factor that may have significant influence on the structure of the resulting metal complexes. Owing to the heterofunctional nature of the ligands, we first set out to establish their coordination behavior by making complexes with platinum metal, which should force the ligand to assume a different configuration, because of the square planar geometry of the metal site. The complexes were prepared by treatment of K_2PtCl_4 with the corresponding ligands in an acetone-water (1:1,V/V) mixture at room temperature. The reaction conditions for both the ligands $[PhSe(CH_2)_2NH\text{-}C(CH_3)CHC(CH_3)(=O)]$ (**L_1H**) and $[PhTe(CH_2)_2NH\text{-}C(CH_3)CHC(CH_3)(=O)]$ (**L_2H**) were sufficient to deprotonate the ligand

and to produce the complexes [Pt(L_1)Cl] (3) and [Pt(L_2)Cl] (4) as pale yellow crystalline material in quantitative yields (see Scheme 1).



Scheme 1

Microanalysis and spectral data confirmed the proposed stoichiometry and geometry. The monomer complexes once isolated are insensitive to oxygen and moisture, and the reactions can be carried out in air with no change in efficiencies or yield. The monomer-dimer association in molecular weight determinations in solution can also be observed by low ionization mass spectroscopy (LI-MS). Because of the stabilizing tridentate nature of these ligand systems, the complexes are extraordinarily thermally stable and no decomposition is observed at temperature below 180°C. The X-ray structure determination of the complex [$PhSe(CH_2)_2N-C(CH_3)CHC(CH_3)$ (=O)PtCl] (3) revealed that the central platinum center is four coordinated in an approximately square-planar (Se, N, O & Cl) environment. At the platinum center the chloride ligand is *trans-* to the nitrogen atom. The Pt-Cl distance is [2.333(4)Å] which is typical of Pt^{II}-Cl bonds and the Pt-Se separation [2.3570(15)Å] lies somewhat below the range [2.376(2)-2.590(7)Å] observed in the various complexes containing Pt-Se bond. Furthermore, the Pt-Cl distance of 2.333(4) Å is rather short compared to a number of platinum complexes having Pt-Cl bonds[11-13]. Apparently, this may be attributed to different *trans*- and *cis*- influence of N- and Se- donors which are part of the ligand (fig.2).

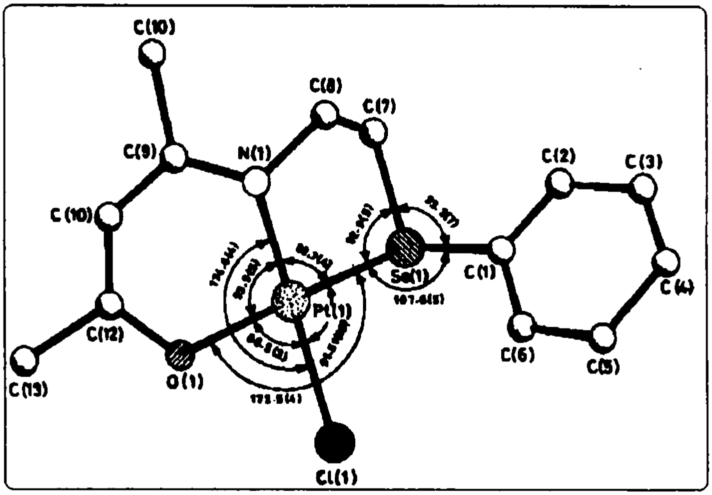


FIGURE 2

We have found no structurally characterized precedents for N, Se/Te, O ligands in the literature. The Pt-Se(1)-C(1) and C(7)-Se(1)-C(1) angles [107.6(5), 99.3(7)°]. The repulsion from the nonbonding pair on the selenium and the tension imposed by the five-membered ring would account for these facts. The N(1)-Pt-Cl(1) axis is almost linear[174.6(4)Å] whereas O(1)-Pt-Se(1) is [172.5(4)Å], probably as a consequence of chelate ring strain. A feature of particular interest is that the molecule crystallizes as dimer in an unit cell showing intermolecular electronic interactions, although not very prominent, such as (Pt...Pt) [3.8375 Å], (Pt...Se) [3.6955 Å] and (Se...Cl) [4.4298 Å] between the two molecule. Oxidative addition at Pt(II), Se(II) and Te(II) centers are very common with halogens or alkyl halides. Surprisingly our attempts to prepare mixed halides by oxidative addition at **3** and **4** gave no detectable reaction products under various reaction conditions. This might be a consequence of the geometric constraints imposed by the presence of three heteroatom donors (N), (O), (Se/Te) in the ligands forming both 5- and 6-membered ring around the central platinum metal. The intermolecular electronic interactions between the two molecules in a dimer might also be responsible for extra stability of the molecule.

In conclusion, we have found easily accessible (N,O,Se) or (N,O,Te) ligands which are relatively free of hydrogen bonds and have comparable steric properties to suit well for investigation of (Pt...Pt) interactions in the absence of other strong intermolecular forces. Such interactions, in analogy to hydrogen bonds, are a useful tool for the controlled assembly of molecules. The electronic properties of the ligands may influence the Pt...Pt interactions and may lead to an organized structure. The complexes of the present study can also be used as precursors in the production of semiconducting metal selenides(Pt/Se) and tellurides(Pt/Te). The complexes also have extra chlorine atoms and open the way to further extension of this chemistry towards the synthesis of multimetallic complexes. Further work in this area is under progress.

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