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NMR investigations on a series of diplatinum(II) complexes possessing phenylpropenoids in $CDCl_3$ and CD_3CN: Crystal structure of a mononuclear platinum complex

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ABSTRACT

The NMR spectra of five diplatinum(II) complexes, Pt(μ-Cl)(arylolefin)]$_2$ [arylolefin = Eug (**1**), ^{i}PrEug (**2**), Meug (**3**), EtEug (**4**), Saf (**5**)], in $CDCl_3$ are studied. All the five complexes are formed by the reaction of K[$PtCl_3$(arylolefinH)] with Ag_2O in the mixture of alcohol-water. A mononuclear platinum complex, PtCl(Saf)(CH_3CN)], which is formed by the crystallization of a dimeric complex **5** in acetonitrile is also investiated. The mononuclear platinum complex is characterized by elemental analysis, ESI mass spectrometry, infrared and NMR spectroscopic studies and single crystal X-ray crystallography. The single X-ray crystal structure reveals the coordination of Pt(II) ion to Saf via C = C_{allyl} and the carbon of the benzene ring. DFT calculations are also performed to collect information about the structural parameter and stability of mononuclear platinum complexes. The findings reveal that the theoretical data agree with the experimental findings of single crystal X-ray structure. In addition, Hirshfeld surface analysis is also carried out to investigate various intermolecular interactions in the crystal structure of mononuclear platinum complex.

1. Introduction

Platinum-based compounds have been extensively investigated as potential chemotherapeutic medicines since the revolutionary discovery of cisplatin and its analogs [1–3]. Despite their remarkable efficacy against various cancers, platinum-based drugs are accompanied by several serious adverse effects [4,5]. This motivates the scientists to see out more effective platinum complexes. Lippard et al discovered a novel platinum complex, cis-[$Pt(NH_3)_2$(Phenanthridine)Cl]NO_3, which is 7–40 times more effective than cisplatin in the early scan of human cancer cells from a range of organs [6].

The strategy of using a natural compound as a ligand in the formation of Pt(II) complexes to minimize their toxicity and consequently harmful consequences has gained a lot of interest in recent years [7–9]. The platinum complex K[$PtCl_3(C_2H_4)$], also known as Zeise's salt, was discovered by William Zeise in 1825 as the first example of a transition metal–olefin complex through the interaction of platinum chloride with ethylene [10]. Olefin ligands, also known as alkene ligands, are good π electron donors and are widely used in the organometallic chemistry of platinum to produce relatively stable complexes [10–13]. Pt(II) complexes with a single geometry and stability are useful models for bonding, structural, and reactivity research [14]. Over the years, several Pt(II) complexes with natural arylolefins as ligands, such as safrole (in sassafras oil), eugenol (in clove oil), and anethole (in anise and fennel oil), and their derivatives have been investigated due to their novel topologies and significant inhibitory activities against human cancer cells, and have shown significant anti-inflammatory and analgesic properties [9,15–17]. In addition, large number of Pt(II) complexes with caffeine [18], theophylline [19], methyleugenol [20,21], safrole [15,16], oleanoic acid [22], propyl gallate [23] have been synthesized and their biological applications explored. Moreover, several diplatinum(II) complexes (Scheme 1) containing phenylpropenoids, [Pt(μ-Cl)(arylolefin)]$_2$ have been reported in mild conditions [16,24–26], which, when combined with other ligands, L, yield monoplatinum(II) complexes with

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