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Thermally induced structural transformations of a series of palladium(II) complexes with *N*-heteroaromatic bidentate hydrazone ligands

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ABSTRACT

Thermal stability of a series of palladium(II) complexes with *N*-heteroaromatic bidentate hydrazone ligands was investigated using a combination of experimental measurements and DFT calculations. All complexes exhibit a reversible second-order transition around 333 K, which can be attributed to structural reorganization of the ligand molecules. Thermal degradation begins in 570–610 K temperature region, with an endothermic peak, followed by exothermic peaks in DSC. TG measurements show a well-defined mass loss corresponding to the initial degradation, while subsequent processes are poorly separated. DFT calculations suggest that the initial degradation step occurs with release of Cl, which then reacts with remaining part of the complex molecule in an exothermic process. This leads to decomposition of the ligand molecule into four fragments corresponding to ethyl chloride, carbon dioxide, methyl amine, and the fragment with the aromatic group. Mass spectrum suggests that creation of these fragments most likely corresponds to the initial degradation, after which some of these coordinate to Pd center, whose coordination sphere is left incomplete by release of Cl. TG measurement to 1123 K indicates that the final degradation product at this temperature is palladium.

1. Introduction

Synthesis and properties of palladium(II) complexes has been a focus of some interest for some time [1–3]. They have been recognized as effective catalysts [4–7], as well as potential metal based anticancer drugs [8–10], since they exhibit the same geometry and electronic configuration as platinum. However, the ligand-exchange kinetics of platinum(II) and palladium(II) derivatives is quite different: hydrolysis of palladium(II) compounds is nearly 10^5 times faster, leading to very reactive species that are unable to reach pharmacological targets [11,12]. It was shown that stabilization of palladium(II) complexes by prevention of possible *cis*–*trans* isomerisation can be achieved by using chelate ligands in complex synthesis which possess similar or even better activity than platinum-approved drugs [13].

In light of this potential application, their thermal stability has been considered as an important issue [14–17], although, to the best of our knowledge, there has been no investigation to the impact of ligand peripheral substitution on thermal stability. Farran and House studied effect of the basicity of the ligands on the enthalpies and the activation energies of thermal decomposition of palladium(II) chloride complexes with pyridine and pyridine derivatives using TG and DSC [18]. During thermal degradation, complexes of type PdL_2Cl_2 lost two ligands in a single step, resulting in $PdCl_2$, with no relationship between the enthalpy values of decomposition and other properties of the complexes. With only a few exceptions, calculated E_a values increased, while the procedural onset temperatures (Te) of decomposition decreased with increase in basicity of the ligands. This was due to *trans* influence of one ligand in the square planar complexes, causing the first ligand to be released easier than the second. Gomez-Vaamonde et al. investigated thermal stability of *trans*-bis (2-amino pyridine)dichloro palladium(II) complex, where palladium(II) is coordinated to two monodentate ligands [19]. The process

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of thermal decomposition occurs through three steps, where two amino-pyridines are released. The mass loss in TG experiment occurred in two separate temperature regions: 533–598 K and 598–718 K. This is contributed to the *trans* influence strengthening the bond of the second ligand to the metal center.

In our previous work, we examined the cytotoxic activity of palladium(II) complexes with NN bidentate chelate hydrazone ligands derived from ethyl hydrazino acetate (haOEt) and various *N*-heteroaromatic carbonyl compounds. The ligands posses the same donor atoms, but differ at ligand periphery backbones [20]. It was shown that such structural differences, which affect their lipophility, had crucial impact on cytotoxic activity. In addition, it is known that substituents in aromatic amines have an effect on activation energy of their reactions [21]. In this paper, we present a systematic investigation of the impact of ligand peripheral substitution on thermal stability of a series of palladium(II) complexes with *N*-heteroaromatic bidentate hydrazone ligands, from the experimental, as well as, the theoretical aspect.

2. Experimental

2.1. Materials

All of the complexes were synthesized from chemicals of analytical purity according to the procedure described in Ref. [20]. The series of palladium(II) complexes with *N*-heteroaromatic bidentate hydrazone ligands was derived from *cis*-dichloro-{[ethyl (2E)-2-(pyridine-ilmethyledene)hydrazynil]acetate-κ^{2}N}Pd(II) complex (complex 1). Complex 2 replaces methyledene with ethyledene group to give *cis*-dichloro-{[ethyl(2E)-2-(pyridine-ilethyledene)hydrazynil]acetate-κ^{2}N}Pd(II), and complex 3 replaces pyridine with quinoline group to give *cis*-dichloro-{[ethyl(2E)-2-(quinoline-ilmethyledene)hydrazynil]acetate-κ^{2}N} Pd(II) complex. The synthesized complex purity was confirmed using elemental analysis and X-ray diffraction (XRD).

2.2. Methods

Thermogravimetric analyses were conducted using a Q500 TGA (TA Instruments) with sample weights of 10.0 ± 0.5 mg, in nitrogen atmosphere with gas flow rate of 50 mL min^{-1}, at a heating rate of 10 K min^{-1}. DSC measurements were carried out using DSC Q1000 (TA Instruments) with typical sample weight of 2.0 ± 0.2 mg, in nitrogen atmosphere with gas flow rate of 50 mL min^{-1} at constant heating rates of 2–40 K min^{-1}. Experimental enthalpies were determined as the average value of three measurements. Values of average apparent activation energies were determined using Kissinger's method [22]. The X-ray powder diffraction (XRD) spectra were obtained using Philips PW-1710 automated diffractometer, using CuKα line, operated at 40 kV and 30 mA, in Bragg–Brentano geometry. The instrument was equipped with diffracted beam curved graphite monochromator and Xe-filled proportional counter. The XRD peaks were indexed using WTREOR as implemented within GSAS program packet. Mass spectroscopy was conducted using quadruple mass spectrometer system, QMG422, incorporated in an argon filled glove-box. The sample was heated to 593 K under argon at 10 K min^{-1}.

All DFT calculations were performed simulating aqueous solution with continuous dielectric model, as this was determined to be the optimal for investigated system, using Gaussian 09 [23] program package. Gaussian package was used for structure optimization and frequency analysis. All structures where fully optimized using C-PCM solvation method with Klamt [24] radii, as implemented in Gaussian 09. In Gaussian 09 calculations, we used the hybrid HF/DFT method with a combination of the three-parameter Becke [25] exchange functional and the Lee–Yang–Parr (B3LYP) [26] non-local correlation functional. Calculated bond dissociation energy (BDE) values for Pd–Cl(1) and N(3)–H(1) refer to reactions in which the products are a single atom and the remainder of the respective complex, while in the all other cases, the products are two or more fragments.

3. Results and discussion

As a part of systematic investigation of palladium(II) complexes with NN bidentate chelate ligands, the influence of substitution at the ligand periphery on thermal stability on a series of three palladium-based complexes with *N*-heteroaromatic bidentate hydrazone ligands (Fig. 1). Investigated complexes are crystalline, as shown in the XRD pattern of complex 1 (Fig. 2). Based on their crystal lattice parameters, the initial structures of complexes were constructed for DFT calculations. Optimized structures of the initial complexes in DFT calculations highlight how changes in functional groups alter complex geometries. Derivatization of complex 1 causes increased deviation from planarity, which is particularly pronounced in complex 2. In order to estimate the relative stabilities of individual complexes, isodesmic reactions were constructed to calculate their respective enthalpies of formation. Calculated values for individual complexes (Table 1) indicate that complex 2 should be the most stable, while complex 3 should be

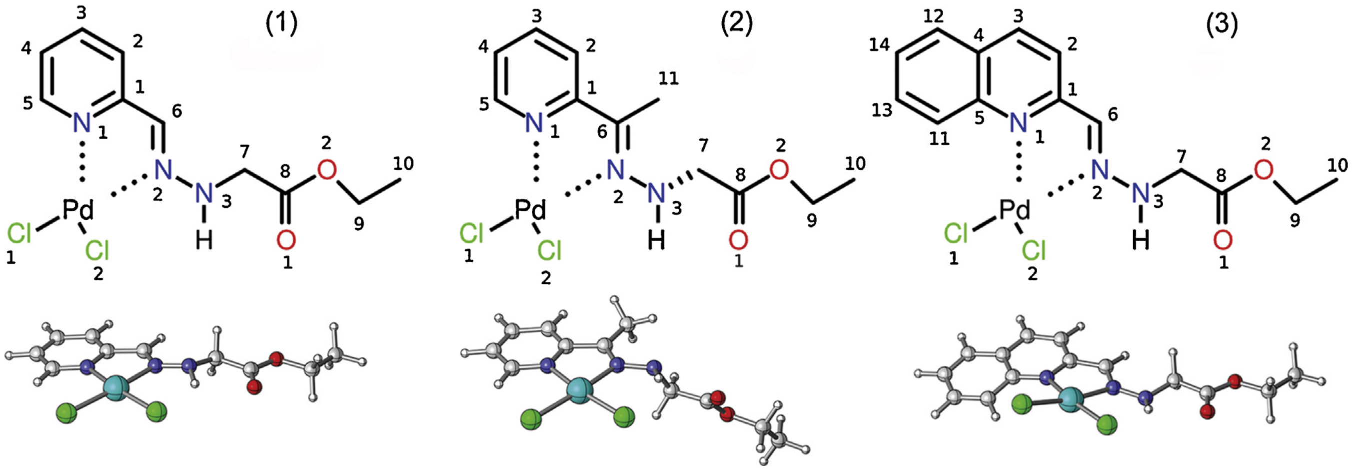

Fig. 1. Chemical formulas (top) and optimized structures from DFT calculations (bottom) of three palladium-based complexes.