Polyhedron 50 (2013) 82–89

Contents lists available at SciVerse ScienceDirect

Polyhedron

journal homepage: www.elsevier.com/locate/poly

Probing the ‘Venus fly-trap’ parameters of cyclo-octadiene in selected β-diketonato complexes of platinum(**II**) and the nickel-triad from a spectroscopic, X-ray crystallographic and DFT study

T.N. Hill, A. Roodt *, G. Steyl

Department of Chemistry and Strategic Academic Cluster: Materials and Nanosciences, University of the Free State, Bloemfontein 9300, South Africa

ARTICLE INFO

Article history:
Received 1 September 2012
Accepted 29 October 2012
Available online 5 November 2012

Keywords:
β-Diketonato
Platinum(**II**)
Crystallography
DFT
Spectroscopy
Cyclooctadiene
Crystal structures
Venus fly-trap angles

ABSTRACT

Synthetic, structural and theoretical studies of Pt(**II**) complexes of a series of β-diketonato ligands with a variation of sterics, namely acetylacetonato (acac) and thenyoltrifluoroactonato (thtfac), are reported. The crystal structures of [Pt(cod)(acac)]PF_6(**I**), [Pt(cod)(acac)]BF_4(**II**) and [Pt(cod)(thtfac)]BF_4(**III**) are presented while the complexes were characterized spectroscopically by IR, ^1H and ^{13}C NMR spectroscopy. DFT calculations of the group 10 transition metals in the nickel triad, utilising the model complex, $[M(cod)(acac)]^+$, to gain further insights in the variation of the transition metal within the complex and the interactions with both the β-diketonato and *cis,cis*-1,5-cyclo-octadiene (cod) co-ordinating ligands are reported. In particular, the variation in the ‘Venus fly-trap’ bite and jaw dihedral angles, χ and ψ, is *ca.* 2° and 4°, respectively, and therefore quite small, but significant. The HOMO and LUMO energy gaps between the Ni(**II**) and Pd(**II**) complexes were insignificant, while that of Pt(**II**) is >1 eV higher than the corresponding 3rd and 4th row congener complexes.

1. Introduction

Diolefins act as ligands for a large number of metal centres and forms an important range of complexes for the study of π-bonding interactions. Bidentate olefins can also act as inhibitors in certain homogeneous catalytic processes and a more detailed knowledge on the bonding modes therein maybe exploited by more detailed and systematic variation of effects, which influences transition metal interactions therewith [1]. Similarly, classic β-diketone and related ligands have been studied for more than a century and their ability to give rise to rich and interesting co-ordination chemistry is well known. β-Diketonato ligand systems act as monovalent *O,O′*-chelating donors capable of stabilizing mononuclear transition metal complexes. These *O,O′*-bidentate ligands may be underutilised in middle and late transition metal complexes [2], to evaluate dynamics and reaction mechanisms [3] as well as potential application in radiopharmaceuticals [4,5] and homogeneous catalysis [6–12]. The keto-enol tautomerism of this class of ligand has been widely studied [13,14]. The stepwise and subtle systematic ligand manipulation ability of β-diketonato ligand systems therefore allow investigation into the bonding modes and co-ordination of *cis,cis*-1,5-cyclo-octadiene (cod).

For these reasons we have focused our investigation to well known β-diketonate ligands which were commercially available (acetylacetone (Hacac) and thenoyltrifluoroacetone (Hthtfac)). In this paper we present the crystal structure of several β-diketonato cod platinum(**II**) complexes of the type [Pt(cod)(LL′-Bid)]A (where LL′-Bid = acac, thtfac; A = BF_4^-, PF_6^-) along with theoretical calculations on the $[M(cod)(acac)]^+$ complex for the nickel triad. The aim is the further understanding of the co-ordination of a model diolefin ligand such as 1,5-cylo-octadiene and the influence that the β-diketonate systems, while varying different counter ions, have on the respective structures and comparing the data for the cod ligand with the previously defined ‘Venus fly-trap’ bite and jaw dihedral angles, χ and ψ, [15] and a simultaneous evaluation of spectroscopic data.

2. Experimental

2.1. Materials and general procedures

All reagents used for synthesis and characterization were of analytical grade, purchased from Sigma–Aldrich, unless otherwise stated. Reagents were used as received, without purification.

NMR spectra were recorded on a Bruker Advance II 600 (^1H: 600.28 MHz; ^{13}C: 150.96 MHz), ^1H NMR spectra were referenced internally using residual protons in the deuterated solvent

---

* Corresponding author.
E-mail address: roodta@ufs.ac.za (A. Roodt).

0277-5387/$ - see front matter © 2012 Elsevier Ltd. All rights reserved.
http://dx.doi.org/10.1016/j.poly.2012.10.043

($CDCl_3$: d 7.28; CD_2Cl_2: s 5.32). ^{13}C NMR spectra were similarly referenced internally to the solvent resonance ($CDCl_3$: t 77.36; CD_2Cl_2: m 53.8) with values reported relative to tetramethylsilane (d 0.0). Chemical shifts are reported in ppm.

Infrared spectra were recorded on a Bruker Tensor 27 Standard System spectrophotometer with a laser range of 4000–370 cm^{-1}. Solid samples were prepared as potassium bromide disks.

Preparation of dichlorido-1,5-cyclo-octadieneplatinum(**II**) starting material was achieved by the previously published method [16] from the reaction of potassium tetrachloroplatinate in water and propanol with *cis,cis*-1,5-cyclo-octadiene (cod).

2.2. Synthesis

2.2.1. Preparation of [Pt(cod)(acac)]PF_6(**I**) and [Pt(cod)(acac)]BF_4(**II**)

[Pt(cod)Cl_2] (100 mg, 0.27 mmol) was dissolved in dichloromethane (5 ml). To this AgA (A = PF_6, BF_4, 135.1 mg or 104.1 mg 0.53 mmol) was added, the resulting solution was stirred for *ca.* 15 min. An equivalent of acetylacetone (Hacac, 27 mg, 0.27 mmol) was added and the mixture stirred for a few minutes to allow the reaction to complete. The solution was filtered and diethyl ether was added to the filtrate to precipitate the product. The resulting solution was again filtered and the precipitate washed with diethyl ether. Crystals suitable for X-ray determination were obtained by DCM/Et_2O vapour diffusion.

Yield (**I**) 42 mg (53%); (**II**) 100 mg (74%).

I: IR_{KBr}: $\nu_{C=C}$ 1526, $\nu_{C=O}$ 1556, ν_{Pt-O} 647 and 473, $\nu_{Pt-[C=C]}$ 558 cm^{-1}. ^1H NMR (600.28 MHz, CD_2Cl_2) δ 2.008 (s, 6H, CH_3), 2.492 (q, 4H, CH_2), 2.836 (d, 4H, CH_2), 5.744 (t, 4H, CH), 5.861 (s, 1H, CH). ^{13}C NMR (150.96 MHz, CD_2Cl_2) δ 26.70 (CH_3), 29.95 (CH_2), 99.51 (CH), 103.02 (CH), 187.84 (CO).

II: IR_{KBr}: $\nu_{C=C}$ 1529, $\nu_{C=O}$ 1555, ν_{Pt-O} 645 and 474, $\nu_{Pt-[C=C]}$ 521 cm^{-1}. ^1H NMR (600.28 MHz, CD_2Cl_2) δ 2.209 (s, 6H, CH_3), 2.499 (q, 4H, CH_2, **IIa**), 2.254 (q, 4H, CH_2, **IIb**), 2.683 (dd, 4H, **IIb**), 2.841 (d, 4H, CH_2, **IIa**), 5.556 (t, 4H, CH, **IIb**), 5.75 (t, 4H, CH, **IIa**), 5.862 (s, 1H, CH). ^{13}C NMR (150.96 MHz, CD_2Cl_2) δ 26.81 (CH_3), 29.97 (CH_2, **IIa**), 31.23 (CH_2, **IIb**), 99.53 (t, CH, **IIa**), 100.94 (CH, **IIb**), 103.02 (CH), 187.81 (CO).

2.2.2. Preparation of [Pt(cod)(thtfac)]BF_4(**III**)

Using the preparation method presented in Section 2.2.1, changing the β-diketonato ligand to thenoyltrifluoroacetone (Hthtfac) complex **III** was synthesized. Crystals suitable for X-ray determination were obtained by DCM/Et_2O vapour diffusion.

Yield (**III**) 90 mg (54%).

III: IR_{KBr}: $\nu_{C=C}$ 1540, $\nu_{C=O}$ 1579, ν_{Pt-O} 613 and 473, $\nu_{Pt-[C=C]}$ 522 cm^{-1}. ^1H NMR(600.28 MHz, $CDCl_3$) δ 2.604 (m, 4H, CH_2), 2.727 (m, 4H, CH_2), 5.626 (t, 4H, CH), 6.717 (s, 1H, CH), 7.969 (d, 1H, CH), 8.085 (d, 2H, CH). ^{13}C NMR (150.96 MHz, $CDCl_3$) δ 30.22 (CH_2), 31.28 (CH_2), 100.42 (t, CH), 120.94 (CH), 130.59 (CH), 136.72 (CH), 139.73 (CF_3), 198.87 (CO).

2.3. X-ray crystallographic data collection and refinement

Data collections for [Pt(cod)(acac)]PF_6(**I**) was obtained on a Bruker APEX II 4K CCD diffractometer. The data for [Pt(cod)(acac)]BF_4(**II**) and [Pt(cod)(thtfac)]BF_4(**III**) were collected on an Oxford Diffraction Xcalibur 3 Crysalis CCD system [17]. Both systems were equipped with a graphite-monochromatted Mo Kα radiation, for the Bruker system all the reflections were merged and integrated with SAINT-PLUS [18] and corrected for Lorentz, polarization and absorption effects with SADABS [19], while Crysalis RED [20] was used for the Oxford Diffraction system.

Structures were solved by direct and conventional Patterson methods using SHELX-97 [21] as part of the WINGX [22] package, and anisotropic refinement was performed on all non-hydrogen atoms by a full-matrix least-squares method. The positions of the hydrogen atoms were calculated using a riding model to the adjacent carbon, unless otherwise stipulated. Hydrogen interactions were calculated using the PLATON [23–25] and PARST [26] programs. Molecular graphics were obtained using DIAMOND [27], while overlay illustrations were generated using HyperChem™ 7.5 [28].

Details of the crystal data, intensity measurements and data processing are summarized in Table 1 for [Pt(cod)(acac)]PF_6(**I**), [Pt(cod)(acac)]BF_4(**II**) and [Pt(cod)(thtfac)]BF_4(**III**) while selected bond distances and angles are given in Table 2. The molecular structure with thermal ellipsoids at 50% probability and numbering scheme for complex **I** are shown in Fig. 1, complex **II** is likewise numbered, the counter-ions and hydrogen atoms have been omitted for clarity. The numbering scheme of complex **III** is represented in Fig. 2, crystallizing with two independent complexes in the asymmetric unit, labelled as **IIIa** and **IIIb**, respectively. The atoms are prefixed with 1 or 2, respectively, e.g. O_{11} and O_{21} for the first oxygen atom of the β-diketonato ligand, and again the counter-ions and hydrogen atoms have been omitted for clarity.

2.4. Computational methodology

The DFT (density functional theory) molecular orbital calculations were carried out using the GAUSSIAN 03 [29] software suite. Becke's three parameter hybrid (B3LYP) [30,31] exchange correlation functional was used. The basis set employed in this study was 6-311++G(d,p) [32–34] for the main group elements and LanL2DZ [35] for the middle to late transition metals. Vibrational frequencies were calculated at the 6-311++G(d,p) level for the main group elements and at the LanL2DZ level for the middle to late transition metals with minimum energies confirmed to have zero imaginary frequencies. The frequencies were unscaled and used to compute the zero-point vibrational energies, while the calculated harmonic wavenumbers were used in the analysis of the experimental IR spectra. The values were scaled down by the factor 0.9982, to account for anharmonicity effects and limitations of the basis set [36].

3. Results and discussion

3.1. Synthesis and characterization

The platinum(**II**) complexes (**I–III**) were synthesized utilising potassium tetrachloroplatinate in a mixture of water and propanol followed by the addition of a catalytic amount of tin chloride and an excess of *cis,cis*-1,5-cyclo-octadiene (cod). The mixture was stirred for several days and allowed to evaporate to dryness where upon it was extracted with dichloromethane. The resulting dichloro(1,5-cyclo-octadiene)platinum(**II**) complex was then further reacted with an equivalent of the β-diketonato ligand in the presence of a silver salt (Scheme 1). The compounds described in this paper were characterized by IR, ^1H and ^{13}C NMR spectroscopy (data in Section 2.2).

The IR spectra of the compounds showed characteristic bands at 613–647 cm^{-1} and ± 474 cm^{-1} assigned to ν_{Pt-O} + Δring (in-plane ring distortion) and ν_{Pt-O} while $\nu_{Pt-[C=C]}$ bands were observed around 558–521 cm^{-1}. These bands were assigned based on the previous assignments of similar compounds by Mikami et al. [37] and Nakamoto et al. [38] who studied a range of bis-acetylacetonato transition metal complexes. The O–Pt–O bite angle decreases when varying the β-diketonato ligands from acac to thtfac leading to an increase in strain on the metallocycle, this is seen in the IR by *ca.* 34 cm^{-1} shift down-field.

The ^1H NMR data is given in Section 2.2 and the complexes have been described considering the atomic numbering scheme given in