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Molecular characterization, DFT and TD-DFT calculations of morpholinium tetra chloropalladate (II)

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ABSTRACT

The paper presents a combined experimental and computational study of new compound morpholiniumtetrachloropalladate(II) (MTCP) which has been synthesized and characterized by FT-IR, UV–Vis and single crystal X-ray diffraction studies. The solid phase FT-IR spectra of the complex salt have been recorded in the regions 4000-400 cm^{-1}. Density functional (DFT and TD-DFT) calculations have been carried out for this complex by using DFT/LANL2DZ functional with the basis set of SDD for Palladium and 6-311G+(d,p) for C, N, H, O and Cl atoms. The calculated results show that the predicted geometry can well reproduce the structural parameters. The complex formed by a discrete $PdCl_4^{2-}$ anion and one protonated $C_4H_{10}NO^+$ cation and the Pd (II) ion is located on an inversion center and is coordinated by four chlorine in a square planar geometry.

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1. Introduction

Various transition metal complexes with some Schiff bases containing nitrogen and oxygen donor atoms play an important role in biological systems and represent interesting models for metal enzymes, which efficiently catalyze the reduction of dinitrogen and dioxygen [1,2] Furthermore, the macrocyclic derivatives of these Schiff bases were found to have many fundamental biological functions such as photosynthesis [3,4] and transport of oxygen in mammalian [5] and other respiratory systems [6]. The metal centers of most reported complexes, [M (Salen)], belong to the first row of transition metals and less attention has been paid to complexes of metals of the second and third rows, such as palladium or platinum. The coordination chemistry of the square planar palladium(II) and platinum(II) complexes of nitrogen and sulfur-oxygen donor ligands have gained importance because of their antitumor, anticancer, and catalytic activities [7,8]. Antiandrogen and antimicrobial aspects of coordination compounds of palladium(II) and platinum(II) have also been reported in recent years [9,10].

Quantum chemical calculations of metal-ligand complexes allow for an in silico approach to identify which interactions help to stabilize the metal ion and which interactions might be improved. Moreover, the calculations may lead to a better understanding of why certain complexes are observed experimentally. A mixed basis set Stuttgart-Dresden (SDD) is an effective core pseudopotential (ECP) on the palladium atom with a Midi! And allowed for efficient computations yielding very good correlation to Pd–Cl containing experimental structures. The structures and energetics of small model systems have been investigated to assess the reliability of combinations of mixed basis sets and the commonly employed B3LYP, 6-311G+(d,p), and SDD methods. The effectiveness of the mixed basis sets was further assessed by comparing calculated geometries to literature crystal structures.

Paul-Gerhard Lassahn et al. [11] used for vinyl polymerisation of norbornene in the palladium (II) compounds which have the pre catalyst of $PdCl_4^{2-}$ and $PdCl_6^{2-}$ anion units in the different organic environment. Due to this, these salts are used for the preparation of mesoporous materials [12]. Indeed, applying current quantum mechanical methods have opened up the way for calculating the frequencies and intensities of spectral bands with a minimum degree of arbitrariness and finding rational explanation for a number of chemical and physical properties. Hence the synthesis and the study of new kinds $PdCl_4^{2-}$ salts are important for the further development of its applications. Hence we have synthesized the protonated Lewis base of morpholine with the $PdCl_4^{2-}$ anion. In this paper we report the synthesis, crystal structure; DFT and TD-DFT calculation of morpholiniumtetrachloropalladate (II) complex.

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2. Experimental

2.1. Synthesis

Morpholine and $PdCl_2.4H_2O$ purchased from E-Merck chemical company were used without further purification. HCl (1.72 ml, 5 mmol) and Palladium(II)chloride tetrahydrate (1.09 g, 5 mmol) was dissolved in 10 ml of absolute ethanol and 3 ml of water mixture. Morpholine (0.9 ml, 10 mmol) was dissolved in 5 ml of ethanol. Then the morpholine solution was slowly added to the metal halide solution. The reaction mixture was refluxed for 2–3 h. After refluxing, the homogenous solution was cooled and stored at room temperature over 2 days for the slow evaporation. The resulting transparent yellowish brown colored square shaped uniform crystals were formed, and washed with the cold ethanol for the removal of any impurity adsorbed on the surface. The purified crystals were used for the further studies. The elemental analysis shows the compositions of the compound, Anal. Calc. for $[C_4H_{10}NO]\ 0.5[PdCl_4]$: C, 14.1; H, 3.1; N, 4.2; Cl, 42.3. Found: C, 14.3; H, 2.9; N, 4.1; Cl, 42.3.

2.2. Spectroscopic measurements

FT-IR spectra were recorded in the region 400–4000 cm^{-1} on a Perkin-Elmer 1600 spectrometer using KBr discs at room temperature. The electronic absorption spectrum of the complex was recorded on a JASCO V-550 UV–Vis spectrophotometer using DMSO as a solvent in the range of 200–900 nm.

2.3. Crystal structure determination

The diffraction data were collected on Enraf – Nonius CAD-4 diffractometer [13] with graphite – monochromated Mo Kα radiation (λ = 0.71069 A°, T = 293 K) using the gauss of 0.20 × 0.16 × 0.16 mm single crystal. The technique used was ù-2è scan mode with limits 3.1–25.0°. The structure of the MTCP was solved by direct methods and refined by least squares on F^2 by using SHELXL97 software package [14]. A summary of the key crystallographic information is given in Table 1. All non – hydrogen atoms were anisotropically refined (Table 2). The hydrogen atom positions were fixed geometrically at calculated distances and allowed to ride on the parent carbon atoms. An ORTEP plot illustrates the anion and cation structures at the 50% probability level.

2.4. Theoretical methods

The density functional theory calculations were performed with a hybrid functional B3LYP (Becke's three parameters hybrid functional using the LYP correlation functional) using the Gaussian03 programmer package using Pentium III computer. The geometry optimization calculations were performed starting from the experimental structures with all the symmetry consideration under a default convergence criterion. The harmonic and unharmonic vibrational spectra were calculated using the same level of theory, which is used for the geometry optimization. The molecular parameters obtained from X-ray and calculated values are given in Tables 3 and 4. The electronic spectrum was computed with the hundred excited states with lop () employing the previously employed theory and basis sets. To validate the prediction and extrapolate the accuracy level for these calculations we have done all the calculations by applying the DFT/B3LYP functional with the basis set of SDD [15] for Palladium and 6-311G+(d,p) for C,N,H,O and Cl atoms because 6-311G+(d,p) basis set does not have the scaling factor. The default spin value state has been taken for all the calculations [16]. The optimized structural parameters used for frequency calculations at DFT level characterize all stationary points as minima. Based on the optimized geometries, vibrational and electronic absorption spectral properties of the title compound was discussed.

Table 1
Crystal data and structure refinement for mtcp.

Identification code	mtcp
Empirical formula	$C_4H_{10}Cl_4N_1Pd_1O_1$
Formula weight	212.23
Temperature	293(2) K
Wavelength	0.71069 A
Crystal system, space group	Orthorhombic, Pcab
Unit cell dimensions	a = 8.288(3) A alpha = 90 deg.
	b = 8.598(4) A beta = 90 deg.
	c = 20.802(5) A gamma = 90 deg.
Volume	1482.4(9) A^{-3}
Z, Calculated density	8, 1.902 Mg/m^{-3}
Absorption coefficient	1.965 mm^{-1}
F(000)	848
Crystal size	0.20 × 0.16 × 0.16 mm
Theta range for data collection	3.07–25.00 deg
Limiting indices	$-9 \le h \le 9$, $-10 \le k \le 7$, $-13 \le l \le 24$
Reflections collected/unique	6905/1303 [R(int) = 0.0215]
Completeness to theta = 25.00	99.8%
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.7475 and 0.6965
Refinement method	Full-matrix least-squares on F^2
Data/restraints/parameters	1303/0/88
Goodness-of-fit on F^2	1.080
Final R indices [I > 2sigma(I)]	R1 = 0.0146, wR2 = 0.0373
R indices (all data)	R1 = 0.0167, wR2 = 0.0398
Extinction coefficient	0.0212(5)
Largest diff. peak and hole	0.239 and −0.376 e.A^{-3}

Table 2
Hydrogen-bond (A°).

D—H···A	D—H	H···A	D···A	D—H···A
N1—H1D···Cl2	0.87 (2)	2.63 (2)	3.273 (2)	132.0 (18)
N1—H1D···Cl1	0.87 (2)	2.63 (2)	3.402 (2)	148.8 (19)
N1—H1C···Cl2ii	0.82 (2)	2.64 (2)	3.294 (2)	137 (2)
N1—H1C···Cl1iii	0.82 (2)	2.68 (2)	3.3977 (18)	148 (2)

Note: D donor. A, acceptor. Symmetry transformations used to generate equivalent atoms.
Symmetry codes: (ii) x−1/2, −y+3/2, z; (iii) −x+1/2, y+1/2, −z.

Table 3
Optimized and experimental geometries Bond lengths [A°] for mtcp.

Parameters	Experimental	B3LYP/6-311 + G**
C(1)–O(1)	1.425(2)	1.4572
C(1)–C(2)	1.492(3)	1.5263
C(1)–H(1A)	0.9700	1.0953
C(1)–H(1B)	0.9700	1.0953
C(2)–N(1)	1.481(3)	1.4810
C(2)–H(2A)	0.9700	1.0953
C(2)–H(2B)	0.9700	1.0953
C(3)–N(1)	1.488(2)	1.5213
C(3)–C(4)	1.497(3)	1.5743
C(3)–H(3A)	0.9700	1.0953
C(3)–H(3B)	0.9700	1.0953
C(4)–O(1)	1.413(2)	1.4361
C(4)–H(4A)	0.9700	1.0953
C(4)–H(4B)	0.9700	1.0953
N(1)–H(1D)	0.87(2)	1.0763
N(1)–H(1C)	0.82(2)	1.0251
Cl(1)–Pd(1)	2.3051(8)	2.3426
Cl(2)–Pd(1)	2.3012(7)	2.3146
Pd(1)–Cl(2i)	2.3012(7)	2.3146
Pd(1)–Cl(1i)	2.3051(8)	2.3426

Symmetry codes: (i) −x+1, -y+1, -z.

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