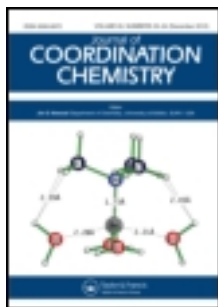


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Synthesis, spectroscopy, X-ray crystal structure, and DFT studies on a platinum(II) Schiff-base complex

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Synthesis, spectroscopy, X-ray crystal structure, and DFT studies on a platinum(II) Schiff-base complex

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[PtCl₂(SMe₂)₂] reacts with (*N,N'*-bis(salicylidene)-1,2-cyclohexanediamine) to give (*N,N'*-bis(salicylidene)cyclohexane-1,2-diamine)platinum(II). The complex has been characterized by elemental analysis, infrared (IR), UV-Vis, and single-crystal X-ray diffraction. Pt(II) is in a square-planar environment, coordinated by a chelating N₂O₂ donor. Density functional theory (DFT) calculations such as geometry optimization, vibrational frequency, electronic properties, and natural bond orbital (NBO) have been performed for the platinum compound using the OLYP method at TZP(6-311G*) basis set. The optimization calculation shows that the geometry parameters can be reproduced with the OLYP/TZP basis set. Experimental IR frequencies and calculated vibrational frequencies support each other. Time-dependent DFT has been used for absorption wavelengths and results were compared with experimental data. Moreover, NBO analysis has been performed.

Keywords: Platinum(II) complex; Crystal structure; Square-planar; DFT

1. Introduction

Condensation between 1,2-diamine and derivatives of salicylaldehyde or analog aldehydes forms a quadridentate N₂O₂ donor that is called salen. Salen ligands and their metal complexes are employed as catalytic [1–3], magnetic [4], luminescence [5], and biological properties such as antimicrobial [6], antitumor [7], antiviral [8], fungicidal [9], and nonlinear optical properties (NLO) [10]. Salen compounds have been shown to mimic biological sites upon complexation with metal ions [11, 12]. Platinum complexes play roles in catalysis [13], materials chemistry [14], and replacement for cisplatin in order to increase efficacy, reduce side effects, and overcome cisplatin resistance [15]. According to the Cambridge structure database, few platinum(II) complexes of salen compounds have been characterized by X-ray diffraction. Few calculations and spectroscopic assignment using density functional

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theory (DFT) have been done on platinum salen complexes. Thus, we have synthesized and characterized (*N,N'*-bis(salicylidene)cyclohexane-1,2-diamine)platinum(II) by spectroscopic methods such as FT-IR, UV-Vis, and ^1H NMR. X-ray diffraction was used to clarify the structure of the complex. Geometry optimization, frequency, natural bond orbital (NBO), and electronic analyses have been performed with DFT [16(a-d)].

2. Materials and methods

Solvents were of analytical reagent grade and used without purification. $[\text{PtCl}_2(\text{SMe}_2)_2]$ was prepared by the previously reported method [17]. Molar conductance measurement was carried out on a Metrohm 712 Conductometer using $1 \times 10^{-3} \text{ mol L}^{-1}$ solution in DMF. Infrared (IR) spectrum was obtained as a KBr pellet using an FT-IR 8400-SHIMADZU infrared spectrophotometer. C, H, and N analyses were carried out with a Thermo Finnigan Flash Elemental Analyzer 1112EA. ^1H NMR spectrum was acquired using a Bruker BRX 500 AVANCE in CDCl_3 . The electronic spectrum was recorded on a SHIMADZU model 2550 UV-Vis spectrophotometer in dilute CHCl_3 . The single-crystal X-ray structure was determined on a Bruker-Nonius KappaCCD diffractometer.

2.1. Synthesis of *N,N'*-bis(salicylidene)-1,2-cyclohexanediamine, H_2L

H_2L was prepared by following the reported procedure [18]. Salicylaldehyde (2.44 g, 20 mmol) and 1,2-cyclohexanediamine (1.14 g, 10 mmol) in 10 mL absolute ethanol were refluxed at 100°C for one hour. After cooling a yellow precipitate separated, washed several times with cold ethanol, and dried in vacuum over silica gel. Yield: 5.2 g (82%); m.p. 98°C . Elemental Anal. for $\text{C}_{20}\text{H}_{22}\text{N}_2\text{O}_2$: Calcd C, 74.51; H, 6.88; N, 8.69. Found: C, 73.20; H, 6.78; N, 8.63.

2.2. Synthesis of PtL complex

Salen (0.645 g, 2 mmol) and triethylamine (0.404 g, 4 mmol) were dissolved in absolute methanol (10 mL), stirred for 30 min and then added dropwise in 10 mL of $[\text{PtCl}_2(\text{SMe}_2)_2]$ (0.780 g, 2 mmol) in the same solvent. The mixture was left to stir at room temperature for 48 h. An orange precipitate obtained was filtered off, washed with ether, and then dried in vacuum over silica gel. Yield: 0.752 g (70%); m.p. 340°C , decomposed. Molar conductivity ($1.0 \times 10^{-3} \text{ mol L}^{-1}$, DMF): $14.5 \Omega^{-1} \text{ cm}^2 \text{ mol}^{-1}$. Elemental Anal. for $\text{C}_{20}\text{H}_{20}\text{N}_2\text{O}_2\text{Pt}$: Calcd C, 46.60; H, 3.91; N, 5.43. Found: C, 46.20; H, 4.01; N, 5.63. ^1H NMR (CDCl_3 , 500 MHz, ppm): $\delta = 1.3\text{--}1.4$ (4H, m), 3.5–3.8(1H, m), 6.1(1H, m), 7(1H, d), 7.2(1H, d), 7.5(1H, m), 7.8(1H, s). IR (KBr, cm^{-1}): 3050vw, 3036vw, 2935w, 2858w, 1604vs, 1594s, 1535s, 1483ms, 1446ms, 1400ms, 1342m, 1315m, 1223mw, 1191m, 1149mw, 1045w, 1026w, 923w, 906mw, 883w, 806w, 740w, 698w, 563ms, 470mw, 453mw, 424mw. UV-Vis [CHCl_3 , λ_{max} nm ($\log \varepsilon/(\text{mol L}^{-1})^{-1} \text{ cm}^{-1}$): 252 (4.74), 316 (4.25), 342 (4.33), 428 (3.92), 512 (2.05).

2.3. Computational details

DFT calculations of the single-crystal X-ray structure were carried out in the gas phase with a generalized gradient approximation functional OLYP [19] at the TZP (6-311G*) basis set for all atoms using the Amsterdam DFT [20]. The corresponding vibrational frequencies were calculated at the same level without any imaginary frequency. The electronic spectrum of [Pt(Salen)] was calculated with the time-dependent DFT (TDDFT) method [21]. NBO calculation was also performed at the same OLYP/TZP level.

2.4. X-ray crystallography

The experimental details of X-ray data collection, structure solution, and refinement of the title compound are given in table 1. A suitable crystal of platinum complex (a yellow plate with $0.23 \times 0.05 \times 0.02$ mm dimensions) was attached to a thin glass fiber. Diffraction data were collected on a Bruker-Nonius KappaCCD diffractometer with graphite-monochromated Mo-K α radiation ($\lambda = 0.71073$ Å, $T = 150$ K). Absorption correction was applied using SADABS [22]. Data reduction included the application of EvalCCD. The structure was solved using direct methods with the SHELXTL NT 6.12 software package [22]. Scattering factors were taken from the literature [23]. All non-hydrogen atoms were refined anisotropically. The compound crystallizes with two

Table 1. Crystal data and structure refinement for [Pt(N₂O₂)].

Empirical formula	C ₂₀ H ₂₀ N ₂ O ₂ Pt
Formula weight	515.47
Temperature (K)	150
Wavelength (Å)	0.71073
Crystal system	Monoclinic
Space group	<i>P</i> 2 ₁ / <i>c</i>
Unit cell dimensions (Å, °)	
<i>a</i>	22.094(2)
<i>b</i>	7.4680(4)
<i>c</i>	24.992(2)
β	123.742(6)
Volume (Å ³), <i>Z</i>	3429.0(4), 8
Calculated density (Mg m ⁻³)	8.200
Absorption coefficient (mm ⁻¹)	8.200
<i>F</i> (000)	1984
Crystal size (mm ³)	0.23 × 0.05 × 0.02
θ range for data collection (°)	6.7–57.4
Limiting indices	−29 ≤ <i>h</i> ≤ 29; −10 ≤ <i>k</i> ≤ 10; −33 ≤ <i>l</i> ≤ 33
Reflections collected	105,207
Independent reflections	8839 [<i>R</i> (int) = 0.0794]
Completeness to $\theta = 99.8$ (%)	28.70
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.849 and 0.478
Refinement method	Full-matrix least-squares on <i>F</i> ²
Data/restraints/parameters	8839/0/451
Goodness-of-fit on <i>F</i> ²	1.160
Final <i>R</i> indices [<i>I</i> > 2 σ (<i>I</i>)]	<i>R</i> ₁ = 0.0298, <i>wR</i> ₂ = 0.0559
<i>R</i> indices (all data)	<i>R</i> ₁ = 0.0517, <i>wR</i> ₂ = 0.0609
Largest difference peak and hole (e Å ⁻³)	1.474 and −0.708

symmetrically independent molecules in its asymmetric unit. All hydrogen atoms were placed in positions of optimized geometry and their isotropic displacement parameters were tied to those of their corresponding carrier atoms by a factor of 1.2 or 1.5. The final residual factors are $R_1 = 0.0298$ and $wR_2 = 0.0609$ for 8839 unique reflections with $I > 2\sigma(I)$ using the weighting scheme, $w = 1/[\sigma^2(F_o^2) + (0.0966P)^2 + 0.1292P]$, where $P = (F_o^2 + F_c^2)/3$.

3. Results and discussion

The platinum complex was obtained in good yield (70%) by the reaction of the quadridentate ligand with $[\text{PtCl}_2(\text{SMe}_2)_2]$ in stirred anhydrous methanol. A suitable crystal for X-ray crystallography was obtained by slow evaporation of $\text{CHCl}_3/\text{MeCN}$ (3/1) over a week in a refrigerator. The platinum complex has excellent solubility in DMSO, DMF, CH_2Cl_2 , and CHCl_3 and is insoluble in alcohol, benzene, acetone, and water. Molar conductance of the complex is $14.5 \Omega^{-1} \text{cm}^2 \text{mol}^{-1}$ for $1.0 \times 10^{-3} \text{mol L}^{-1}$ solution in DMF, indicating a non-electrolyte [24].

3.1. ^1H NMR study

^1H NMR spectra of the platinum(II) complex and H_2L were recorded in CDCl_3 . In the ^1H NMR spectrum of the complex, the OH resonance disappears upon complexation, indicating coordination through deprotonated phenolic oxygen. Cyclohexane resonances of the $\text{CH}_2\text{--CH}_2$ and N--CH--CH--N moieties are at 1.3–1.4 and 3.5–3.8 ppm, respectively. The azomethine proton ($\text{HC}=\text{N}$) appears at 7.8 ppm revealing N coordinated to Pt(II) since it is upfield shifted with respect to the free ligand. Peaks of the phenyl ring protons were observed at 6.1–7.5 ppm.

3.2. Description of crystal structure

Single-crystal X-ray diffraction analysis was performed for the platinum complex, confirming the spectroscopic results. An ORTEP diagram of the platinum complex is presented in figure 1 and relevant bond length and angle data are collected in table 2. There are two molecules in the asymmetric unit with slightly different structures (figure 2). The central Pt(II) of both structures is square-planar. Here, we describe general information about $[\text{Pt}(1)(\text{ONNO})]$ and related parameters of $[\text{Pt}(2)(\text{ONNO})]$ are given in table 2. H_2L is doubly deprotonated, acting as a double negatively charged quadridentate N_2O_2 chelate, coordinated to Pt(II) *via* azomethine N(1) and N(2) and phenolic O(1) and O(2). The average Pt–N and Pt–O bond lengths are 1.955 Å and 1.995 Å, respectively, consistent with those found in other platinum compounds [25–27]. The sum of the four angles around Pt is exactly 360° , indicating the square-planar geometry. But, the O(1)–Pt(1)–N(2) and O(2)–Pt(1)–N(1) bond angles are 178.58° and 178.47° , respectively, showing a little distortion. The cyclohexane ring adapts a distorted chair conformation. Displacements of C(7), C(13), N(1), and N(2) from the least-squares plane drawn through the chelate ring $[\text{Pt}(1)\text{--N}(1)\text{--C}(9)\text{--C}(13)\text{--N}(2)]$ are 0.248 Å, -0.252 Å, 0.131 Å, and 0.139 Å, respectively, in agreement with results from

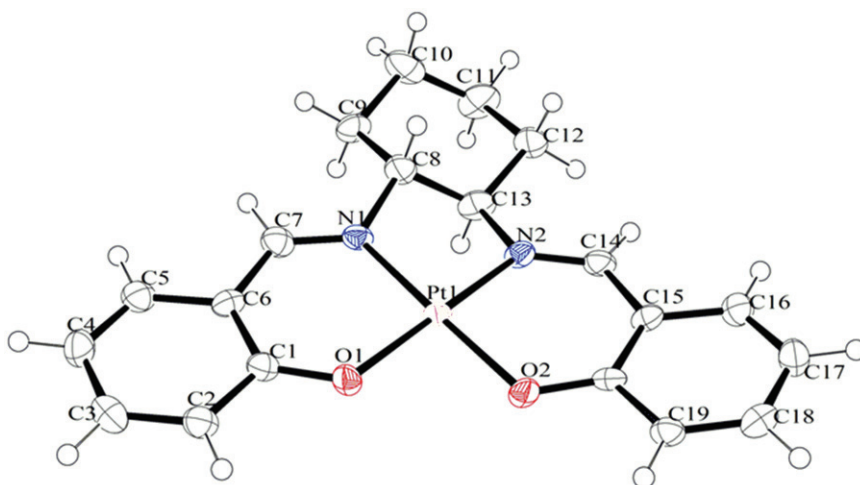


Figure 1. The ORTEP drawing of molecular structure of platinum complex.

Table 2. The experimental and optimized bond lengths (Å) and angles (°) for platinum complex.

Bond types	Experimental	Optimized	Bond types	Experimental	Optimized
Pt(1)–O(1)	2.003(2)	2.123	O(1)–Pt(1)–O(2)	85.3(1)	91.8
Pt(1)–O(2)	1.997(4)	2.121	O(1)–Pt(1)–N(1)	95.4(2)	92.8
Pt(1)–N(1)	1.961(5)	2.058	O(1)–Pt(1)–N(2)	178.6(2)	174.3
Pt(1)–N(2)	1.950(3)	2.059	O(2)–Pt(1)–N(1)	178.5(2)	175.2
O(1)–C(1)	1.312(6)	1.301	O(2)–Pt(1)–N(2)	95.1(2)	93.0
O(2)–C(20)	1.324(5)	1.301	N(1)–Pt(1)–N(2)	84.2(2)	82.50
N(1)–C(7)	1.279(6)	1.300	Pt(1)–O(1)–C(1)	122.5(3)	122.0
N(1)–C(8)	1.486(5)	1.479	Pt(1)–O(2)–C(20)	122.4(3)	122.3
N(2)–C(13)	1.510(7)	1.480	Pt(1)–N(1)–C(7)	124.6(3)	123.8
N(2)–C(14)	1.287(7)	1.301	Pt(1)–N(1)–C(8)	112.2(3)	111.3
C(6)–C(7)	1.445(5)	1.433	Pt(1)–N(2)–C(13)	110.7(3)	111.4
C(8)–C(13)	1.490(7)	1.548	Pt(1)–N(2)–C(14)	124.9(3)	123.7
C(14)–C(15)	1.448(8)	1.433	N(1)–C(7)–C(6)	125.9(4)	127.7
Pt(2)–O(3)	2.003(3)		C(15)–C(14)–N(2)	126.2(4)	127.8
Pt(2)–O(4)	2.008(4)		O(3)–Pt(2)–O(4)	86.1(1)	
Pt(2)–N(3)	1.948(5)		O(3)–Pt(2)–N(3)	94.8(2)	
Pt(2)–N(4)	1.960(4)		O(3)–Pt(2)–N(4)	178.3(1)	
O(3)–C(21)	1.324(7)		O(4)–Pt(2)–N(3)	179.1(2)	
O(4)–C(40)	1.304(7)		O(4)–Pt(2)–N(4)	94.8(1)	
N(3)–C(27)	1.298(8)		N(3)–Pt(2)–N(4)	84.4(2)	
N(3)–C(28)	1.493(5)		Pt(2)–O(3)–C(21)	122.6(3)	
N(4)–C(33)	1.505(5)		Pt(2)–O(4)–C(40)	122.9(3)	
N(4)–C(34)	1.274(8)		Pt(2)–N(3)–C(27)	124.7(3)	
C(34)–C(35)	1.452(6)		Pt(2)–N(3)–C(28)	112.0(3)	
C(28)–C(33)	1.496(8)		Pt(2)–N(4)–C(33)	112.0(3)	
C(26)–C(27)	1.436(5)		Pt(2)–N(4)–C(34)	124.6(3)	
			N(3)–C(27)–C(26)	126.1(4)	
			C(35)–C(34)–N(4)	126.4(4)	

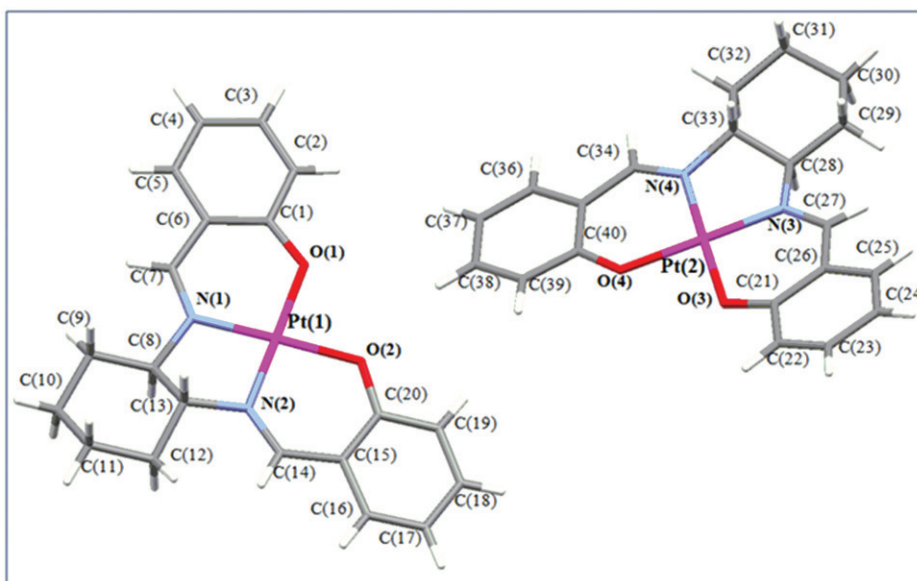


Figure 2. The asymmetric unit showing two crystallographically independent molecules.

most Schiff-base metal complexes containing $\text{NCH}_2\text{CH}_2\text{N}$ moieties [28]. The dihedral angle between $\text{Pt}(1)\text{N}(2)\text{C}(14)\text{C}(15)\text{C}(19)\text{O}(2)$ and its counterpart chelate ring [$\text{Pt}(1)\text{N}(1)\text{C}(7)\text{C}(5)\text{C}(6)\text{O}(1)$] is 3.49° . The mean plane of the two chelating rings are nearly coplanar with the benzene planes (Calcd 8.2° between $[\text{C}(19)\text{C}(20)\text{C}(15)\text{C}(16)\text{C}(17)\text{C}(18)]$, $[\text{O}(2)\text{Pt}(1)\text{N}(2)\text{C}(14)\text{C}(15)\text{C}(20)]$ and *ca* 6.79° between $[\text{C}(20)\text{C}(19)\text{C}(18)\text{C}(17)\text{C}(16)\text{C}(15)]$, $[\text{Pt}(1)\text{N}(2)\text{C}(14)\text{C}(15)\text{C}(20)\text{O}(2)]$), supporting a large π -electron delocalization. The partial double-bond character of $\text{C}(6)\text{C}(7)$ and $\text{C}(14)\text{C}(15)$ in the molecule favor conjugation of the delocalized π -electrons with d electrons of platinum.

3.3. General optimization and NBO analysis

The optimized geometry of the compound has been obtained at the OLYP/6-311G* level. Some of the optimized geometric parameters are also listed in table 2 and show good agreement with experimental values. The bond lengths and angles determined from the OLYP method are slightly larger than the experimental values; the largest difference in bond length and angle occur at $\text{Pt}(1)\text{O}(1)$ and $\text{O}(1)\text{Pt}(1)\text{O}(2)$ with a difference of 0.12 \AA and 6.46° , respectively. The reason for this is that the theoretical calculation is performed for an isolated molecule in the gas phase and the experimental results are obtained for a molecule in the solid state. The geometry of the solid-state structure is affected by intermolecular, crystal packing forces, and other types of supramolecular interactions [29].

The natural charges on donors and platinum were calculated by NBO analysis. The NBO analysis shows calculated net charges for N(1), N(2), O(1), and O(2) are -0.6098 a.u. , -0.6076 a.u. , -0.6472 a.u. , and -0.6474 a.u. , respectively. The calculated

charge on platinum is 1.1685 a.u., lower than the formal charge +2. This confirms charge donation from the oxygen and nitrogen of the ligand toward platinum.

3.4. Vibrational assignments

The platinum molecule has C1 symmetry with 45 atoms that should have 129 normal vibrational modes [30]. The frequency calculation could predict all of them without any imaginary frequencies. Some of the most important vibrational modes are discussed here.

The IR spectrum of the complex does not show any peak related to $\nu(\text{OH})$, indicating oxygen is coordinated to platinum. Very weak bands at 3050 cm^{-1} and 3036 cm^{-1} are assigned to C–H stretches of aromatic and cyclohexane rings, respectively [31]. The corresponding calculated values are at 3091 cm^{-1} and 3059 cm^{-1} . Experimentally the out of plane bending vibration of C–H is at 740 cm^{-1} [32]. The related vibration is computed at 724 cm^{-1} . The asymmetric and symmetric vibrations of CH_2 for cyclohexane are at 2935 cm^{-1} and 2858 cm^{-1} , respectively [33]. The theoretically scaled values are at 3000 cm^{-1} and 2905 cm^{-1} . The C=N stretch is expected at $1600\text{--}1630\text{ cm}^{-1}$ [34, 35] and in this study, this mode appears at 1604 cm^{-1} as a very strong band and at 1588 cm^{-1} in the calculated with the same intensity. The C=C band is reported at $1350\text{--}1600\text{ cm}^{-1}$ [36]. In this work, the C=C stretch is mixed with the other stretching or bending vibrations, observed at 1594 cm^{-1} . The DFT calculation gives this mode at 1584 cm^{-1} . The medium intensity band found in the complex spectrum at 1342 cm^{-1} could be attributed to the C–O stretch [37]. In the calculated spectrum of the complex, this band is at 1354 cm^{-1} .

3.5. Electronic spectrum

The electronic spectrum of the Pt(II) complex was recorded from 230 to 1000 nm in chloroform. In addition, the TDDFT method was used to predict the UV-Vis spectrum with 0.72 scale factor [38] at the OLYP/TZP level. The experimental spectrum of the complex exhibits three bands at 252, 316, and 342 nm due to interligand transitions ($\pi \rightarrow \pi^*$) [39]. Electronic spectra for square-planar geometry with d^8 electronic configuration predicts three d–d transitions [40], but the platinum complex just exhibits one d–d transition at 512 nm attributed to $^1A_{1g} \rightarrow ^1A_{2g}$ [41]. Other d–d transitions are masked by ligand-to-metal charge transfer (LMCT) and metal-to-ligand charge transfer (MLCT) bands. A broad band is observed between 380 and 482 nm with maximum at 426 nm due to combination of LMCT, MLCT, and d–d transitions [42].

Figure 3 depicts selected, occupied, and unoccupied frontier orbitals. To compare between calculated and experimental results, some of the most important details such as absorption wavelengths (λ_{max}), oscillator strength, and excitation energies are collected in table 3. The HOMO-1 and LUMO are 100% contribution from the ligand. HOMO-3 is 52% contribution from Pt(II) and 48% contribution from ligand. HOMO, LUMO + 1, and LUMO + 2 are dominated by ligand (>65%). Accordingly, the intense transitions at <450 nm originate mainly from interligand transitions ($\pi \rightarrow \pi^*$) and also two bands at 510 and 534 nm are a mixture of MLCT, LMCT, and d–d transitions.

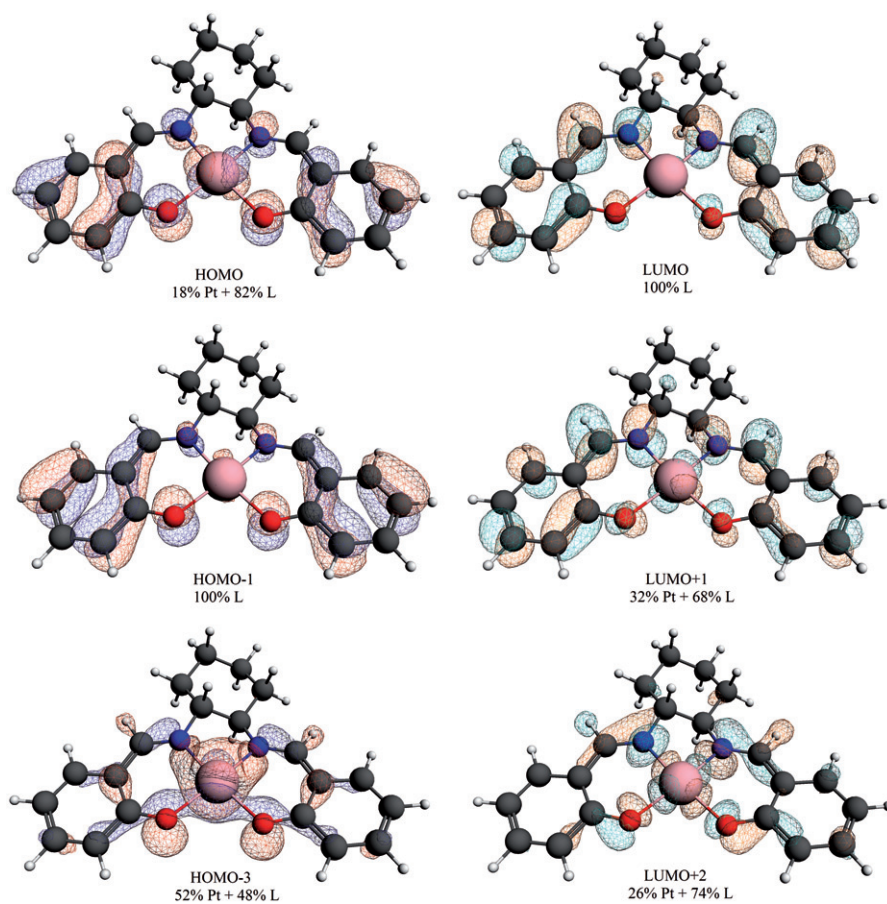


Figure 3. Selected contour plots of MOs of the Pt(II) complex.

Table 3. Experimental and calculated absorption wavelengths (λ), excitation energies (E), and oscillator strength (f) of platinum complex.

Most important orbital excitations	Character	Calculated			Experimental		
		λ (nm)	E (eV)	f	λ (nm)	E (eV)	ϵ
HOMO-3 \rightarrow LUMO	LLCT, MLCT	254	4.88	0.001042	252	4.92	55,850
HOMO-1 \rightarrow LUMO+2	LLCT, LMCT	291	4.26	0.05628	316	3.92	18,000
HOMO-1 \rightarrow LUMO+1	LLCT, LMCT						
HOMO-1 \rightarrow LUMO	LLCT	305	4.06	0.002814	342	3.62	21,700
HOMO \rightarrow LUMO+2	LMCT, LLCT, MLCT, d-d	367	3.37	0.01800	428	2.9	8450
HOMO \rightarrow LUMO+1	LMCT, LLCT, MLCT, d-d						
HOMO \rightarrow LUMO	MLCT, LLCT	384	3.22	0.009571	—	—	—
		—	—	—	512	2.42	114

4. Conclusion

We synthesized and characterized a platinum(II) complex containing an N₂O₂ quadridentate ligand. X-ray diffraction reveals that the ligand is a binegative chelate. The crystal structure shows platinum(II) is square-planar. The compound crystallized in the monoclinic, space group *P*2₁/*c* with two molecules in the asymmetric unit. Geometry optimization calculation based on DFT provided a satisfactory match with the crystallographic structure and spectral properties. The frequency calculation results show that the predicted vibrations compare well with the experimental results. The molecular orbital (MOs) diagram has been drawn by DFT calculation and also the TDDFT method at OLYP/6-311G* level can be used to improve understanding of the electronic excitation.

Supplementary data

CCDC 888714 contains the supplementary crystallographic data for the platinum complex. This data can be obtained free of charge *via* <http://www.ccdc.cam.ac.uk/conts/retrieving.html>, or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; Fax: (+44) 1223-336-033; or E-mail: deposit@ccdc.cam.ac.uk

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