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Synthesis, characterization and crystal structure of platinum(II) complexes with thiourea derivative ligands

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ABSTRACT

Thiourea derivatives [*N*-(*di-n*-propylcarbamothioyl)-4-fluorobenzamide (HL¹) and *N*-(*di-n*-propylcarbamothioyl)-4-bromobenzamide (HL²)] and their platinum complexes have been successfully synthesized and structurally characterized by spectroscopic ¹H NMR, ¹³C NMR, COSY, HMQC, and FT-IR techniques. The structure of both complexes was also confirmed by single crystal X-ray diffraction studies. The study of X-ray single crystal diffraction shows that the supramolecular aggregation of the complexes is stabilized *via* weak interactions as well as stacking interactions such as C-H... π and π ... π . The *cis*-[Pt(L¹-S,O)₂] showed C-H... π and π ... π stacking interactions, whereas only C-H... π stacking interaction was observed in *cis*-[Pt(L²-S,O)₂]. In addition, the strong classical and non-classical intermolecular hydrogen bonds are not found in the prepared complexes. Therefore, it can be said that the C-H... π and π ... π stacking interactions play an important role in the formation of supramolecular structures of the complexes.

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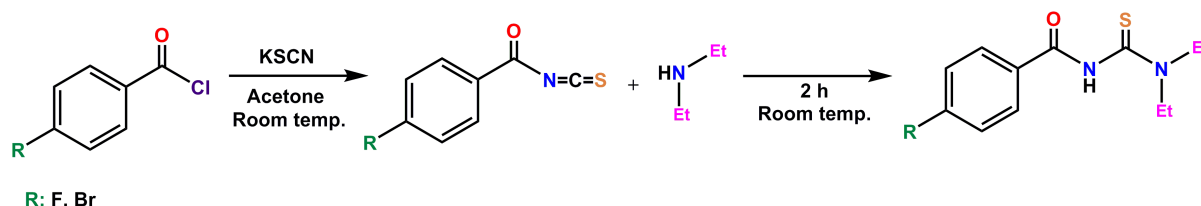
1. Introduction

Thiourea containing compounds are versatile molecules which are capable of coordinating with metal ions to form stable complexes. For example *N*-(alkyl/aryl)-*N'*-acylthiourea and *N*-di(alkyl/aryl)-*N'*-acylthiourea derivatives which have oxygen, nitrogen and sulphur donor atoms, exhibit prevalent coordination modes. Organic ligands that have thiourea moiety are able to bind metal ions in several ways, like: (i) acting as monodentate ligands through sulphur atom in mononuclear complexes [1-4] (ii) binding to metal ions forming S-bridges in dinuclear complexes [4-8] or (iii) chelating sulphur and nitrogen atoms [4,6,8-16]

Thiourea derivatives as a ligand have a large dipole moment and these ligands can also form extensive network of hydrogen bonds due to their unique structures. For example in 3-monosubstituted arylthioureas [17-19], the carbonyl group and the proton on the nitrogen attach in a strong hydrogen bond interaction which unite into a planar six-membered ring structure forming an "S" shaped conformation of the C=O and C=S groups [20,21]. Further, it can also be stated that amine-

thiourea compounds might have bifunctional properties due to the intra- and inter-molecular interactions *via* hydrogen bonding [22-25]. The interplay of intermolecular and intramolecular hydrogen bonding has direct relevance on chemical properties of these compounds, including their use as ligand in metal complexes [26] and also their conformational properties, which have influence in the applied fields [27]. Metal complexes of these compounds have long been known not only for their wide range of biological applications but also for their role in analytical sciences [28-30], as inhibitors in the corrosion field [31] and as catalysts in chemical reactions [21,32].

Because of the significant properties that thiourea derivatives have, their synthesis, structure, biological activity and application to these kinds of compounds have drawn attention from the past to the present. Numbers of studies, involving structural ligand design and the synthesis of complexes for different purposes in various fields, have increased. As a part of our research, we report herein the synthesis and characterization of thiourea derivative ligands (*N*-(*di-n*-propylcarbamothioyl)-4-fluorobenzamide (HL¹) and *N*-(*di-n*-propyl-



Scheme 1. Synthesis of thiourea ligands.

carbamothioyl)-4-bromobenzamide (HL²) and their platinum complexes (*cis*-[Pt(L¹-S,O)₂] and *cis*-[Pt(L²-S,O)₂]). Conformational properties of synthesized complexes have also been investigated by intermolecular contacts obtained from X-ray single crystal diffraction study.

2. Experimental

2.1. Instrumentation

Infrared measurement was recorded in the range 400–4000 cm⁻¹ on a Perkin Elmer Spectrum 100 series FT-IR/FIR/NIR Spectrometer Frontier, ATR Instrument. The NMR spectra were recorded in CDCl₃ solvent on Bruker Avance III 400 MHz NaNoBay FT-NMR spectrophotometer using tetramethylsilane as an internal standard.

The X-ray diffraction data were recorded on a Bruker APEX-II CCD diffractometer. A suitable crystal was selected and coated with Paratone oil and mounted on a Nylon loop on a Bruker APEX-II CCD diffractometer. The crystal was kept at *T* = 100 K during data collection. The data were collected with MoK α (λ = 0.71073 Å) radiation at a crystal-to-detector distance of 40 mm. Using Olex2 [33], the structure was solved with the Superflip [34–36] structure solution program, using the Charge Flipping solution method and refined by full-matrix least-squares techniques on *F*² using ShelXL [37] with refinement of *F*² against all reflections. Hydrogen atoms were constrained by difference maps and were refined isotropically, and all non-hydrogen atoms were refined anisotropically.

2.2. Reagents

Potassium thiocyanate, 4-fluorobenzoyl chloride and 4-bromobenzoylchloride were purchased from Merck and used as received. All other chemicals and solvents were obtained from commercial suppliers and used without further purification.

2.3. Synthesis and characterization

2.3.1. General procedure for the synthesis of ligands (HL^{1,2})

HL^{1,2} ligands were prepared according to previously published methods [38–40]. A solution of substituted benzoyl chloride (4-fluorobenzoyl chloride and 4-bromobenzoyl chloride, 5 mmol) in dry acetone (50 mL) was added dropwise to a suspension of potassium thiocyanate (5 mmol, 0.490 g) in acetone (30 mL). The reaction mixture was heated under reflux for 30 min and then cooled to room temperature. A solution of di-*n*-propylamine (5 mmol, 0.54 g) was added and the resulting mixture was stirred for 2 h. After that, the reaction mixture was poured into hydrochloric acid (0.1 M, 300 mL), and the solution was filtered. The solid product was washed with water and purified by recrystallization from an ethanol:dichloromethane mixture (1:1, v:v) (Scheme 1).

N-(Di-*n*-propylcarbamothioyl)-4-fluorobenzamide (HL¹): Colour: White. Yield: %70. FT-IR (ATR, ν , cm⁻¹): 3271 (NH), 2968, 2934, 2877 (CH), 1643 (C=O), 1275 (C=S), 753 (C-F). ¹H

NMR (400 MHz, CDCl₃, δ , ppm): 8.42 (s, 1H, NH), 7.86 (d, 2H, Ar-*H*), 7.15 (d, 2H, Ar-*H*), 3.92 (t, 2H, N-CH₂), 3.51 (t, 2H, N-CH₂), 1.83 (m, 2H, -CH₂-), 1.71 (m, 2H, -CH₂-), 1.02 (t, 3H, CH₃), 0.88 (t, 3H, CH₃). ¹³C NMR (100 MHz, CDCl₃, δ , ppm): 180.10 (C=S), 162.83 (C=O), 130.61 (C-Ar), 130.52 (C-Ar), 115.96 (C-Ar), 115.74 (C-Ar), 54.99 (C-N), 54.89 (C-N), 21.46 (CH₂), 19.73 (CH₂), 11.31 (CH₃), 11.27 (CH₃).

N-(Di-*n*-propylcarbamothioyl)-4-bromobenzamide (HL²): Colour: White. Yield: %88. FT-IR (ATR, ν , cm⁻¹): 3207 (NH), 2962, 2947, 2871 (CH), 1685 (C=O), 1261 (C=S), 750 (C-Br). ¹H NMR (400 MHz, CDCl₃, δ , ppm): 8.38 (s, 1H, NH), 7.64 (d, 2H, Ar-*H*), 7.62 (d, 2H, Ar-*H*), 3.95 (s, 2H, N-CH₂), 3.50 (s, 2H, N-CH₂), 1.84 (m, 2H, -CH₂-), 1.67 (m, 2H, -CH₂-), 1.04 (s, 3H, CH₃), 0.91 (s, 3H, CH₃). ¹³C NMR (100 MHz, CDCl₃, δ , ppm): 179.88 (C=S), 162.97 (C=O), 132.02 (C-Ar), 131.40 (C-Ar), 129.55 (C-Ar), 127.78 (C-Ar), 55.02 (C-N), 54.95 (C-N), 21.48 (CH₂), 19.75 (CH₂), 11.35 (CH₃), 11.31 (CH₃).

2.3.2. General procedure for the synthesis of platinum complexes

A solution of HL^{1,2} (2.0 mmol, HL¹: 0.56 g; HL²: 0.67 g) in ethanol (50 mL) at 70 °C was added dropwise to a solution of potassium tetrachloroplatinate(II) (1.0 mmol, 0.416 g) in water (50 mL) at 70 °C. The reaction mixture was stirred for 30 min and then cooled to room temperature. A yellow-brown precipitate formed, which was filtered off and recrystallized from ethanol:dichloromethane (2:1, v:v) (Scheme 2) [41–50].

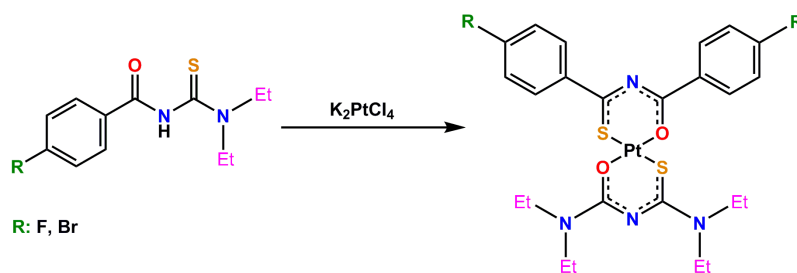
Bis[4-Fluoro-*N*-(di-*n*-propylcarbamothioyl)benzamido-*O*, *S*] platinum(II), *cis*-[Pt(L¹-S,O)₂]: Color: Yellow. Yield: 78%. FT-IR (ATR, ν , cm⁻¹): ν (C-H) 2962, 2927, 2868 (w), ν (C-N) 1578 (w), ν (C-O) 1487 (vs), ν (C-S) 1088 (s). ¹H NMR (400 MHz, CDCl₃, δ , ppm): 8.16 (td, 4H, Ar-*H*), 7.01 (td, 4H, Ar-*H*), 3.65 (q, 4H, N-CH₂), 3.58 (q, 4H, N-CH₂), 1.76 (p, 4H, N-CH₂-CH₂), 1.63 (p, 4H, N-CH₂-CH₂), 0.90 (m, 12H, CH₃). ¹³C NMR (100 MHz, CDCl₃, δ , ppm): 167.68 (C-S), 167.40 (C-O), 133.82 (C-Ar), 133.79 (C-Ar), 131.64 (C-Ar), 131.55 (C-Ar), 115.15 (C-Ar), 114.93 (C-Ar) 54.54 (C-N), 53.75 (C-N), 21.27 (CH₂), 20.53 (CH₂), 11.40 (CH₃).

Bis[4-Bromo-*N*-(di-*n*-propylcarbamothioyl)benzamido-*O*, *S*] platinum(II), *cis*-[Pt(L²-S,O)₂]: Color: Yellow. Yield: 72%. FT-IR (ATR, ν , cm⁻¹): ν (C-H) 2972, 2957, 2898 (w), ν (C-N) 1565 (w), ν (C-O) 1492 (vs), ν (C-S) 1090 (s). ¹H NMR (400 MHz, CDCl₃, δ , ppm): 8.10 (td, 4H, Ar-*H*), 7.57 (td, 4H, Ar-*H*), 3.75 (q, 4H, N-CH₂), 3.67 (q, 4H, N-CH₂), 1.85 (p, 4H, N-CH₂-CH₂), 1.76 (p, 4H, N-CH₂-CH₂), 0.99 (m, 12H, CH₃). ¹³C NMR (100 MHz, CDCl₃, δ , ppm): 167.74 (C-S), 167.47 (C-O), 136.64 (C-Ar), 131.36 (C-Ar), 131.13 (C-Ar), 130.85 (C-Ar), 126.27 (C-Ar), 54.60 (C-N), 53.51 (C-N), 20.49 (CH₂), 20.53 (CH₂), 11.40 (CH₃).

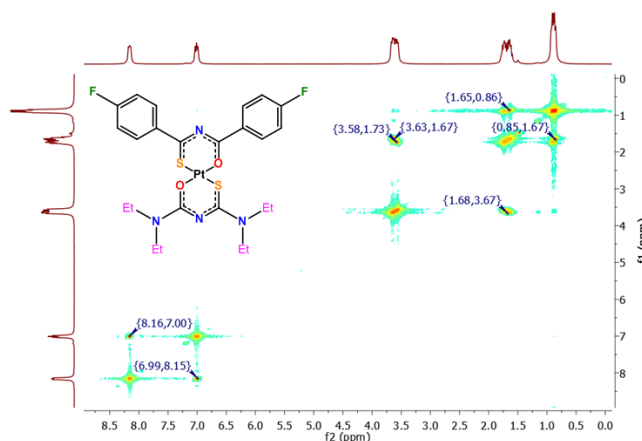
3. Results and discussion

3.1. NMR and FT-IR spectral analysis

The synthesized compounds have been characterized by spectroscopic ¹H NMR, ¹³C NMR, COSY, HMQC and FT-IR techniques. The NMR spectra of the ligands and their platinum complexes were recorded in CDCl₃.



Scheme 2. Synthesis of thiourea complexes.

Figure 1. COSY NMR spectrum of *cis*-[Pt(L¹-S,O)₂] complex.

The NMR data of the compounds are given in the experimental section and are consistent with the structural results. In the ¹H NMR of the ligands (HL^{1,2}) characteristic NH proton signals were observed at δ 8.42 and 8.38 ppm, respectively, as a singlet. After the complexation, the signals that belong to NH group were not observed due to the deprotonation. The ligands have shown bidentate coordination *via* the sulfur and oxygen atoms to platinum metal atom. Slight differences were observed in the ¹H NMR spectra of the complexes related to attached substituent groups (F or Br), altering the electronic structure of the ligand. The signals for the aromatic protons were observed in the range of δ 7.15-7.86 ppm for each ligand, with small differences in their environments. After the metalation, differently from the free ligand, the aromatic proton resonance values shifted to downfield, between the range of δ ~7-8 ppm. The resonance values, obtained from the ¹H NMR spectra of the complexes, were almost similar. The most observed distinct shift values were aliphatic protons in *cis*-[Pt(L²-S,O)₂] complexes. Compared to free ligands, the resonance values that were obtained for the aliphatic protons shifted to upfield, only the observed signals, which belong to the methyl group shifted to downfield region in *cis*-[Pt(L¹-S,O)₂] and *cis*-[Pt(L²-S,O)₂] complexes. In ¹³C NMR spectrum of free ligands, thiocarbonyl (C=S) and carbonyl (C=O) carbons appeared at δ 180-162 ppm range. It has been observed from the ¹³C NMR spectra of the complexes, that the C-S carbon resonance values shifted to upfield while the resonance values of the C-O appeared at the downfield region for both complexes as a result of the complexation process.

The two-dimensional nuclear magnetic resonance spectra is used for resolving the interactions between carbon and hydrogen atoms, or neighboring protons. These spectral analysis are based on effective magnetic fields, interactions of the nuclear spin with adjacent atoms and the number of equivalent protons. To elucidate the structures of compounds, 2D NMR experiments (HMQC and COSY) were carried out. According to the COSY spectrum of the platinum complexes,

for the benzamide moiety, correlations between aromatic protons were observed at δ 8.16; 7.00 and 8.15; 6.99 ppm for *cis*-[Pt(L¹-S,O)₂] and δ 8.12; 7.58 and 8.10; 7.57 ppm for *cis*-[Pt(L²-S,O)₂] complexes, respectively. In addition, the COSY spectrum of the complexes revealed the CH₂-CH₂ and CH₂-CH₃ interactions between aliphatic neighboring protons (Figures 1 and 2). CH₂-CH₂ interactions were detected between the peaks, appearing as a quartet close to the electronegative N atom and as a pentet, for both complexes. Also, the correlations of CH₂-CH₃ protons were observed between the peaks at δ 1.65 (CH₂) with 0.86 (CH₃) and 1.67 (CH₂) with 0.85 (CH₃) ppm for *cis*-[Pt(L¹-S,O)₂] complex and between the peaks at δ 1.77 (CH₂) with 0.97 (CH₃) and 1.83 (CH₂) with 0.99 (CH₃) ppm for *cis*-[Pt(L²-S,O)₂] complex (Figures 1 and 2). The HMQC shows the interactions between the protons and their attached heteronuclei through the heteronuclear coupling. In the HMQC spectrum of the complexes, it is evident that the peaks which were observed in the ¹³C NMR spectra (δ 167.68 (C-S) and 167.40 (C-O) ppm for *cis*-[Pt(L¹-S,O)₂], 167.74 (C-S) and 167.47 (C-O) ppm for *cis*-[Pt(L²-S,O)₂]) did not appear because of being non-protonated carbons. The aromatic and aliphatic carbons that have coupled with protons appeared to be compatible with the peaks in the HMQC spectra. Besides, the interactions between carbon and proton atoms, which have attached to electronegative N atom, were detected at δ 3.60 with 54.01 and 3.65 with 53.73 ppm for *cis*-[Pt(L¹-S,O)₂] complex and δ 3.71 with 54.54 ppm, for *cis*-[Pt(L²-S,O)₂] complex, respectively (Figures 3 and 4) [51,52].

The infrared spectra of ligands with their metal complexes have been studied in order to characterize their structures and to confirm the presence of characteristic groups. The IR spectra of free ligands and metal chelates were carried out in the 4000-400 cm⁻¹ range. In the IR spectrum of the ligands the vibration band was observed nearly at ~3200 cm⁻¹ assigned to ν(NH) stretching vibration.

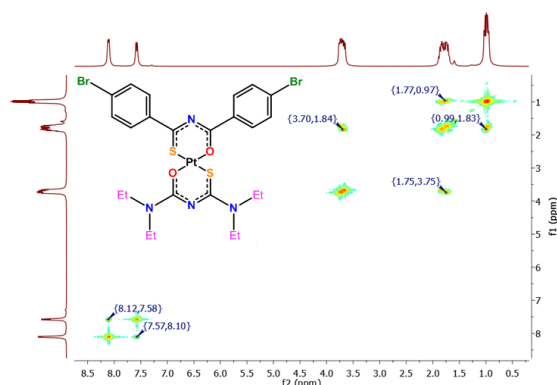


Figure 2. COSY NMR spectrum of *cis*-[Pt(L²-S,O)₂] complex.

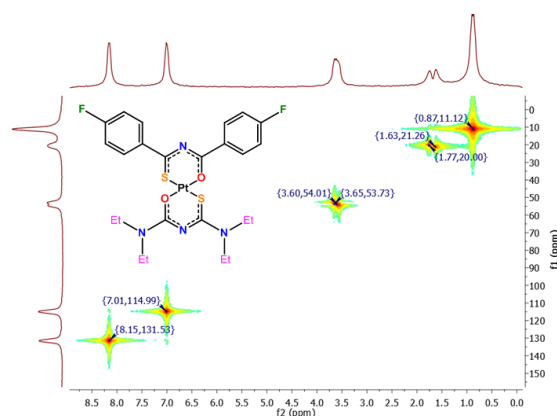


Figure 3. HMQC NMR spectrum of *cis*-[Pt(L¹-S,O)₂] complex.

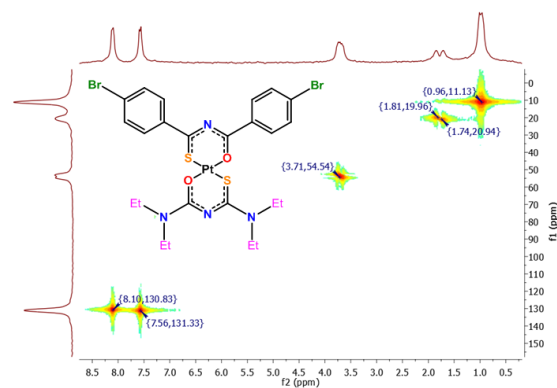


Figure 4. HMQC NMR spectrum of *cis*-[Pt(L²-S,O)₂] complex.

This band disappears upon metal complex formation. The vibration band observed at 1643 and 1685 cm^{-1} are assigned to carbonyl $\nu(\text{C}=\text{O})$ for HL¹ and HL², respectively. The vibration bands for HL¹ and HL² ligands, which belong to $\nu(\text{C}=\text{S})$ group, appeared at 1275 and 1261 cm^{-1} , respectively. After the complexation, carbonyl $\nu(\text{C}=\text{O})$ and thiocarbonyl $\nu(\text{C}=\text{S})$ vibration bands shifted to lower values as a result of the coordination via sulfur and oxygen atoms to platinum ions [53-55].

3.2. Crystal structure analysis

The molecular structure of the obtained complexes was determined with single crystal X-ray diffraction. Block shaped yellow coloured crystal of the complexes was obtained by slow evaporation of their ethanol:dichloromethane solution (2:1,

v:v). The complexes *cis*-[Pt(L¹-S,O)₂] and *cis*-[Pt(L²-S,O)₂] crystallized in orthorhombic space group *Fdd2* and triclinic space group *P1*, respectively. The crystal and structure refinement data are given in Table 1. The asymmetric unit of the *cis*-[Pt(L¹-S,O)₂] consists of half unique molecules, while four crystallographically independent molecules are observed in the *cis*-[Pt(L²-S,O)₂] (Figures 5 and 6).

Calculating the root mean square deviations between the X-ray geometries of the four independent molecules of the *cis*-[Pt(L²-S,O)₂] we can see that all molecules are slightly differ (propyl regions) from the equilibrium geometry (RMSD_(A-C) = 0.692 Å with inversion, RMSD_(A-C) = 0.992 Å without inversion, RMSD_(A-B) = 1.113 Å with inversion, RMSD_(A-B) = 0.716 Å without inversion, RMSD_(A-D) = 0.084 Å with inversion, RMSD_(A-D) = 1.299 Å without inversion).

Table 1. Crystal data and details of the structure refinement for complexes.

Compound	<i>cis</i> -[Pt(L ¹ -S,O) ₂]	<i>cis</i> -[Pt(L ² -S,O) ₂]
Empirical formula	C ₂₈ H ₃₆ F ₂ N ₄ O ₂ PtS ₂	C ₂₈ H ₃₆ Br ₂ N ₄ O ₂ PtS ₂
Formula weight	757.82	879.64
Temperature (K)	298	99.99
Crystal system	Orthorhombic	Triclinic
Space group	<i>Fdd2</i>	<i>P1</i>
a, (Å)	26.819(9)	15.7174(6)
b, (Å)	12.131(5)	17.5696(6)
c, (Å)	18.880(6)	25.3974(9)
α, (°)	90	80.253(2)
β, (°)	90	85.604(2)
γ, (°)	90	63.8880(10)
Volume (Å ³)	6142(4)	6206.7(4)
Z	8	8
ρ _{calc} (g/cm ³)	1.639	1.883
μ (mm ⁻¹)	4.748	12.990
F(000)	3008.0	3424.0
Crystal size (mm ³)	0.21 × 0.21 × 0.12	0.18 × 0.17 × 0.12
Radiation	MoKα (λ = 0.71073)	CuKα (λ = 1.54178)
2θ range for data collection (°)	6.058 to 53.434	5.666 to 146.486
Index ranges	-33 ≤ h ≤ 33, -15 ≤ k ≤ 15, -23 ≤ l ≤ 23	-19 ≤ h ≤ 19, -20 ≤ k ≤ 21, -31 ≤ l ≤ 31
Reflections collected	45369	257871
Independent reflections	3256 [R _{int} = 0.0754, R _{sigma} = 0.0368]	24579 [R _{int} = 0.0527, R _{sigma} = 0.0235]
Data/restraints/parameters	3256/1/179	24579/0/1421
Goodness-of-fit on F ²	1.075	1.052
Final R indexes [I ≥ 2σ (I)]	R ₁ = 0.0267, wR ₂ = 0.0476	R ₁ = 0.0322, wR ₂ = 0.0743
Final R indexes [all data]	R ₁ = 0.0425, wR ₂ = 0.0516	R ₁ = 0.0483, wR ₂ = 0.0818
Largest diff. peak/hole (e.Å ⁻³)	0.97/-0.92	1.56/-2.36

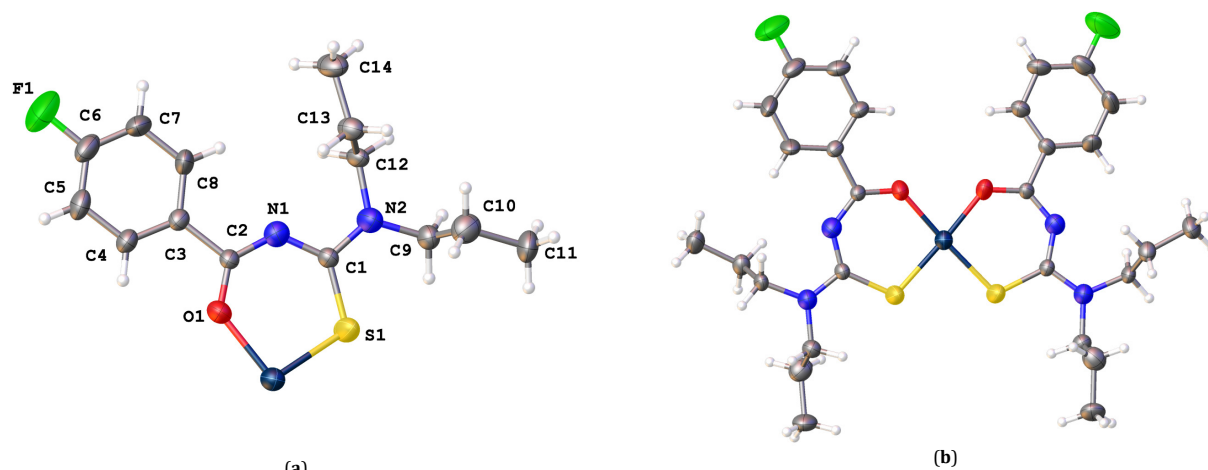
**Figure 5.** (a) The asymmetric unit of the *cis*-[Pt(L¹-S,O)₂] and (b) molecular structure of *cis*-[Pt(L¹-S,O)₂].

Figure 7a shows the overlay diagram of four independent molecules in *cis*-[Pt(L²-S,O)₂]. The overlay diagram illustrates that the conformation of the molecule A is more similar to the molecule D, while the conformation of the molecule B is more similar to the molecule C. The packing diagram of *cis*-[Pt(L²-S,O)₂] is shown in Figures 7b. In the crystal packing of *cis*-[Pt(L²-S,O)₂], molecules A, B, C and D are represented in green, red, pink and blue, respectively, forming an inverted head-to-tail arrangement without any significant hydrogen bond interactions.

In both complexes, the reactions between ligands and Pt(II) produces metal-complexes with the expected ligand-metal ratio of 2:1 in a square-planar geometry. The chelating two benzamide ligands are coordinated with Pt ion in a monoanionic bidentate mode, forming two six membered chelate rings (Pt-SCNCO). The six membered rings are formed via oxygen and sulphur atoms, and dihedral angles between these rings in the *cis*-[Pt(L¹-S,O)₂] and *cis*-[Pt(L²-S,O)₂] are 6.89 and 20.37°, respectively.

The bond angles around the platinum ion are S1-Pt1-O1 = 94.99(17)° for *cis*-[Pt(L²-S,O)₂] and S1-Pt1-O1 = 94.91(9) and S2-Pt1-O2 = 93.89(10)° for *cis*-[Pt(L¹-S,O)₂] (Table 3). The platinum center, surrounded by oxygen and sulphur atoms in complexes, is caused by a slightly distorted square planar geometry as shown in Figure 3. The bite angles of the complexes deviate slightly from the ideal angle (90°). The value of the smallest and largest bite angles are 93.89(10) and 94.99(17)°, respectively. The sum of the equatorial angles S1-Pt1-O1, S2-Pt1-O2, S1-Pt1-S2 and O1-Pt1-O2 are 360.01° and equal to the ideal value of 360.00°, which is consistent with square planar geometry. Other values of bond angles are given in Table 3.

In the both complexes, the C(O) and C(S) bond lengths are 1.292(9) and 1.721(8) Å for *cis*-[Pt(L¹-S,O)₂] and 1.277(5) and 1.736(4) Å for *cis*-[Pt(L²-S,O)₂], which are slightly longer than the corresponding distance found in similar free ligands [47].

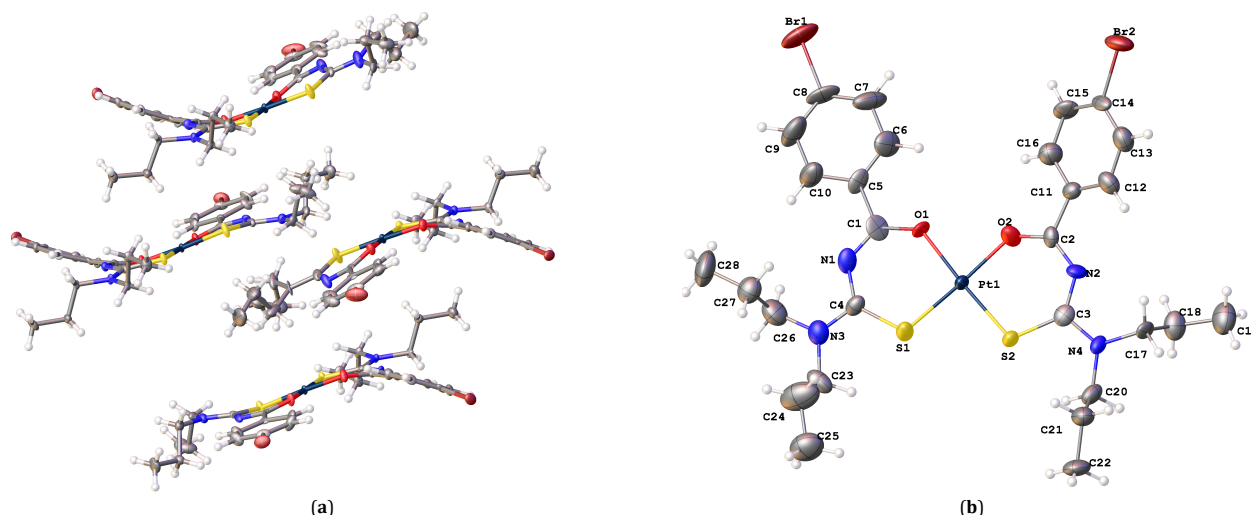


Figure 6. (a) The asymmetric unit of the *cis*-[Pt(L¹-S,O)₂], (b) molecular structure of molecule A in *cis*-[Pt(L²-S,O)₂].

Table 2. Selected bond lengths of the complexes.

Atom	Atom	Length (Å)
<i>cis</i> -[Pt(L ¹ -S,O) ₂]		
Pt(1)	S(1) ⁱ	2.238(3)
Pt(1)	S(1)	2.238(3)
Pt(1)	O(1)	2.002(7)
Pt(1)	O(1) ⁱ	2.002(7)
S(1)	C(1)	1.721(8)
F(1)	C(6)	1.360(11)
O(1)	C(2)	1.292(9)
N(1)	C(1)	1.342(10)
N(1)	C(2)	1.307(9)
N(2)	C(1)	1.338(9)
N(2)	C(9)	1.470(10)
<i>cis</i> -[Pt(L ² -S,O) ₂]		
Pt(1)	S(1)	2.2344(12)
Pt(1)	S(2)	2.2355(10)
Pt(1)	O(2)	2.021(3)
Pt(1)	O(1)	2.013(3)
N(1)	C(1)	1.322(6)
N(1)	C(8)	1.345(6)
C(1C)	C(2C)	1.488(6)
N(2)	C(12)	1.476(6)
N(2)	C(9)	1.472(5)
N(2)	C(1)	1.338(9)
N(2)	C(9)	1.470(10)

ⁱ1/2-x, 1/2-y, +z.

This indicates the existence of an electron delocalization over the six-member chelate ring due to the coordination of the oxygen and sulfur atoms with the platinum ion. All other bond lengths are within normal ranges (Table 2).

The planar configuration of *cis*-[Pt(L¹-S,O)₂] molecule is stabilized by intramolecular C-H...O, C-H...S and C-H...N hydrogen bonds (C-H...O 2.41 Å and ∠ 101°, C-H...S 2.45 Å and ∠ 112°, and C-H...N 2.42 Å and ∠ 100°). All the four independent molecules form similar intramolecular C-H...O, C-H...S and C-H...N hydrogen bonds that stabilize the structure of complexes.

In the both complexes, there are no strong classical and non-classical intermolecular hydrogen bonds to be found. Overall, our data suggest that the supramolecular aggregation of the complexes is stabilized by weak interactions as well as stacking interactions such as C-H...π and π...π. The crystal packing of *cis*-[Pt(L¹-S,O)₂] is stabilized by C-H...π and π...π staking cooperative interactions, and van der Waals forces. In the *cis*-[Pt(L¹-S,O)₂], the two strongest C-H...π interactions

occur between dipropylamine hydrogen atoms and platinum chelate rings (C9-H9A...π 2.76 Å with symmetry code 3/4-x, 1/4+y, -1/4+z and C9-H9B...π with symmetry code 1/4+x, 3/4-y, -1/4+z), as seen in Figure 8. The C-H...π angles, 137° for both interactions, are still below the optimal value (180°) for the strongest CH...π interaction, which may be due to the steric constraints in the molecules [56].

Table 3. Selected bond angles of the complexes.

Atom	Atom	Atom	Angle (°)
<i>cis</i> -[Pt(L ¹ -S,O) ₂]			
S(1) ⁱ	Pt(1)	S(1)	87.42(15)
O(1)	Pt(1)	S(1) ⁱ	175.9(2)
O(1)	Pt(1)	S(1)	94.99(17)
O(1) ⁱ	Pt(1)	S(1)	175.9(2)
O(1) ⁱ	Pt(1)	S(1) ⁱ	94.98(17)
O(1)	Pt(1)	O(1) ⁱ	82.8(4)
C(1)	S(1)	Pt(1)	108.1(3)
C(2)	O(1)	Pt(1)	128.6(6)
C(2)	N(1)	C(1)	128.5(7)
C(1)	N(2)	C(9)	124.0(6)
C(1)	N(2)	C(12)	119.9(6)
<i>cis</i> -[Pt(L ² -S,O) ₂]			
S(1)	Pt(1)	S(2)	88.48(4)
O(2)	Pt(1)	S(1)	176.61(8)
O(2)	Pt(1)	S(2)	94.91(9)
O(1)	Pt(1)	S(1)	93.92(10)
O(1)	Pt(1)	S(2)	176.74(11)
C(26)	N(4)	C(23)	116.6(3)
C(22)	N(4)	C(23)	122.7(4)
C(22)	N(4)	C(26)	120.7(4)
C(15)	N(3)	C(22)	127.6(4)
O(1)	C(1)	N(1)	131.1(4)
O(1)	C(1)	C(2)	112.9(4)

ⁱ1/2-x, 1/2-y, +z.

The crystal packing is also supported by π...π staking interactions. In the crystal packing of *cis*-[Pt(L¹-S,O)₂], Cg1, Cg2 and Cg3 are centroids of the Pt(1)-S(1)-C(1)-N(1)-C(2)-O(1) chelate ring, Pt(1)-S(1)-C(1)-N(1)-C(2)-O(1) chelate ring and C3-C8 ring, respectively. Cg1 exhibits a series stacking interactions with Cg3 of the adjacent molecule with a centroid-to-centroid distance of 3.902(5) Å (Cg(1)...Cg(3) 3.901(5) Å with symmetry code: 3/4-x, 1/4+y, -1/4+z; Cg(1)...Cg(3) 3.902(5) Å with symmetry code: -1/4+x, 1/4-y, -1/4+z;

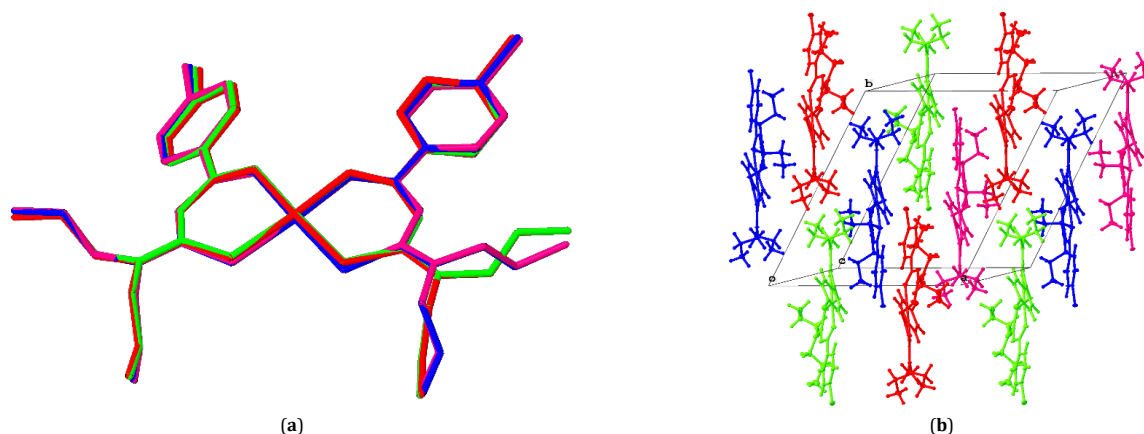


Figure 7. (a) Overlay diagrams of the *cis*-[Pt(L²-S,O)₂], (b) packing diagram of the *cis*-[Pt(L²-S,O)₂] coloured by symmetry equivalence (Green molecule A, red molecule B, pink molecule C and blue molecule D).

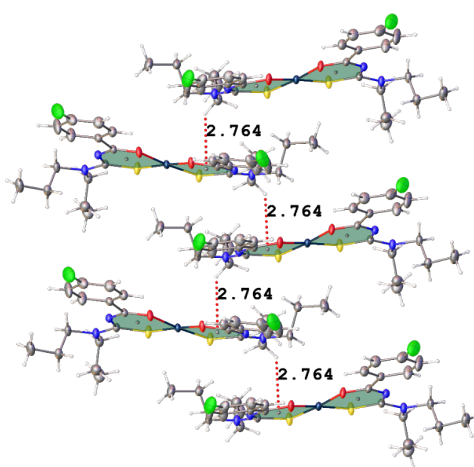


Figure 8. Supramolecular structure in *cis*-[Pt(L¹-S,O)₂] generated via C-H... π stacking interactions.

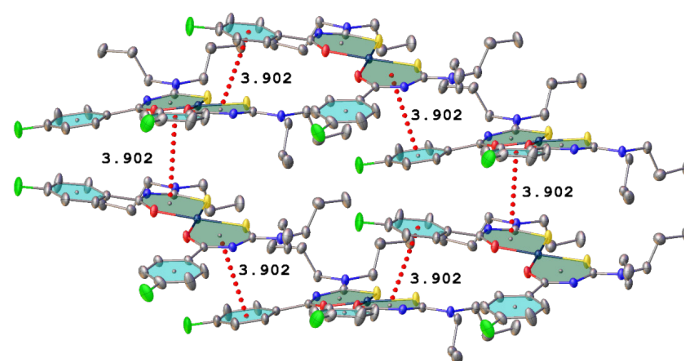


Figure 9. Supramolecular structure in *cis*-[Pt(L¹-S,O)₂] generated via π ... π stacking interactions.

Cg(3)...Cg(1) 3.902(5) Å with symmetry code: $3/4-x, -1/4+y, 1/4+z$ and Cg(3)...Cg(1) 3.902(5) Å with symmetry code: $1/4+x, 1/4-y, 1/4+z$ (Figure 9). These two important stacking interactions in the *cis*-[Pt(L¹-S,O)₂] contribute to the stability of its three dimensional supramolecular structure.

The supramolecular structure of *cis*-[Pt(L²-S,O)₂] is governed by the formation of a series C-H... π stacking interactions, which contribute to the stability of the complex, namely the asymmetric unit of *cis*-[Pt(L²-S,O)₂]. The four independent molecules in the asymmetric unit of *cis*-[Pt(L²-S,O)₂] are kept together via C-H... π stacking interactions. These

interactions occur between the hydrogen atoms of dipropyl moiety and the platinum chelate rings (Figure 10). In the crystal lattice, molecules of *cis*-[Pt(L²-S,O)₂] are again held together by strong C-H... π stacking interactions. However, these interactions occur between the hydrogen atoms of dipropyl moiety and the hydrogen atoms, which are different from the others (C11-H11B... π 2.92 Å, \angle 156° with symmetry code: x, y, z ; C11C-H11E... π 2.89 Å, \angle 156° with symmetry code: $x, 1+y, z$; C11A-H11H... π 2.92 Å, \angle 164° with symmetry code: $x, -1+y, z$; C11B-H11K... π 2.95 Å, \angle 162° with symmetry code: x, y, z).

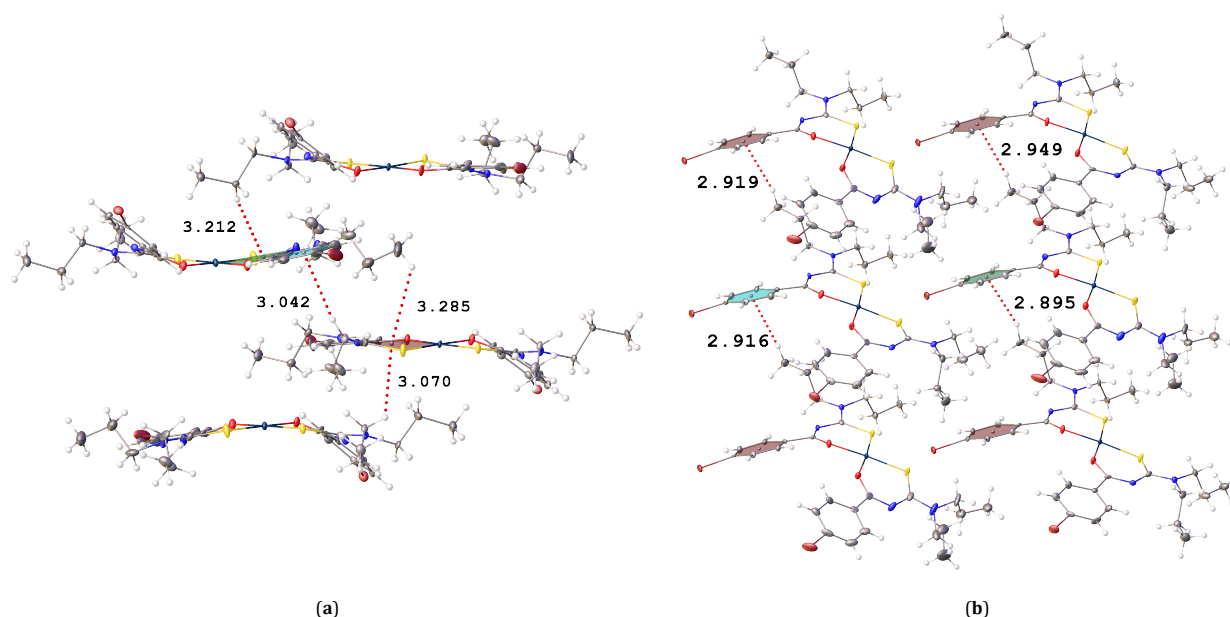


Figure 10. (a) C-H... π stacking interactions in asymmetric unit of *cis*-[Pt(L²-S,O)₂], (b) strong C-H... π stacking interactions in crystal lattice of *cis*-[Pt(L²-S,O)₂].

The C-H... π lengths in the crystal lattice are about 2.90 Å, and are very close to the optimal values (from 2.8 to 3.2 Å) for the strongest CH... π interactions [57-59].

4. Conclusion

Two platinum(II) compounds, having the general formula, *cis*-[Pt(L^{1,2}-S,O)₂] with ligands *N*-(di-*n*-propylcarbamothioyl)-4-fluoro benzamide and *N*-(di-*n*-propylcarbamothioyl)-4-bromo benzamide, have been prepared and characterized, where two monobasic *O,S* donor ligands coordinate to platinum in a *cis*-O₂S₂ conformation. The obtained complexes *cis*-[Pt(L¹-S,O)₂] and *cis*-[Pt(L²-S,O)₂] crystallized in an orthorhombic space group *Fdd2* with half molecules per unit cell and in a triclinic space group *P1* with four molecules per unit cell, respectively. The supramolecular structure of studied compounds were further examined by non-covalent interaction studies. The results of non-covalent interaction studies revealed that both complexes lack strong hydrogen bonds between classical and non-classical molecules. However, the supramolecular aggregation of the complexes is stabilized by van der Waals forces as well as stacking interactions such as C-H... π and π ... π .

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Supporting information

CCDC-1882277 and 1882278 contain the supplementary crystallographic data for compounds *cis*-[Pt(L¹-S,O)₂] and *cis*-[Pt(L²-S,O)₂], respectively. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif or by e-mailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44(0)1223-336033.

Disclosure statement

Conflict of interests: The authors declare that they have no conflict of interest.

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