

Synthesis, characterization and crystal structure of *cis-bis*[4-fluoro-*N*-(diethylcarbamothioyl)benzamido- κ^2 O,S]platinum(II)

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ABSTRACT

cis-Bis[4-fluoro-*N*-(diethylcarbamothioyl)benzamido- κ^2 O,S]platinum(II), *cis*-[Pt(L-O,S)₂], was synthesized and characterized by elemental analyses, FT-IR and NMR techniques. The obtained metal complex was also characterized by a single crystal X-ray diffraction study. Molecule formula of the title compound is C₂₄H₂₈F₂N₄O₂PTS₂: tetragonal, space group I4₁/a, *a* = 19.7530(4) Å, *b* = 19.7530(4) Å, *c* = 13.7137(3) Å, *V* = 5350.83(19) Å³, *Z* = 8, *D*_{calc} = 1.742 g/mm³, 22890 reflections measured (3.62 ≤ 2θ ≤ 52.72), 2733 (R_{int} = 0.0272), which were used in all calculations. A square-planar coordination geometry is formed around the Pt atom by two S atoms and two O atoms of the *N*-(diethylcarbamothioyl)-4-fluorobenzamide ligand which are a *cis* configuration.

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1. Introduction

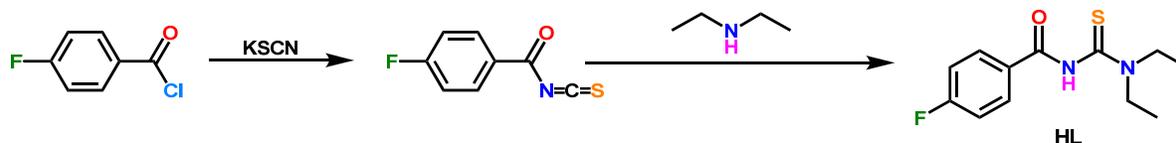
Thioureas are important organic compounds possessing significant biological activities, act as corrosion inhibitors, catalyst and antioxidant, and are polymer components [1-13]. Moreover, the hydrogen-bonding ability of the thiourea moiety has been extensively used in the construction of anion receptors. Thiourea derivatives have attracted considerable attention due to their potential applications [14-22]. Thiourea-based compounds are good candidates for coordination to transition metals as they have sulfur and oxygen donor atoms [13,23-30]. They are also able to bind through multiple bonding modes with one metal ion: chelation through both S and O, just through S, or just through O atoms [31]. Thioureas are selective ligands for the platinum group metals such as rhodium, platinum and palladium [32]. Platinum-thiourea complexes have attracted interest because of their luminescence properties [33] that find applications in optoelectronic devices [34-36], luminescent probes for biomolecules [37,38] and chemical sensors [38-41].

In the present study, we combined thiourea group with fluorine-containing organic compound was report the preparation and characterization of new *N*-(diethylcarbamothioyl)-4-fluoro benzamide (HL) thiourea compound and its Pt(II) complex (Scheme 1). The crystal and molecular structures of Pt (II) complex were characterized by single crystal X-ray diffraction study.

2. Experimental

2.1. Instrumentation

C, H, and N analyses were carried out on a Carlo Erba MOD 1106 elemental analyzer. Infrared measurement was recorded in the range 400-4000 cm⁻¹ on FT-IR/FIR/NIR Spectrometer Frontier, ATR Instrument. The ¹H NMR spectrums were recorded in CDCl₃ solvent on Bruker 400 MHz spectrophotometer using tetramethylsilane as an internal reference. Crystallographic measurements of the compound were carried out at 296(2) K using a Bruker APEX-II CCD area-detector diffractometer.



Scheme 1

The intensity data were collected using graphite monochromated Mo-K α radiation ($\lambda = 0.71073 \text{ \AA}$). Absorption corrections were applied with the program SADABS [42]. The structure was solved by direct methods SHELXS-97 [43], and refined by full-matrix least-squares techniques on F^2 using SHELXL-97 [43] with refinement of F^2 against all reflections. Hydrogen atoms were constrained by difference maps and were refined isotropically, and all non-H atoms were refined anisotropically. Crystallographic data and details of data collections and structure refinements of compound *cis*-[Pt(L-O,S) $_2$] are listed in Table 1. The molecular structure plots were prepared using PLATON [44] and ORTEP III [44]. The anisotropic thermal parameters and structure factors (observed and calculated), full list of bond distances, bond angles and torsional angles are given in supplementary materials. The geometric special details: all esds (except the esd in the dihedral angle between two planes) are estimated using the full covariance matrix. The cell esds are taken into account individually in the estimation of esds in distances, angles and torsion angles; correlations between esds in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell esds is used for estimating esds involving planes.

Table 1. Crystal data and structure refinement for *cis*-[Pt(L-O,S) $_2$].

Empirical formula	C $_{24}$ H $_{28}$ F $_2$ N $_4$ O $_2$ PtS $_2$
Formula weight	701.74
Temperature (K)	296.15
Crystal system	Tetragonal
Space group	I4 $_1$ /a
<i>a</i> (Å)	19.7530(4)
<i>b</i> (Å)	19.7530(4)
<i>c</i> (Å)	13.7137(3)
Volume (Å 3)	5350.83(19)
Z	8
ρ_{calc} (g/cm 3)	1.742
<i>M</i> (mm $^{-1}$)	5.443
<i>F</i> (000)	2752.0
Crystal size (mm 3)	0.45 \times 0.15 \times 0.15
Radiation	Mo K α ($\lambda = 0.71073 \text{ \AA}$)
2 θ range for data collection ($^\circ$)	3.616 to 52.724
Index ranges	-27 $\leq h \leq$ 29 -26 $\leq k \leq$ 31 -21 $\leq l \leq$ 20
Reflections collected	22890
Independent reflections	2733 [R $_{\text{int}}$ = 0.0272, R $_{\text{sigma}}$ = 0.0268]
Data/restraints/parameters	2733/44/158
Goodness-of-fit on F^2	1.058
Final R indexes [$I \geq 2\sigma(I)$]	R $_1$ = 0.0303, wR $_2$ = 0.0787
Final R indexes [all data]	R $_1$ = 0.0405, wR $_2$ = 0.0847
Largest diff. peak/hole (eÅ $^{-3}$)	0.61/-0.72

2.2. Reagents

4-Fluorobenzoyl chloride, potassium thiocyanate, diethylamine were purchased from Merck and used as received. Acetone and dichloromethane used without further purification. Ethanol was dried and distilled before the using. All the other chemicals used for the preparation of the ligand and platinum complex were of reagent grade quality.

2.3. Synthesis of ligand

HL was prepared according to previously published method [45-47]. A solution of 4-fluoro benzoyl chloride (5.10 $^{-2}$

mol) in acetone (50 mL) was added dropwise to a suspension of potassium thiocyanate (5.10 $^{-2}$ mol) in acetone (30 mL). The reaction mixture was heated under reflux for 30 min, and then cooled to room temperature. A solution of diethylamine (5.10 $^{-2}$ mol) in acetone (10 mL) was added and the resulting mixture was stirred for 2 h. Hydrochloric acid (0.1 N, 300 mL) was added and the solution filtered. The solid product was washed with water and purified by recrystallization from an ethanol:dichloromethane mixture (1:1, v:v) (Scheme 1).

N-(diethylcarbamothioyl)-4-fluorobenzamide, (HL): Color: White. Yield: 88 %. FT-IR (ATR, ν , cm $^{-1}$): 3293 (w) (NH), 2998, 2977, 2933 (vw) (CH), 1647 (s) (C=O), 1275 (m) (C=S), 761 (w) (C-F). ^1H NMR (400 MHz, CDCl $_3$, δ , ppm): 8.41 (s, 1H, NH), 7.88 (d, 2H, Ar-H), 7.16 (d, 2H, Ar-H), 4.04 (q, 2H, N-CH $_2$), 3.70 (q, 2H, N-CH $_2$), 1.38 (t, 3H, CH $_3$), 1.32 (t, 3H, CH $_3$). ^{13}C NMR (100 MHz, CDCl $_3$, δ , ppm): 179.39 (C=S), 166.76 (C=O), 130.61 (C-Ar), 130.52 (C-Ar), 116.01 (C-Ar), 115.78 (C-Ar), 47.94 (C-N), 47.63 (C-N), 13.28 (CH $_3$), 11.47 (CH $_3$). Anal. calcd. for C $_{12}$ H $_{15}$ FN $_2$ OS: C, 56.67; H, 5.94; N, 11.01; Found: C, 56.50; H, 5.90; N, 11.01%.

2.4. Synthesis of the complex

The solution of *N*-(diethylcarbamothioyl)-4-fluoro benzamide in ethanol (50 mL) at 70 $^\circ\text{C}$ was added dropwise a solution of potassium tetrachloroplatinate(II) (10.0 mmol) in water (50 mL). The reaction mixture was stirred for 30 min, and then cooled to room temperature. A brown precipitate was formed which was filtered off and recrystallized from ethanol:dichloromethane mixture (2:1, v:v) (Scheme 2).

Cis-bis[4-fluoro-*N*-(diethylcarbamothioyl)benzamido- $\kappa^2\text{O}$, *S*] platinum(II), (*cis*-[Pt(L-O,S) $_2$]): Color: Yellow. Yield: 83 %. FT-IR (ATR, ν , cm $^{-1}$): 2989, 2939, 2871 (w) (C-H), 1597 (w) ν (C-N), 1489 (vs) ν (C-O), 759 (w) ν (C-F). ^1H NMR (400 MHz, CDCl $_3$, δ , ppm): 8.22 (d, 4H, Ar-H $_a$), 7.10 (d, 4H, Ar-H $_b$), 3.80 (dd, 8H, N-CH $_2$), 1.28 (t, 12H, CH $_2$ -CH $_3$). ^{13}C NMR (100 MHz, CDCl $_3$, δ , ppm): 167.50 (2C, C-S), 167.07 (2C, C-O), 131.60 (2C, C-Ar), 131.68 (2C, C-Ar), 115.19 (4C, C-Ar), 114.97 (4C, C-Ar), 47.07 (2C-N), 45.97 (2C-N), 13.12 (2CH $_3$), 12.44 (2CH $_3$). Anal. calcd. for C $_{24}$ H $_{28}$ F $_2$ N $_4$ O $_2$ PtS $_2$: C, 41.08; H, 4.02; N, 7.98; Found: C, 40.20; H, 4.00; N, 7.9 %.

3. Results and discussion

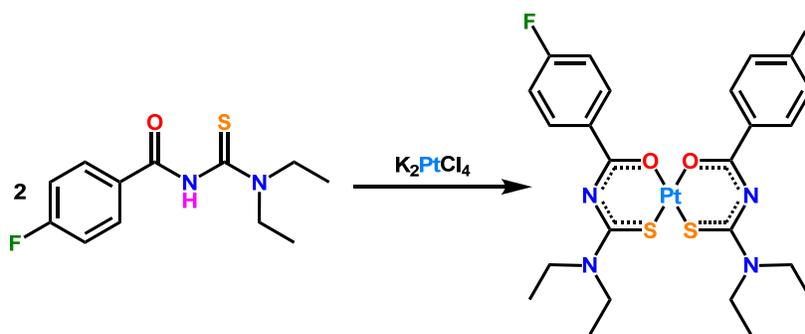
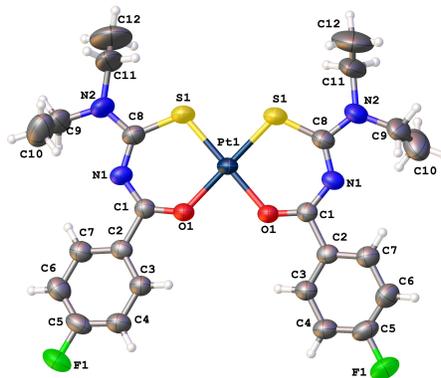
3.1. Synthesis and characterization

4-Fluoro benzoyl isothiocyanate was synthesized by reaction of 4-fluoro benzoyl chloride with an equimolar amount of potassium thiocyanate in dry acetone. HL was synthesized from 4-fluorobenzoyl isothiocyanate and diethyl amine in dry acetone. Both HL and *cis*-[Pt(L-O,S) $_2$] compounds were characterized by elemental analysis, FT-IR, ^1H NMR and ^{13}C NMR techniques. Data of the synthesized compounds confirmed the proposed structures given in Scheme 1 and 2.

The FT-IR spectra of HL was showed characteristic bands at 3293 and 1647 cm $^{-1}$ corresponding to ν (NH) and ν (C=O), respectively. Moreover synthesized free ligand showed weak intensity C=S stretching vibration in the 1275 cm $^{-1}$. The FT-IR spectra of the platin complex displayed important differences when compared with the FT-IR spectra of the corresponding ligand.

Table 2. Selected bond lengths (Å) and bond angles (°) for *cis*-[Pt(L-O,S)₂].

Atom	Atom	Length, Å	Atom	Atom	Atom	Angle, °
Pt1	S1 ¹	2.2232(13)	S1 ¹	Pt1	S1	86.08(7)
Pt1	S1	2.2232(12)	O1	Pt1	S1	94.49(9)
Pt1	O1	2.033(3)	O1 ¹	Pt1	S1 ¹	94.49(9)
Pt1	O1 ¹	2.033(3)	O1 ¹	Pt1	S1	178.19(10)
S1	C8	1.710(5)	O1	Pt1	S1 ¹	178.19(10)
F1	C5	1.362(5)	O1	Pt1	O1 ¹	84.98(15)
O1	C1	1.262(5)	C8	S1	Pt1	108.42(15)
N1	C1	1.313(5)	C1	O1	Pt1	128.8(2)
N1	C8	1.346(5)	C1	N1	C8	127.1(4)
N2	C8	1.340(6)	C8	N2	C9	120.9(4)
N2	C9	1.460(7)	C8	N2	C11	122.0(5)
N2	C11	1.500(8)	C9	N2	C11	116.5(5)
C1	C2	1.504(5)	O1	C1	N1	131.1(4)
C2	C3	1.386(6)	O1	C1	C2	114.6(3)
C2	C7	1.370(6)	N1	C1	C2	114.3(4)
C9	C10	1.489(9)	F1	C5	C6	118.3(5)
C11	C12	1.127(16)	C4	C5	F1	118.7(5)
			N1	C8	S1	129.7(3)
			N2	C8	S1	116.0(3)
			N2	C8	N1	114.3(4)
			N2	C9	C10	110.7(6)
			C12	C11	N2	124.6(15)

¹1-x, 1/2-y, +z**Scheme 2****Figure 1.** The molecular structure of the title compound. Displacement ellipsoids are drawn at the 50% probability level.

The most important differences are the $\nu(\text{N-H})$ band of free ligand disappeared completely in the spectra of the Pt(II) complex indicating that the deprotonation of the NH group and coordination via the thiolate S-atom and carbonyl O-atom. These results agree with the data in the literature [45,46].

The ^1H NMR spectra of the HL ligand and its platinum complex were recorded in CDCl_3 . The ^1H NMR data of the obtained compounds were given in the experimental section and consistent with the structural results. The N-H signal in the ^1H NMR spectrum for the ligand at 8.41 ppm disappeared upon the complexation reaction. All other proton signals were appeared in appropriate place (Section 2.3 and 2.4).

The molecular structures and packing diagrams of *cis*-[Pt(L-O,S)₂] are depicted in Figures 1 and 2, respectively. Crystallographic information was briefly given in Table 1 for the title compound. Selected bond lengths and angles of the compounds are presented in Table 2.

The structure of the platinum complex shows that the platinum atom with 4-fold coordination set up by two oxygen and two sulfur atoms [S(1)-Pt(1)-O(1): 178.19(10) and O(1)-Pt(1)-S(1): 94.49(9)°] in a *cis* geometry. The bond distances of the C-S [S(1)-C(8): 1.710(5)] and C-O [C(1)-O(1): 1.262(5) Å] in the chelate ring are longer than average C-S and C=O double bond distances of thiourea derivatives [47].

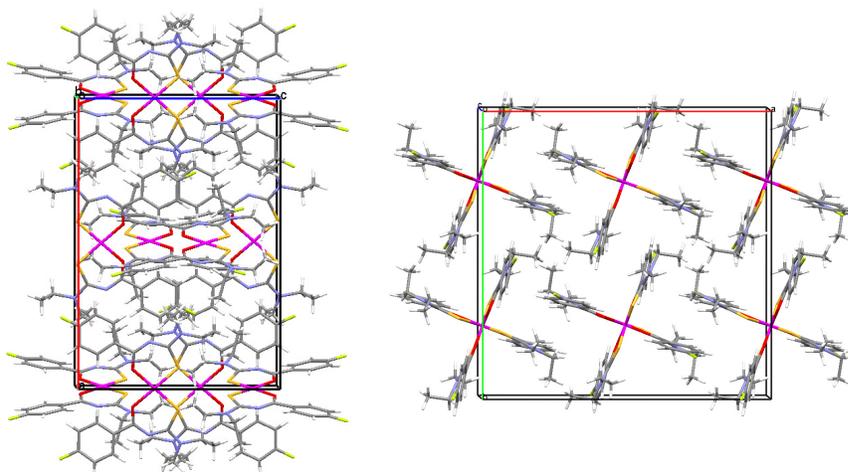


Figure 2. Packing diagram for the title compound.

The bond lengths of all C-N bonds in the chelate rings (C1-N1 1.313(5), N1-C8 1.346(5), C8-N2 1.340(6) Å) are shorter than the normal C-N single bond (1.48 Å) and longer than normal C=N double bond (1.25 Å) due to the strong delocalization in the chelate rings. As expected, the Pt-O bond distance [2.033(3) Å] is shorter than Pt-S bond distance [2.2232(13) Å]. These parameters indicate that shift from the square planar structure to tetrahedral structure. These results are confirmed by C1-N1-C8-N2 showing sp^2 hybridization in N1 atoms [48-51]. All the other bond lengths and bond angles fall within the expected range.

4. Conclusions

In this work, *N*-(diethylcarbamothioyl)-4-fluorobenzamide ligand and its Pt(II) complex has been synthesized and characterized by elemental analysis, FT-IR spectroscopy, ^1H NMR and ^{13}C NMR techniques. Crystal and molecular structures of metal complex was analyzed by X-ray single crystal diffraction method. *Cis*-bis[4-fluoro-*N*-(diethylcarbamothioyl)benzamido- $\kappa^2\text{O,S}$]platinum(II) has been reported to crystallize in the tetragonal space group $I4_1/a$. The crystal structure of *cis*-[Pt(L,O,S) $_2$] confirms that the *N*-(diethylcarbamothioyl)-4-fluoro benzamide ligand is a bidentate chelating ligand, coordinating to the platinum through thio-carbonyl and carbonyl groups. The comparative analysis was performed with literature data. The structure of this compound is consistent with the structure of other thiourea derivatives. The bond lengths and angles also agree well with other thiourea derivatives.

Acknowledgements

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Supplementary material

CCDC-1420142 contains the supplementary crystallographic data for this paper. 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.

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