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Research paper

Synthesis and characterization of ethylenediamine platinum(II) complexes containing thiourea derivatives. X-ray crystal structures of [Pt(en)(2-imidazolidinethione)$_2$](NO$_3$)$_2$ and [Pt(en)(1-phenyl-2-thiourea)$_2$](NO$_3$)$_2$

Ashwaq Bahkali, Jacob Wei, Yuanjian Deng *

Department of Chemistry, Texas Southern University, Houston, TX 77004, USA

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ABSTRACT

Reactions of ethylenediamineplatinum(II) nitrate with thiourea derivatives afford new complexes of the form [Pt(en)L$_2$](NO$_3$)$_2$ [en = ethylenediamine, L = 1-benzyl-2-thiourea (bztu), 1-cyclohexyl-2-thiourea (chtu), 1,3-diethyl-2-thiourea (detu), 1,3-diisopropyl-2-thiourea (diptu), 1-ethyl-2-thiourea (etu), 1-heptyl-2-thiourea (htu), 2-imidazolidinethione (imt), 1-isopropyl-2-thiourea (iptu), 1-phenyl-2-thiourea (phtu), 1-(3-pyridyl)-2-thiourea (pytu), and 1-*tert*-butyl-2-thiourea (tbtu)]. These complexes are soluble in high polarity solvents and have been characterized by elemental analysis, IR spectroscopy and NMR spectroscopy. IR analyses reveal the characteristic vibrations of the functional groups and the nitrate counter ions. NMR studies show that the chemical shifts of proton and carbon signals of the bonded en are about the same, indicating the bonding of thioureas to the platinum(II) center exert limited *trans* effect on the en ligand. The observation that thioamide proton signals shift downfield and the thiocarbonyl carbon signals shift upfield as compared to the free thioureas suggests a decrease in thiocarbonyl bond order and an increase in thiocarbonyl carbon-amide nitrogen bond order upon coordination to the platinum(II) center. Good quality single crystals of [Pt(en)(2-imidazolidinethione)$_2$](NO$_3$)$_2$ (**7**) and [Pt(en)(1-phenyl-2-thiourea)$_2$](NO$_3$)$_2$ (**9**) are grown by slow evaporation of methanol solution at room temperature. Their molecular structures have been identified by the single crystal X-ray diffraction. Complex **7** crystallizes in the orthorhombic space group *Pccn* whereas **9** crystallizes in the monoclinic space group *P*2(1)/n. X-ray crystallographic analysis indicates that the geometry about the platinum atom is square-planar and the crystal packings are dominated by intermolecular en N—H···O (NO$_3$) and thioureas N—H···O (NO$_3$) hydrogen bonds. The two imidazole rings in **7** and the two phenyl rings in **9** are oriented above and below the PtN$_2$S$_2$ plane, respectively, to minimize the steric interaction.

1. Introduction

Cisplatin has been in use for cancer treatment for more than 40 years and proven to be effective in treating various types of cancers [1]. Along with other platinum(II)-based anticancer drugs such as carboplatin and oxaliplatin, they account for about 50% of all chemotherapies [2]. But their clinical use has been restricted due to serious problems such as neurotoxicity, nephrotoxicity, myelosuppression, and resistance [3,4]. To reduce toxicity and to circumvent resistance, scientists have synthesized and evaluated thousands of cisplatin like platinum complexes. As a result, carboplatin and oxaliplatin plus a few others such as nedaplatin have been obtained therapeutic approval [5]. All these drugs are bifunctional compounds and possess vicinal amines. They employ the same mechanism of action by forming coordinate covalent bonds with DNA molecules, which interrupt transcription and generate DNA damage responses, leading to cancer cell apoptosis. Thus, searching for novel platinum(II) complexes is mainly focusing on compounds that are structurally like cisplatin with a comparable mechanism of action [6]. This can be done by varying the carrier ligands and leaving groups. Reedijk suggested the development of the coordination chemistry of platinum compounds with rescue and protective agents that are sulfur containing compounds [7,8]. The commonly used S-donor ligands include sodium thiosulfate, thiourea, sodium diethyldithiocarbamate, and glutathione [7–11]. Among them, thioureas are of special interest because they can be used as anticancer agents and enhance biological activities of other anticancer drugs [12–17]. Although ethylenediamine

* Corresponding author.
E-mail address: yuanjian.deng@tsu.edu (Y. Deng).

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is commonly used as a bidentate ligand to form very stable chelating compounds with transition metals including platinum, some anticancer drugs also contain this ligand [18–24]. Therefore, in the present study we choose ethylenediamine as a carrier ligand that forms a five-membered chelate ring with platinum(II) and prevents its replacement by incoming S-donor ligands such as thioureas because S-donor ligands have stronger *trans* effect than *N*-donor ligands. In addition, the chelate ring in the complexes not only dictates the *cis* isomer but also enhances the complex stability. In this paper we report the synthesis and characterization of 11 new platinum(II) complexes that contain substituted thioureas with a general formula of $[Pt(en)L_2](NO_3)_2$, where en is ethylenediamine, L is thiourea derivatives, including 1-benzyl-2-thiourea (bztu), 1-cyclohexyl-2-thiourea (chtu), 1,3-diethyl-2-thiourea (detu), 1,3-diisopropyl-2-thiourea (diptu), 1-ethyl-2-thiourea (etu), 1-heptyl-2-thiourea (htu), 2-imidazolidinethione (imt), 1-isopropyl-2-thiourea (iptu), 1-phenyl-2-thiourea (phtu), 1-(3-pyridyl)-2-thiourea (pytu), and 1-*tert*-butyl-2-thiourea (tbtu). In addition, X-ray crystallographic analyses were also performed for $[Pt(en)(imt)_2](NO_3)_2$ and $[Pt(en)(phtu)_2](NO_3)_2$.

2. Experimental

2.1. Materials

Potassium tetrachloroplatinate (K_2PtCl_4) was purchased from Johnson Matthey Electronics. En, etu, imt, and silver nitrate were purchased from Sigma–Aldrich, bztu, chtu, htu, and pytu were purchased from Matrix Scientific, detu was purchased from Tokyo Chemical Industry, diptu, iptu, and tbtu were purchased from Oakwood Chemical, phtu was purchased from Acros Organics, and potassium iodide was purchased from Fisher Scientific. All chemicals and solvents were used without further purification. Deuterated dimethylsulfoxide (DMSO-d_6) was supplied by Cambridge Isotope Laboratories.

2.2. Physical measurements

Carbon, hydrogen and nitrogen analyses were carried out by Robertson Microlit Laboratories. FTIR spectra were recorded on a Nicolet 380 or iS50 FTIR spectrometer using diamond ATR accessories over the range 4000–400 cm^{-1}. ^1H and ^{13}C NMR spectra were obtained on a JEOL 400 MHz spectrometer. The NMR experiments were conducted in DMSO-d_6 on which signals were locked. Chemical shifts for ^1H and ^{13}C NMR spectra were referenced to the residual signals of DMSO-d_6 at 2.500 ppm and 39.50 ppm, respectively.

2.3. Synthesis of starting complex

Ethylenediaminediiodoplatinum(II) ($Pt(en)I_2$) was the starting complex that was used to prepare the thiourea complexes. $Pt(en)I_2$ was synthesized by reacting K_2PtCl_4 with potassium iodide and then en as follows. To a filtered 100 mL of K_2PtCl_4 solution (12.5 g, 30 mmol) was added 40 mL of KI solution (39.8 g, 240 mmol). The solution immediately turned from yellow to dark brown. After stirring for 15 min, one equivalent of ethylenediamine (2.1 mL, 30 mmol) was added dropwise. Yellow precipitate was formed. The mixture was stirred further for one more hour. The yellow solid was then filtered, washed extensively with water, and recrystallized from a DMF/H_2O mixture. The product was then washed with water, methanol, and diethyl ether, each two times in sequence, and dried in vacuum oven at room temperature. Yield, 92%. The purity of the complex was checked with ^1H NMR.

2.4. Preparation and characterization of Pt(II) complexes

$[Pt(en)(bztu)_2](NO_3)_2$ (**1**). To a 10 mL aqueous suspension of $Pt(en)I_2$ (0.513 g, 1.01 mmol) was added 5 mL of $AgNO_3$ solution (0.340 g, 2.00 mmol). Then a small amount of acetone was added to the suspension. The mixture was stirred at room temperature in the dark for 24 h. The precipitate AgI was then filtered off, and to the filtrate was added 5 mL of bztu solution (0.339 g, 2.00 mmol). Upon stirring at room temperature overnight, the solution was filtered again to remove any insoluble residue, and the solvent was evaporated at 60 °C under reduced pressure. The solid was then collected by using a small amount of hexane. After filtration, it was washed with hexane and diethyl ether, and dried in vacuum oven at room temperature. Yield, 63%. Anal. Calc. for $C_{18}H_{28}N_8O_6PtS_2$: C, 30.38; H, 3.97; N, 15.75. Found: C, 30.49; H, 3.90; N, 15.74%. IR (cm^{-1}): 3380–3151, 1617s, 1572s, 1447m, 1368s, 1316vs, 1204w, 1148s, 1078w, 1053m, 1045m, 1027w, 952w, 887w, 827s, 763w, 694s, 604w, 523m, 449m (s, strong; m, medium; w, weak; br, broad; vs, very strong). ^1H NMR 9.223 (s, 2H, NH), 8.847–8.227 (m, 4H, bztu-NH_2), 7.365–7.249 (m, 10H), 5.508 (br, 4H, en-NH_2), 4.482 (s, 4H, bztu-CH_2), 2.558 (br, 4H, en-CH_2). ^{13}C NMR 171.830 (*C*═S), 136.457 (bztu-*C*H_2), 128.496, 128.295, 127.380, 127.170, 126.894 (Ph-*C*N), 46.250 (en-*C*H_2).

The following ten complexes were prepared by the same procedure.

$[Pt(en)(chtu)_2](NO_3)_2 \cdot H_2O$ (**2**). Yield, 87%. Anal. Calc. for $C_{16}H_{38}N_8O_7PtS_2$: C, 26.92; H, 5.37; N, 15.70. Found: C, 26.79; H, 5.18; N, 15.83%. IR (cm^{-1}): 3387–3076, 2928m, 2852w, 1613s, 1590s, 1453m, 1373s, 1316s, 1220w, 1191w, 1158s, 1055m, 968w, 890w, 826w, 717m, 559m. ^1H NMR 8.515–8.156 (m, 6H, chtu-NH and NH_2), 5.447 (br, 4H, en-NH_2), 3.468 (br, 2H, chtu-CH), 2.567 (br, 4H, en-CH_2), 1.788–1.569 (m, 10*H*), 1.267 (m, 10*H*). ^{13}C NMR 169.656 (*C*═S), 52.601 (chtu-*C*N), 47.519 (en-*C*H_2), 31.539, 24.731, 24.369.

$[Pt(en)(detu)_2](NO_3)_2$ (**3**). Yield, 71%. Anal. Calc. for $C_{12}H_{32}N_8O_6PtS_2$: C, 22.39; H, 5.01; N, 17.41. Found: C, 22.52; H, 5.09; N, 17.20%. IR (cm^{-1}): 3229vs, 3124w, 2981w, 1583vs, 1504s, 1452m, 1317vs, 1247s, 1164m, 1138m, 1090w, 1054s, 928m, 826m, 795s, 702w, 533s, 454w. ^1H NMR 8.350 (br, 4H, detu-NH_2), 5.518 (br, 4H, en-NH_2), 3.463 (br, 4H, detu-CH_2), 3.296 (br, 4H, detu-CH_2), 2.568 (br, 4H, en-CH_2), 1.129 (br, 12H, detu-CH_3). ^{13}C NMR 170.353 (*C*═S), 47.576 (en-*C*H_2), 37.688 (detu-*C*N), 14.653, 14.424, 13.461.

$[Pt(en)(diptu)_2](NO_3)_2 \cdot H_2O$ (**4**). Yield, 72%. Anal. Calc. for $C_{16}H_{42}N_8O_7PtS_2$: C, 26.77; H, 5.90; N, 15.61. Found: C, 26.92; H, 5.74; N, 15.56%. IR (cm^{-1}): 3245m, 3115w, 2975w, 1576vs, 1506s, 1462w, 1310vs, 1259w, 1163m, 1128m, 1055m, 980m, 879w, 827m, 741m, 562m, 449w. ^1H NMR 8.062 (br, 2H, diptu-NH), 7.872 (br, 2H, diptu-NH), 5.594 (br, 4H, en-NH_2), 4.224 (br, 2H, diptu-CH), 3.972 (br, 2H, diptu-CH), 2.571 (br, 4H, en-CH_2), 1.185 (d, 24H, diptu-CH_3). ^{13}C NMR 168.427 (*C*═S), 47.576 (en-*C*H_2), 44.582 (diptu-*C*N), 22.338, 21.775.

$[Pt(en)(etu)](NO_3)_2$ (**5**). Yield, 90%. Anal. Calc. for $C_8H_{24}N_8O_6PtS_2$: C, 16.35; H, 4.12; N, 19.08. Found: C, 16.34; H, 4.10; N, 18.70%. IR (cm^{-1}): 3387–3121 (multiple), 2975w, 1615s, 1579s, 1485w, 1452s, 1366vs, 1320vs, 1214w, 1159s, 1047s, 920w, 887w, 826m, 810w, 810w, 697m, 607w, 546s, 460s. ^1H NMR 8.698 (s, 2H, etu-NH), 8.448 (d, 2H, etu-NH_2), 8.048 (br, 2H, etu-NH_2), 5.440 (s, 4H, en-NH_2), 3.216 (m, 4H, etu-CH_2), 2.554 (br, 4H, en-CH_2), 1.086 (t, 6H, etu-CH_3). ^{13}C NMR 170.829 (*C*═S), 47.538 (en-*C*H_2), 38.318 (etu-*C*N), 13.566, 13.461.

$[Pt(en)(htu)_2](NO_3)_2$ (**6**). Yield, 37%. Anal. Calc. for $C_{18}H_{44}N_8O_6PtS_2$: C, 29.70; H, 6.09; N, 15.40. Found: C,29.43; H,6.02; N,15.33%. IR (cm^{-1}): 3395–3124, 2933m, 2855w, 1615vs, 1459s, 1370vs, 1326vs, 1223w, 1160s, 1054m, 889w, 824m, 712s, 608w, 547s, 496m, 453w. ^1H NMR 8.688 (t, 2H, htu-NH), 8.479 (br, 1H, htu-NH_2), 8.384 (br, 1H, htu-NH_2), 8.054 (br, 2H, htu-NH_2), 5.424 (s, 4H, en-NH_2), 3.157 (m, 4H, htu-CH_2N), 2.547 (br, 4H, en-CH_2), 1.469 (br, 4H), 1.255 (br, 16H), 0.865 (t, 6H, htu-CH_3). ^{13}C NMR 170.915 (*C*═S), 47.557 (en-*C*H_2), 43.485 (htu-*C*N), 31.224, 28.421, 27.973, 26.142, 22.080, 13.966.

$[Pt(en)(imt)_2](NO_3)_2$ (**7**). Crystals suitable for X-ray crystallographic analysis were grown by slow evaporation of methanol solution at room temperature. Yield, 89%. Anal. Calc. for $C_8H_{20}N_8O_6PtS_2$: C, 16.47; H, 3.45; N, 19.21. Found: C, 16.72; H, 3.40; N, 19.16%. IR (cm^{-1}): 3190m, 3124m, 2897w, 1514vs, 1478w, 1399w, 1305s, 1273s, 1188m, 1040m,

996w, 921m, 874w, 827m, 726m, 676m, 570m, 490m. ^{1}H NMR 9.153 (s, 4H, imt-NH_2), 5.520 (s, 4H, en-NH_2), 3.737 (s, 8H, imt-CH_2), 2.555 (br, 4H, en-CH_2). ^{13}C NMR 174.328 (*C*═S), 47.700 (en-*C*H_2), 44.916 (imt-*C*H_2).

[Pt(en)(iptu)$_2$](NO$_3$)$_2$ ***(8)***. Yield, 91%. Anal. Calc. for $C_{10}H_{28}N_8O_6PtS_2$: C, 19.51; H, 4.58; N, 18.21. Found: C, 19.55; H, 4.56; N, 18.05%. IR (cm^{-1}): 3388–3114, 2970w, 1615s, 1676s, 1445m, 1364vs, 1315vs, 1216w, 1178m, 1159m, 1126w, 1054m, 951w, 884w, 863w, 827m, 690s, 552s, 490w, 458w. ^{1}H NMR 8.558 (d, 1H, iptu-NH), 8.431 (br, 1H, iptu-NH), 8.111 (br, 1H, iptu-NH), 5.454 (s, 4H, en-NH_2), 3.800 (m, 2H, iptu-C*H*), 2.554 (br, 4H, en-CH_2), 1.123 (d, 12H, CH_3). ^{13}C NMR 169.79 (*C*═S), 47.490 (en-*C*H_2), 45.678 (iptu-*C*H), 22.138 (*C*H_3), 21.527 (*C*H_3).

[Pt(en)(phtu)$_2$](NO$_3$) ***(9)***. Crystals suitable for X-ray crystallographic analysis were grown by slow evaporation of methanol solution at room temperature. Yield, 74%. Anal. Calc. for $C_{16}H_{24}N_8O_6PtS_2$: C, 28.11; H, 3.54; N, 16.39. Found: C, 28.01; H, 3.51; N, 16.08%. IR (cm^{-1}): 3107br, 1614w, 1594w, 1534w, 1495w, 1305vs, 1155w, 1053w, 823w, 746w, 691m, 498w. ^{1}H NMR 10.384 (br, 2H, phtu-NH), 8.882 (br, 2H, phtu-NH_2), 8.209 (br, 2H, phtu-NH_2), 7.491–7.243 (m, 10*H*), 5.571 (s, 4H, en-NH_2), 2.592 (br, 4H, en-CH_2). ^{13}C NMR 172.99 (*C*═S), 47.566 (en-*C*H_2), 136.467, 129.554, 127.256, 125.311.

[Pt(en)(pytu)$_2$](NO$_3$)$_2$ · H$_2$O ***(10)***. Yield, 85%. Anal. Calc. for $C_{14}H_{24}N_{10}O_7PtS_2$: C, 23.90; H, 3.44; N, 19.91. Found: C, 23.94; H, 3.33; N, 19.67%. IR (cm^{-1}): 3094br, 1615w, 1532w, 1481w, 1308s, 1189w, 1027w, 879w, 822w, 701m. ^{1}H NMR 9.799 (s, 2H, pytu-NH), 9.045 (br, 4H, pytu-NH_2), 8.541 (dd, 2H), 8.289 (m, 2H), 7.694 (dt, 2H), 7.534–7.502 (m, 2H), 5.621 (s, 4H, en-NH_2), 2.587 (br, 4H, en-CH_2). ^{13}C NMR 173.909 (*C*═S), 148.127, 146.745, 145.057, 144.619, 136.114, 133.149, 130.498, 124.367, 123.271, 47.614 (en-*C*H_2).

[Pt(en)(tbtu)$_2$](NO$_3$)$_2$ ***(11)***. Yield, 49%. Anal. Calc. for $C_{12}H_{32}N_8O_6PtS_2$: C, 22.39; H, 5.01; N, 17.41. Found: C, 22.26; H, 5.04; N, 17.16%. IR (cm^{-1}): 3392–3107, 2976w, 1583s, 1481w, 1440m, 1370s, 1317s, 1231w, 1206w, 1160w, 1053w, 1044w, 921w, 827m, 797w, 704vw, 671m, 568s, 484w, 455w. ^{1}H NMR 8.194 (s, 2H, tbtu-NH), 5.534 (s, 4H, en-NH_2), 2.561 (br, 4H, en-CH_2), 1.366 (s, 18H, CH_3). ^{13}C NMR 170 (*C*═S, estimated), 54.002 (tbtu-*C*N), 47.538 (en-*C*H_2), 28.144 (*C*H_3)

2.5. X-ray Crystallography

[Pt(en)(imt)$_2$](NO$_3$)$_2$ (**7**). A hemisphere of data (1272 frames at 6 cm detector distance) was collected using a narrow-frame algorithm with scan widths of 0.30 deg in omega and an exposure time of 35 s/frame. Final cell constants were refined using 6200 reflections having I > 10σ (I). The Laue symmetry was determined to be mmm. The space group was shown unambiguously to be *Pccn*. The asymmetric unit consists of one-half organometallic complex situated on a two-fold axis and one nitrate anion in a general position. Crystal data and structure refinement are listed in Table 1.

[Pt(en)(phtu)$_2$](NO$_3$) (**9**). A hemisphere of data (1272 frames at 6 cm detector distance) was collected using a narrow-frame algorithm with scan widths of 0.30 deg in omega and an exposure time of 40 s/frame. Final cell constants were refined using 8115 reflections having I > 10σ (I). The Laue symmetry was determined to be 2/m. The space group was shown unambiguously to be *P*2(1)/c. Crystal data and structure refinement are listed in Table 1.

Table 1
Crystallographic data and structure refinement for [Pt(en)(imt)$_2$](NO$_3$)$_2$] (**7**) and [Pt(en)(phtu)$_2$](NO$_3$)$_2$] (**9**).

	7	**9**
Empirical formula	$C_8H_{20}N_8O_6PtS_2$	$C_{16}H_{24}N_8O_6PtS_2$
Formula weight	583.53	683.64
Temperature (K)	123(2)	123(2)
Wavelength (Å)	0.71073	0.71073
Crystal color and shape	Colorless thin plate	Orange thick column
Crystal dimensions (mm)	0.40 × 0.15 × 0.08 mm	0.40 × 0.25 × 0.20 mm
Crystal system	Orthorhombic	Monoclinic
Space group	*Pccn*	*P*2(1)/c
Unit cell		
a (Å)	18.750(2)	13.4793(8)
b (Å)	6.001(1)	7.1655(4)
c (Å)	15.819(2)	24.1874(14)
α (°)	90 deg.	90 deg.
β (°),	90 deg.	91.524(1) deg.
γ (°)	90 deg.	90 deg.
V (Å^3)	1779.9(4)	2335.3(2)
Z	4	4
D $_{calc}$ (g cm^{-3})	2.178	1.944
F(000)	1128	1336
θ Range for data collection (°)	2.58 to 27.49 deg.	1.68 to 27.48 deg.
Limiting indices	$-24 \le h \le 20$, $-7 \le k \le 7$, $-18 \le l \le 20$	$-14 \le h \le 17$, $-8 \le k \le 9$, $-30 \le l \le 31$
Reflections collected/ unique	11,027 / 2038 [R_{int} = 0.0198]	14,503 / 5330 [R_{int} = 0.0176]
Max, min transmission	0.7456 and 0.4336	0.7456 and 0.4844
Refinement method	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2
Data/restraints/ parameters	1750 / 2 / 120	5065 / 6 / 316
Goodness-of-fit (GOF) on F^2	1.038	1.097
Final R indices [I > 4σ (I)]	R1 = 0.0124, wR_2 = 0.0315	R1 = 0.0147, wR_2 = 0.0375
R indices (all data)	R1 = 0.0148, wR_2 = 0.0331	R1 = 0.0157, wR_2 = 0.0384
Largest difference peak and hole	0.967 and −0.732 e.A^{-3}	1.249 and −1.306 e.A^{-3}

3. Results and discussion

3.1. Synthesis

Although all new platinum(II) complexes were prepared from potassium tetrachloroplatinate(II) by following the same procedure, the more useful starting material was actually Pt(en)I_2, from which the thiourea complexes were eventually synthesized. In the precipitation reaction to remove iodide from Pt(en)I_2, less than the stoichiometric amount of silver nitrate was acquired to assure the silver ions were completely reacted. Then the thiourea ligand (L) in exactly the same number of moles of the silver nitrate was added to the filtrate to form the desired complex [Pt(en)L_2](NO$_3$)$_2$. Upon removing water under reduced pressure, the final products were collected in hexane. The synthetic pathway to the final products is shown in the following scheme.

$$K_2PtCl_2 \xrightarrow[2.en]{1.KI} Pt(en)I_2 \xrightarrow[4.L]{3.AgNO_3} [Pt(en)L_2](NO_3)_2$$

Except complexes **1**, **6** and **11**, the other complexes were obtained in good yield (>70%). All the complexes are either off-white or pale-yellow powders and soluble in high polarity solvents such as water and methanol but insoluble in acetone. Slow evaporation of saturated methanol solution at room temperature afforded X-ray quality single crystals **7** and **9**.

3.2. IR spectroscopy

The IR spectra of **1**–**11** exhibit either multiple or broad bands between 3094 and 3395 cm^{-1} assignable to NH stretching vibrations. Since both the en ligand and the thioureas contain either NH or NH_2 groups, it is difficult and unnecessary to distinguish them. Miller and Wilkins reported that common inorganic nitrate salts showed doubly degenerate stretching vibrations in the region of 1350–1380 cm^{-1} [25] while Kirishnamaline et al pointed out that a mixed vibration of C—N stretching

and N—H bending modes was also possible [26]. All complexes showed strong bands at 1305–1370 cm^{-1} that may be more reasonably to ascribe to the C—N stretching vibrations because free en ligand showed a broad band at 1354 cm^{-1}. Absorption bands at 822–828 cm^{-1} (see Table 2) are due to the out-of-plane deformation vibrations for the ionic nitrate, being consistent with the previously reported values of 815–840 cm^{-1} for simple nitrate salts [25], 813–819 cm^{-1} [27] and 832 cm^{-1} [28] for silver(I) thiourea nitrates. The thiocarbonyl stretching vibration occurs in a large range of 930–670 cm^{-1}, depending on the chemical environment [26,29]. Definitive assignment of C═S vibrations is sometimes difficult because of strong coupling that results in thioamides as a mixed vibration [30]. Thus, we have also recorded IR spectra of free thioureas. A careful comparison of the IR spectra between the free thioureas and their complexes reveals all thiocarbonyl C═S vibrations occurring between 671 and 717 cm^{-1} except **3** at 795 cm^{-1} and **4** at 741 cm^{-1} (see Table 2). Nevertheless, these results are comparable to previously reported values for other transition metal thiourea complexes [31–36].

3.3. NMR spectroscopy

The ^{1}H and ^{13}C NMR spectra of **1**–**11** exhibited several sets of signals for the same functional groups. Some of these groups in the ligands are more affected than the others. In an attempt to give more definitive assignment of resonance signals, we also took the NMR spectra of the free en ligand, free thioureas, and the complexes of $Pt(en)I_2$ and $Pt(en)(NO_3)_2$. For the convenience of comparison, we tabulate the chemical shifts of the groups that are more prone to changing in chemical environment in Table 2. The free en ligand did not show the NH_2 signals in its ^{1}H NMR spectra because these protons underwent fast exchange reaction with the solvent. But when a five-membered chelate ring was formed with platinum in $[Pt(en)L_2](NO_3)_2$, one NH_2 resonance at 5.424–5.621 ppm was found for all complexes. The ethylene proton signals of the bonded en in $[Pt(en)L_2](NO_3)_2$ were broadened as one peak around 2.547–2.694 ppm, about 1 ppm downfield shift from the free en ligand's signal at 1.668 ppm but similar to the signal of 2.729 ppm in $Pt(en)(NO_3)_2$. All complexes displayed one ethylene carbon signal. It is worth noting that the chemical shifts of proton and carbon signals of the en ligand in all the complexes are about the same, indicating the bonding of thioureas to the platinum(II) center exert limited *trans* effect on the bonded bidentate en ligand.

Unlike the en ligand, the thioamide protons in bonded thioureas showed greater chemical shifts in their NMR spectra. The variation depends on the nature of the substituents such as alkyl or aryl groups. Complexes **3**, **7** and **11**, exhibited one thioamide proton signal while all other complexes showed more than one peak, indicating the nonequivalence of these protons. It is of interest to note the thioamide proton chemical shifts in complexes **9** and **10** were in opposite directions, i.e. one group of protons shifted downfield while the other group of protons shifted upfield. The presence of a benzene ring in **9** and a pyridyl ring in **10** created magnetic anisotropy and led to opposite shifts but to a different extent.

The ^{13}C NMR spectra of all complexes show high frequency peaks at 168.446–174.328 ppm. These recorded shifts reflected an upfield shift about 10 ppm from the free thioureas, suggesting increased electron density on the thiocarbonyl carbon. As can be seen from Table 2, the patterns of ^{1}H and ^{13}C coordination shifts were similar in all complexes, that is, all thioamide protons were shifted downfield and all thiocarbonyl carbons were shifted upfield. These opposite chemical shifts demonstrate there is an electron density transfer from the amide nitrogen to thiocarbonyl carbon upon thioureas complexation to the platinum(II) center. Consequently, the C═S bond order is decreased, and C—N bond order is increased in accordance with other similar thiourea complexes [35–40].

3.4. X-ray crystallography

Figs. 1 and 2 show the structures of **7** and **9** with the atom labeling scheme adopted and the hydrogen bonding network between the complex cation and nitrate anions, respectively. Both complexes have a near square-planar geometry with the platinum in the center and being coordinated by one bidentate en ligand and two monodentate thioureas via the sulfur atoms. Selected bond lengths, bond angles, and torsion angles are given in Table 3. The Pt–S bond distances are about the same in the two complexes (~2.3 Å), agreeing well with reported values for other analogous complexes containing thioureas [38–41]. The Pt–N bond distances fall in the range expected for other ethylenediamine platinum(II) complexes [42]. The C—S bond lengths in the coordinated thioureas in **7** and **9** are 1.712(2) Å and 1.719 Å, respectively. These values are typical of those seen for other complexes containing thiourea derivative ligands [28,38,39,43] but slightly larger than 1.692(1) Å in free imt [44] and 1.6915(16) Å in free phtu [45]. The lengthening of C═S bond lengths further supports the conclusion drawn from the NMR data, i.e. the bond order of C═S was decreased. The N1–C1–C2–N2 torsion angles in the two complexes are about the same. Obviously, the coordination of thioureas has limited effect on the bond lengths, bond angles and torsion angles of the en ligand, a result consistent with the NMR data in previous section. In **7**, both imidazole planes (not quite flat) are perpendicular to the molecular plane of the complex. In the structure of **9** the interactions between C16-H and N5-H and between C12-H and S2 make the phenyl ring is not coplanar with the plane of sp^2 C(═S), resulting in an exterior torsion angle C10-N5-C11-C12 of −49.1°. This tilting alleviates close contact between the ortho hydrogens of the phenyl group on the amino hydrogen and sulfur. Furthermore, the NH_2 groups were bent over toward the molecular plane while the phenyl rings were oriented away from the plane of the complex. It is of interest to notice that the two imidazole rings in **7** and the two phenyl rings in **9**

Table 2
Selected NMR and IR data for the thiourea ligands and their ethylenediamine platinum(II) complexes $[Pt(en)L_2](NO_3)_2$.*

	NH ^{1}H Shift (ppm)		C═S ^{13}C Shift (ppm)		en Ligand Shift (ppm)		IR band (cm^{-1})	
	Free L	Bonded L	Free L	Bonded L	NH_2 Proton	CH_2 Carbon	C═S	NO_3^-
1	7.972, 7.094	9.223, 8.847–8.227	183.443	171.830	5.508	46.250	694	827
2	7.461, 6.782	8.515–8.156	181.794	169.656	5.447	47.519	717	826
3	7.276	8.350	181.251	170.353	5.518	47.576	795	826
4	6.993	8.062, 7.872	179.925	168.427	5.594	47.566	741	827
5	7.623, 7.502, 6.864	8.698, 8.448, 8.048	182.862	170.829	5.440	47.538	697	826
6	7.510, 7.198, 6.831	8.688, 8.479, 8.384, 8.054	183.062	170.915	5.424	47.557	712	824
7	7.990	9.153	183.434	174.328	5.520	47.700	676	827
8	7.430, 7.210, 6.766	8.558, 8.431, 8.112	181.813	169.790	5.454	47.490	690	827
9	9.670	10.384, 8.884, 8.218	180.974	172.990	5.571	48.122	691	823
10	9.766	9.799, 9.057	181.832	173.909	5.621	47.614	701	822
11	7.274, 6.753	8.194	181.661	170[a]	5.534	47.538	671	827

* Details of the spectroscopic data and assignments can be found in Section 2.4.
[a] Estimated value.

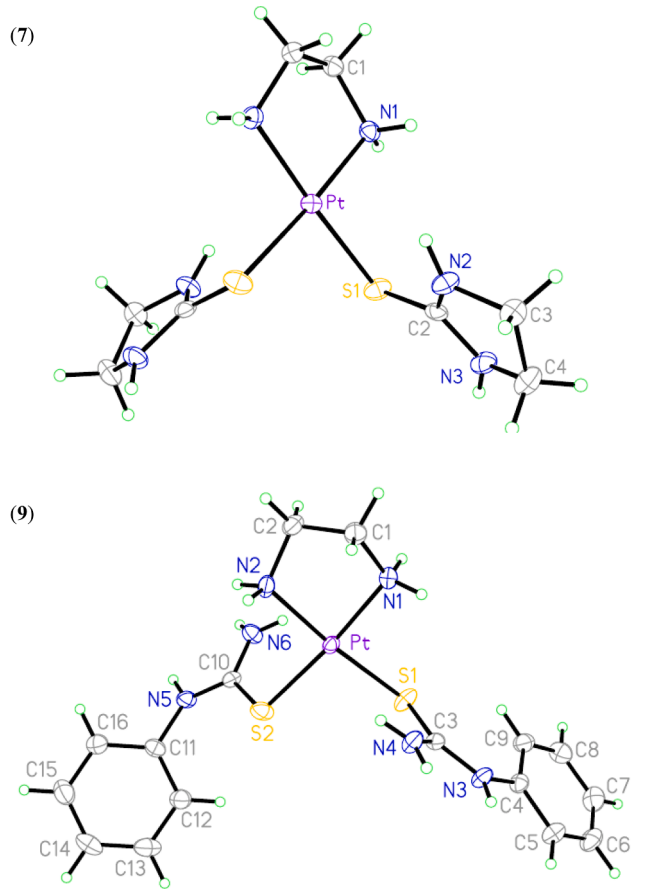

Fig. 1. View of the cation showing the atom numbering scheme. Thermal ellipsoids are 60% equiprobability envelopes, with hydrogens as spheres of arbitrary diameter.

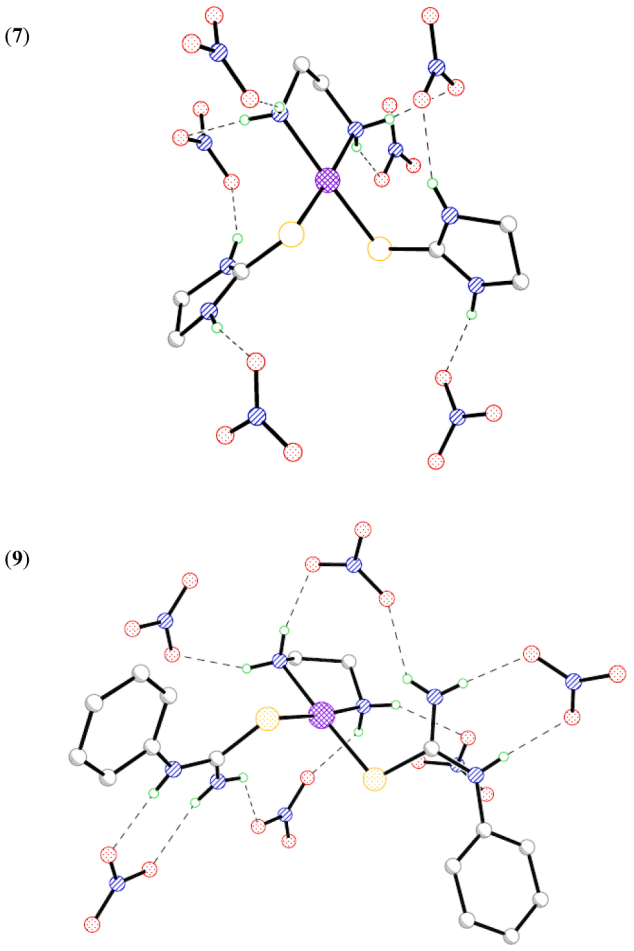

Fig. 2. Intermolecular hydrogen bonding arrangement.

are oriented above and below the PtN_2S_2 plane, respectively, to minimize the steric interaction. The stable crystal structures of **7** and **9** were facilitated by an extended network of hydrogen bond interactions as shown in Fig. 2. These hydrogen bonds are intermolecular, involving the nitrate oxygens and the amino hydrogens of the en and thioureas, either at 2.03 or 2.04 Å in **7** and at 2.01–2.27 Å in **9**. The en N—H···O hydrogen bond angles are 161.4 and 163.3° in **7** and vary from 143.8 to 165.2° in **9**. The variation in N—H···O bond lengths and angles in **7** is smaller than in **9**, suggesting stronger hydrogen bonding interactions in **7** than those in **9**. Even though there are no X-ray crystallographic data for other complexes in this report, it is anticipated that similar hydrogen bonding interactions should also exist. The presence of hydrogen bonds in the complexes may also contribute somewhat to the proton NMR signals shifted downfield. Moloto et al reported that the thioamide hydrogen and the thiocarbonyl sulfur in monosubstituted *N*-alkylthiourea can take either *cis* and *trans* positions with respect to each other [46]. Though phenyl is a bulky substituent complex **9** takes the *trans* configuration because of the formation of strong hydrogen bonds between the NH/NH_2 protons and oxygens from the same nitrate ion on the same side to form an 8-membered ring (N5-H···O4 and N6-HA···O5, see Fig. 2).

4. Conclusion

A series of ethylenediamine platinum(II) complexes containing substituted thiourea ligands (L) with a general formula of $[Pt(en)L_2](NO_3)_2$ have been prepared and characterized by elemental analysis, IR spectroscopy and NMR spectroscopy. Good quality single crystals of $[Pt(en)(2\text{-imidazolidinethione})_2](NO_3)_2$ (**7**) and $[Pt(en)(1\text{-phenyl-2-thiourea})_2](NO_3)_2$ (**9**) are grown by slow evaporation of methanol solution

Table 3
Selected bond length (Å), bond angles (°), and torsion angles (°).

	7 [a]	**9**
Bond lengths		
Pt-N(1)	2.0648(14)	2.0622(16)
Pt-N(2)	2.0648(14)	2.0577(16)
Pt-S(1)	2.3048(5)	2.2935(5)
Pt-S(2)	2.3047(5)	2.2975(5)
S(1)-C(2)	1.712(2)	1.7187(19)[b]
S(2)-C(10)	1.712(2)[c]	1.7195(19)
Bond angles		
N(1)-Pt-N(2)	83.01(8)	82.48(6)
N(1)-Pt-S(1)	92.26(4)	92.68(5)
N(1)-Pt-S(2)	174.84(4)	173.80(5)
N(2)-Pt-S(2)	92.26(4)	91.47(5)
N(2)-Pt-S(1)	174.84(4)	174.81(5)
S(1)-Pt-S(2)	92.53(3)	93.41(2)
Torsion angles		
N(1)-C(1)-C(2)-N(2)	−49.1(2)	53.6(2)
Pt-S(1)-C(3)-N(3)	177.98(15)[d]	−177.62(14)
Pt-S(1)-C(3)-N(4)	−1.95(19)[d]	4.29(18)
Pt-S(2)-C(10)-N(5)	177.98(15)	−168.49(14)
Pt-S(2)-C(10)-N(6)	−1.95(19)	9.99(18)

[a] Symmetry transformations used to generate equivalent atoms: #1 $-x + ½, -y + ½, z$.
[b] C(3).
[c] S(1)#1-C(2)#1.
[d] C(2).

at room temperature. IR analyses reveal the characteristic vibrations of the functional groups and the nitrate counter ions. NMR studies show that the chemical shifts of proton and carbon signals of the bonded en are about the same, indicating the bonding of thioureas to the platinum (II) center exert limited *trans* effect on the en ligand. The observation that thioamide proton signals shift downfield and the thiocarbonyl carbon signals shift upfield as compared to the free thioureas suggests a decrease in thiocarbonyl bond order and an increase in thiocarbonyl carbon-amide nitrogen bond order upon coordination to the platinum (II) center. The molecular structures of **7** and **9** have been identified by the single crystal X-ray diffraction. Complex **7** crystallizes in the orthorhombic space group *Pccn* whereas **9** crystallizes in the monoclinic space group *P*2(1)/n. X-ray crystallographic analysis indicates that the geometry about the platinum atom is square-planar and the crystal packings are dominated by intermolecular en N—H···O and thioureas N—H···O hydrogen bonds. The two imidazole rings in **7** and the two phenyl rings in **9** are oriented above and below the PtN_2S_2 plane, respectively, to minimize the steric interaction.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix A. Supplementary data

Crystallographic data have been deposited with the Cambridge Crystallographic Data Center. CCDC No. 2004587 [**7**, $[Pt(en)(imt)_2](NO_3)_2$], CCDC No. 2004754 [**9**, $[Pt(en)(phtu)_2](NO_3)_2$]. Copies of the data can be obtained, free of charge, on application to The Director, CCDC, Union Road 12, Cambridge CB2 1EZ, UK (fax: +44 1223/336 033 or e-mail: deposite@ccdc.cam.ac.uk). Supplementary data to this article can be found online at https://doi.org/10.1016/j.ica.2021.120302.

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