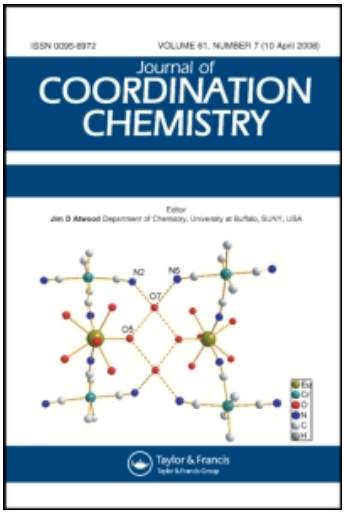

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Synthesis and characterization of platinum(II) complexes with 2-imidazolidinethione. X-ray crystal structure of tetra(2-imidazolidinethione-*S*)platinum(II) iodide dimethylsulfoxide solvate monohydrate

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Preparations of *trans*-$[PtX_2(Imt)_2]$ (Imt = 2-imidazolidinethione, X=Cl^- or I^-) and $[Pt(Imt)_4]I_2$ are described. These complexes were characterized by elemental analysis, thermal analysis, mid- and far-IR spectroscopy, and NMR (^1H and ^{13}C) spectroscopy. The crystal and molecular structure of $[Pt(Imt)_4]I_2 \cdot DMSO \cdot H_2O$ was determined by X-ray diffraction methods. The structural data reveal the following features: (a) the platinum atom in $[Pt(Imt)_4]^{2+}$ is essentially in a square-planar environment, (b) the entire dication possesses approximately C_{2h} symmetry, (c) no appreciable hydrogen bonding exists between the iodide ions and the Imt ligands in the dication, (d) two pairs of two mutually *cis* Imt ligands are arranged above and below the PtS_4 plane, respectively, and (e) two planes defined by two *trans* Imt rings are perpendicular to each other.

Keywords: Platinum(II) complexes; 2-Imidazolidinethione; Thermal analysis; X-ray

1. Introduction

Cisplatin (*cis*-diamminedichloroplatinum(II)) is one of the most widely used anticancer drugs to treat various types of cancers [1]. Due to its severe side effects, e.g., dose-dependent nephrotoxicity, nausea/vomiting, ototoxicity, neurotoxicity, and myelotoxicity, application of cisplatin has been restricted [1, 2]. Therefore, it is desirable to develop new platinum-based anticancer drugs with a broader spectrum of activity, improved clinical effectiveness, and reduced toxicity. Extensive research in this field has resulted in thousands of platinum compounds being synthesized and evaluated in preclinical animal studies [3, 4]. Among this large group, only about two dozen platinum complexes have entered human clinical trials [4]. Clinical differences among

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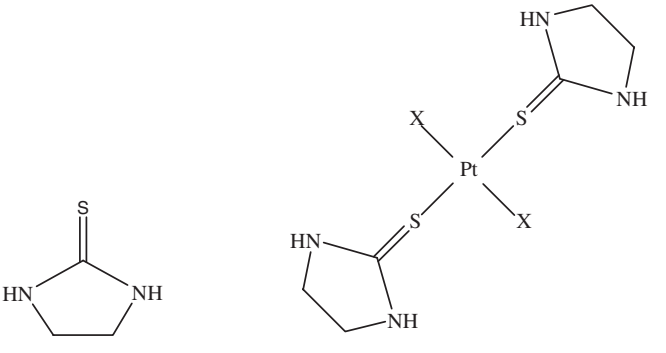
these complexes are minor and their chemical structures share some common structural features, namely, each contains a *cis*-PtN_2 unit [4]. Exploration of new structural classes of platinum-based anticancer drugs has led to the discovery of new agents that do not follow the classical structure/activity relationships established for cisplatin-like complexes. Thus, there has been a growing interest in research on platinum complexes with sulfur-containing ligands in recent years. It has been found that cisplatin-like drugs can induce renal toxicity in chemotherapy due to their reactions with the methionine and cysteine groups of proteins [5–7]. On the other hand, platinum(II) complexes with sulfur-containing ligands, such as dithiocarbamates [8], thiosemicarbazones [9, 10], and xanthate [11], have shown superior or equal efficacy towards some human tumor cell lines yet with less toxicity than cisplatin. Thiourea and its derivatives are one type of such S-donor ligands that have been used as chemoprotectants against nephrotoxicity after cisplatin treatment [5], inhibitors for HIV-1 and HIV-2 reverse transcriptases [12], and antifungal agents against some plant pathogenic fungi [13]. The chemistry of platinum complexes with thiourea and its derivatives has long been known although initial interest in these compounds was not related to their biological activities. For example, the crystal and molecular structure of tetra(thiourea)platinum(II) chloride was reported first in 1973 [14] to investigate the electronic effects of thiourea metal bonding and again in 1988 [15] because of the discovery of thiourea's ability to restore the biological activity of platinated DNA by reversing the cross-links induced by Pt(II) compounds. Platinum(II) complexes with other thiourea derivatives, such as tetra(1-methyl-2(3H)-imidazolinethione)platinum(II) chloride and nitrate, were also crystallographically characterized in 1982 [16] and in 2004 [17], respectively, for interest in new platinum-based anticancer compounds having S,N-containing heterocyclic ligands. The fact that platinum complexes with S-donor ligands have demonstrated anticancer activity prompted us to prepare platinum complexes with 2-imidazolidinethione (Imt), which is also known as N,N-ethylenethiourea, and characterize them using various analytical techniques. In this study, we have synthesized two neutral *trans*-platinum(II) complexes that contain two Imt molecules of the type *trans*-$[PtX_2(Imt)_2]$ ($X{=}Cl^-$ or I^-) shown in chart 1, and a third ionic complex that contains four coordinated Imt molecules $[Pt(Imt)_4]I_2$ (see figure 2). The crystal structure of the latter complex with dimethylsulfoxide solvate monohydrate was also characterized by X-ray diffraction methods.



2-imidazolidinethione (Imt) *trans*-$[PtX_2(Imt)_2]$ ($X = Cl^-, I^-$)

Chart 1. Two neutral *trans*-platinum(II) complexes.

2. Experimental

2.1. *Materials and measurements*

Potassium tetrachloroplatinate ($K_2[PtCl_4]$) was purchased from Johnson Matthey Electronics (Ward Hill, MA). 2-Imidazolidinethione (Imt), cisplatin (*cis*-$[PtCl_2(NH_3)_2]$) and transplatin (*trans*-$[PtCl_2(NH_3)_2]$) were obtained from Sigma-Aldrich Chemical Co. (St. Louis, MO). All other chemicals and solvents were obtained from commercial suppliers and used without further purification. Deuterated solvents were supplied by Cambridge Isotope Laboratories, Inc. (Andover, MA). 0.20 μm nylon acrodis syringe filters were purchased from Gelman Scientific (Ann Arbor, MI).

Carbon, hydrogen and nitrogen analyses were carried out by Robertson Microlit Laboratories (Madison, NJ). Thermogravimetric analysis (TGA) was performed on a Q5000 IR TGA (TA Instruments, New Castle, DE) at a heating rate of 20°C min^{-1} with air purge (air flow rate: 25 mL min^{-1}). 5–10 mg samples were measured in a platinum TGA pan. Melting points were determined from differential scanning calorimetry (DSC) measurements using a Q2000 DSC (TA Instruments, New Castle, DE) at the same heating rate with N_2 purge (N_2 flow rate: 50 mL min^{-1}). Approximately 10 mg samples were contained in crimped aluminum DSC pans and lids. Attenuated Total Reflection (ATR) mid-IR spectra were recorded for pure solids on a ThermoNicolet NEXUS 470 FTIR spectrometer. The far-IR spectra were obtained from Thermo Fisher Scientific (Schaumburg, IL) in the range 275–600 cm^{-1}. ^1H and ^{13}C NMR spectra were obtained on a JEOL 400 MHz spectrometer. The NMR experiments were conducted in deuterated dimethylsulfoxide (DMSO-d_6) on which signals were locked. Chemical shifts for ^1H and ^{13}C NMR spectra were referenced to the instrument's locked values for DMSO-d_6 at 2.4662 and 40.0370 ppm, respectively.

2.2. *Synthesis of complexes*

2.2.1. Synthesis of *trans*-$[PtCl_2(Imt)_2]$. To a 10 mL solution of $K_2[PtCl_4]$ (0.419 g, 1.0 mmol) was added dropwise 15 mL of Imt (0.245 g, 2.4 mmol), immediately generating a beige colored, turbid solution. After stirring for 10 minutes, the solid was collected by vacuum filtration, washed with several portions of water, methanol and ethyl ether in sequence, and dried under vacuum at 30°C overnight; yield, 95.1% (0.470 g), m.p. 210°C. The compound is soluble in DMSO, less soluble in DMF, and insoluble in water and all other common organic solvents. Anal. Calcd for $C_6H_{12}Cl_2N_4PtS_2$(%): C, 15.32; H, 2.57; N, 11.91. Found: C, 15.76; H, 2.51; N, 12.13. IR (pure solid) bands (cm^{-1}): 3368w, 3274sh, 3220m, 2879w, 1562vs, 1520s, 1479m, 1315s, 1281s, 1198m, 1038m, 989w, 916m, 659w, 596s, 498m. Far-IR (cm^{-1}): 322w, 310s. ^1H NMR (DMSO-d_6, δ in ppm): δ 3.65–3.68 (m, 4H, CH_2), 9.04–9.61 (m, 2H, N*H*); ^{13}C NMR (DMSO-d_6, δ in ppm): δ 45.56 (*C*H_2), 174.86 (*C*S).

2.2.2. Synthesis of *trans*-$[PtI_2(Imt)_2]$. This compound was prepared by reacting Imt with K_2PtI_4 formed *in situ* according to the literature method [18]. A typical synthetic procedure is described as follows. Addition of 5 mL solution of KI (1.63 g, 10.0 mmol) solution to a 10 mL solution of $K_2[PtCl_4]$ (0.419 g, 1.0 mmol) gave a dark brown solution immediately. To the resulting solution was added 20 mL of Imt (0.245 g,

2.4 mmol), resulting in immediate deposition of a brown precipitate. Upon stirring for 10 min, the brown precipitate was filtered, washed with several portions of water, and then recrystallized from a DMF/H_2O mixture. After being washed with water, methanol and diethyl ether, the final brown precipitate was dried under vacuum at 30°C overnight; yield, 72% (0.469 g), m.p. 241°C. The compound is soluble in DMSO, DMF, less soluble in acetone, methanol, acetonitrile, and insoluble in water, chloroform, dichloromethane, carbon tetrachloride, and carbon disulfide. Anal. Calcd for $C_6H_{12}I_2N_4PtS_2$(%): C, 11.03; H, 1.85; N, 8.58. Found: C, 11.20; H, 1.83; N, 8.33. IR (pure solid) bands (cm^{-1}): 3331br, 2890w, 1512vs, 1472m, 1337m, 1302m, 1276s, 1187m, 1038w, 984m, 913m, 643m, 533s, 501s. ^{1}H NMR (DMSO-d_6, δ in ppm): δ 3.65–3.71 (m, 4H, CH_2), 8.84–9.17 (m, 2H, N*H*); ^{13}C NMR (DMSO-d_6, δ in ppm): δ 45.48 (*C*H_2), 174.78 (*C*S).

2.2.3. Synthesis of $[Pt(Imt)_4]I_2 \cdot DMSO \cdot H_2O$. The brown solid *trans*-$[PtI_2(Imt)_2]$ was dissolved in DMSO to nearly saturation, filtered through a 0.20 μm nylon acrodis syringe filter, and vapor diffused with water at room temperature. During the recrystallization process, a dark-brown solid was precipitated along with the title compound. Yellow crystals suitable for structure determination were obtained in 5–7 weeks and were physically separated from the dark-brown solid. To separate the dark-brown solid from the yellow crystals, the solvents were first removed by filtration and the mixture of the solids was dried in vacuum at room temperature. To the dried solids a large quantity of water was added, and the mixture was stirred for three days at room temperature. The insoluble dark-brown solid was filtered off, washed with water, methanol and diethyl ether and dried under vacuum at 30°C. The filtrate was condensed to about 3 mL to yield a light brown solid via a rotary evaporator under reduced pressure at 45°C. The light-brown solid was filtered, washed with water, methanol and diethyl ether, and dried under vacuum at 30°C and later identified as an anhydrous tetra Imt platinum(II) complex, $[Pt(Imt)_4]I_2$, m.p. 266°C. The compound is soluble in DMSO, DMF, less soluble in water, acetone, methanol, acetonitrile, and insoluble in chloroform, dichloromethane, carbon tetrachloride, and carbon disulfide. Anal. Calcd for $C_{12}H_{24}I_2N_8PtS_4$(%): C, 16.81; H, 2.82; N, 13.07. Found: C, 16.41; H, 2.72; N, 12.65. IR (pure solid) bands (cm^{-1}): 3235br, 2891vw, 1527s, 1509s, 1478s, 1343m, 1313s, 1280s, 1228w, 1189s, 1035w, 991m, 916m, 661m, 584s(br), 497s. ^{1}H NMR (DMSO-d_6, δ in ppm): δ 3.70 (s, 4H, CH_2), 9.03 (s, 2H, N*H*); ^{13}C NMR (DMSO-d_6, δ in ppm): δ 45.48 (*C*H_2), 174.77 (*C*S).

2.3. *X-ray crystallography*

Diffraction data for $[Pt(Imt)_4]I_2 \cdot DMSO \cdot H_2O$ were collected using a Rigaku SCXmini diffractometer with graphite-monochromated Mo-Kα radiation ($\lambda = 0.71075$ Å) at 110 K operating at 50 kV and 40 mA. Important parameters and results are given in table 1. The crystal samples proved to be very slightly twinned, and the initial cell indexing was determined with the TwinSolve program [19]. Since the second component was determined to consist of less than 5% of the crystal volume, this component was ignored and the few overlapping reflections were removed later during the structure refinement stage. The structure was solved by direct methods [20] and expanded using Fourier techniques. The non-hydrogen atoms were refined anisotropically. Hydrogen atoms were included using the riding model. A total of 32 reflections that exhibited

Table 1. Crystallographic data and structure refinement for $[Pt(Imt)_4]I_2 \cdot DMSO \cdot H_2O$.

Empirical formula	$C_{14}H_{32}I_2N_8O_2PtS_5$
Formula weight	953.67
Crystal color and habit	yellow plate
Crystal dimensions (mm^3)	$0.20 \times 0.17 \times 0.04$
Crystal system	Triclinic
Space group	$P\bar{1}$ (No. 2)
Unit cell dimensions (Å, °)	
a	9.5630(5)
b	11.6780(6)
c	14.7271(8)
α	105.6331(11)
β	103.4525(12)
γ	105.7530(12)
Z	2
D_{calc} ($g\,cm^{-3}$)	2.201
$F(000)$	904
μ (Mo-Kα, cm^{-1})	74.11
θ range for data collection (°)	6.09–55.32
Reflections collected	14994
Absorption correction	6556 [$R_{int} = 0.081$]
Max. and min. transmission	0.732, 0.319
Refinement method	full-matrix least-squares on F^2
Data/restraints/parameters	6553/0/294
Goodness-of-fit on F^2	1.073
Final R indices [$I > 2\sigma(I)$][a]	$R_1 = 0.0554$, $wR_2 = 0.1341$
R indices (all data)	$R_1 = 0.0721$, $wR_2 = 0.1432$
Largest difference peak and hole ($e\text{Å}^{-3}$)	4.60 and −3.17

[a] $R_1 = \sum \|F_o| - |F_c\| / \sum |F_o|$, $wR_2 = \left[\sum\left(w\left(F_o^2 - F_c^2\right)^2\right) / \sum w\left(F_o^2\right)^2\right]^{1/2}$.

severe deviations from F_{calc} due to overlap with the minor twin component were manually removed from the refinement process. Neutral atom scattering factors were taken from Cromer and Waber [21]. Anomalous dispersion effects were included in F_{calc} [22]; the values for $\Delta f'$ and $\Delta f''$ were those of Creagh and McAuley [23]. All calculations were performed using the CrystalStructure [24] crystallographic software package including refinement with SHELXL-97 [25].

3. Results and discussion

3.1. *Synthesis of complexes*

Direct treatment of an aqueous solution of tetrachloroplatinate ($[PtCl_4]^{2-}$) with 2-imidazolidinethione (Imt) with a mole ratio of 1 : 2 resulted immediately in an off-white precipitate which was separated from the solution by filtration. On the basis of stereochemical considerations and the stronger trans-labilizing effect of S-donor ligands, the resulting complex is expected to be a *trans* isomer, *trans*-$[PtCl_2(Imt)_2]$. Similarly, the reaction of stoichiometric amounts of tetraiodoplatinate ($[PtI_4]^{2-}$) prepared *in situ* from $[PtCl_4]^{2-}$ and excess potassium iodide (KI) and Imt gave a structurally similar complex, *trans*-$[PtI_2(Imt)_2]$. Unlike the free Imt that is soluble in water and most polar solvents, *trans*-$[PtCl_2(Imt)_2]$ and *trans*-$[PtI_2(Imt)_2]$ are only

soluble in DMSO and DMF. The powdered forms of both complexes are stable in air and can be kept in a desiccator for a long period without obvious sign of degradation.

Initially, we intended to recrystallize *trans*-$[PtI_2(Imt)_2]$ from a DMSO/H_2O system to grow crystals that would be suitable for structural analysis. To our surprise, in the process of recrystallization, *trans*-$[PtI_2(Imt)_2]$ underwent a series of reactions, possibly dissociation/recombination reaction, eventually leading to a new yellow crystalline platinum(II) complex, determined as $[Pt(Imt)_4]I_2 \cdot DMSO \cdot H_2O$ via X-ray crystallography. The ligand to platinum ratios (Imt:Pt) in the starting material (*trans*-$[PtI_2(Imt)_2]$) and in the final recrystallization product ($[Pt(Imt)_4]I_2 \cdot DMSO \cdot H_2O$) are 2 : 1 and 4 : 1, respectively. Concomitant deposition of a dark-brown solid with the yellow crystal was observed in the recrystallization process. We have separated this dark-brown solid by filtration and attempted to determine its identity using all the analytical methods involved in this study except X-ray crystallography. Unfortunately, analyses of the dark-brown solid proved inconclusive as to its identification. No further efforts have been pursued from this respect. However, from its spectroscopic features, the dark-brown solid may be construed to be a mixture that comprises mainly the starting material and a small amount of dissociation/decomposition products from *trans*-$[PtI_2(Imt)_2]$. If one accepts the assertion that there was a gradual dissociation of the Imt ligand from the coordination core of *trans*-$[PtI_2(Imt)_2]$, then it is not difficult to explain why higher Imt:Pt ratio complexes were formed in the recrystallization process even though there were no other sources of the Imt ligand in the recrystallization DMSO/H_2O system. Dissociation of Imt from some *trans*-$[PtI_2(Imt)_2]$ provides additional Imt ligands *in situ* to react with undissociated *trans*-$[PtI_2(Imt)_2]$ to form $[Pt(Imt)_4]I_2 \cdot DMSO \cdot H_2O$. The precise pathway that led to the higher Imt : Pt ratio complex remains unknown and we do not intend to propose a possible mechanism for the formation of $[Pt(Imt)_4]I_2 \cdot DMSO \cdot H_2O$ from *trans*-$[PtI_2(Imt)_2]$ in the DMSO/H_2O system. The mixture containing the dark-brown solid and the yellow crystals was separated by dissolution of the solids with a large quantity of water followed by filtration. Condensing the filtrate afforded a light-brown solid, which was determined to be an anhydrous $[Pt(Imt)_4]I_2$. Similar to the two *trans* isomers, $[Pt(Imt)_4]I_2$ is soluble in most polar solvents but insoluble in nonpolar solvents. The low solubility of $[Pt(Imt)_4]I_2$ in water suggests that the bonding between the $[Pt(Imt)_4]^{2+}$ cation and iodide anions is more covalent than ionic. Results from the elemental analyses for all three complexes are reported in section 2 and are in good agreement with the theoretical calculations.

3.2. *Thermal analyses*

TGA thermograms of the complexes are presented in figure 1 and the thermal analysis results are summarized in table 2. As anticipated, the melting points of all three complexes are higher than that of free Imt and increase in the order of *trans*-$[PtCl_2(Imt)_2]$, *trans*-$[PtI_2(Imt)_2]$, and $[Pt(Imt)_4]I_2$ (see table 2). Loss of chloride or iodide might be in the form HCl or HI [26]. *Trans*-$[PtCl_2(Imt)_2]$ was degraded by a partial loss of one chlorine atom, followed by one Imt molecule, and then concomitant loss of the other chlorine atom and the other Imt molecule. *Trans*-$[PtI_2(Imt)_2]$ showed a two-step degradation process, each step involving simultaneous evolution of one iodine atom and one Imt molecule. $[Pt(Imt)_4]I_2$ underwent three steps to platinum metal, first involving the release of one iodine atom, followed by two Imt molecules, and finally

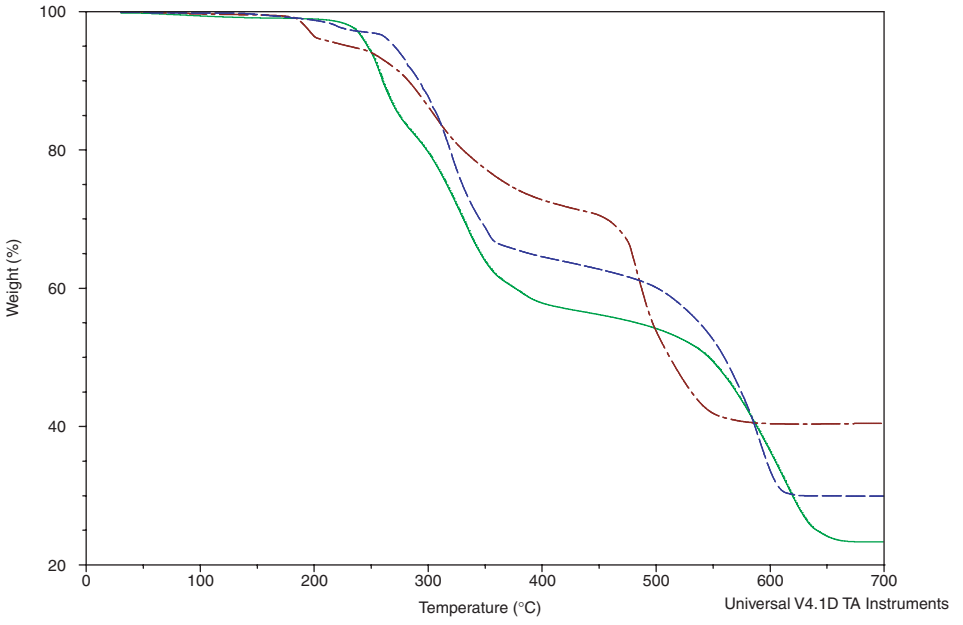


Figure 1. TGA thermograms of *trans*-[$PtCl_2(Imt)_2$] (broken dash), *trans*-[$PtI_2(Imt)_2$] (dash line), and $[Pt(Imt)_4]I_2$ (solid line).

Table 2. Thermal analysis results.

Compound	Decomposition range (°C)	Weight loss (%) Exp.	Calcd	m.p. (°C)
Imt ($C_3H_6N_2S$)				203
trans-[$PtCl_2(Imt)_2$]	179–432	27.9	29.2 (-Cl, -Imt)	210
	432–592	30.9	29.2 (-Cl, -Imt)	
		40.5	41.5 (Residual Pt)	
trans-[$PtI_2(Imt)_2$]	129–403	35.5	35.1 (-I, -Imt)	241
	403–633	34.5	35.1 (-I, -Imt)	
		30.0	29.9 (Residual Pt)	
$[Pt(Imt)_4]I_2$	226–286	15.9	14.8 (-I)	266
	286–413	25.1	23.8 (-2Imt)	
	413–670	37.8	38.6 (-I, -2Imt)	
		23.4	22.8 (Residual Pt)	

another iodine atom and the other two Imt molecules. The offset thermal degradation temperatures for *trans*-[$PtCl_2(Imt)_2$] and *trans*-[$PtI_2(Imt)_2$] were at 549°C and 607°C, respectively. This temperature difference is much smaller than similar dithioester and dithiocarbamato complexes of platinum(II) chloride and bromide [26]. $[Pt(Imt)_4]I_2$ required an even higher temperature (639°C) to release all the ligands. At the end of the pyrolysis, the TGA profile from *trans*-[$PtCl_2(Imt)_2$] presented the highest amount of platinum remaining (40.4%), $[Pt(Imt)_4]I_2$ exhibited the lowest amount of platinum remaining (23.3%), and *trans*-[$PtI_2(Imt)_2$] was in the middle (30.0%).

Agreement between the experimentally determined and theoretically calculated platinum metal residuals upon complete pyrolysis further substantiates the compositions of the complexes.

3.3. *Spectroscopic characterization*

The bands corresponding to NH stretching vibrations were observed in the 3220–3368 cm^{-1} region for all platinum complexes but did not shift to lower frequencies on formation of Pt-Imt complexes. Assignments to NH and CH_2 vibrations are in general straightforward; but definitive assignments to the thiocarbonyl C=S vibrations in IR spectra become difficult because of the strong coupling between the C=S bond and other bonds in the structure [27, 28]. The main IR bands of the complexes are listed in section 2. In the fingerprint region, absorptions at 1204, 1047, 1002, 921, 679, and 508 cm^{-1} in the free Imt shift to lower frequencies in the platinum complexes from a few wavenumbers to a maximum of 19 cm^{-1}, indicating that all these bands might be associated with the C=S vibration in various degrees [27]. The IR absorption band at 508 cm^{-1} with moderate intensity becomes very strong in its Raman spectrum and is assignable to a pure C=S deformation since sulfur is more polarizable than other atoms in the compounds [27, 28]. The bands at 921 and 679 cm^{-1} in Imt may also be ascribed to the contributions of C=S stretching and deformation vibrations, respectively [27–30]. Williams *et al.* have observed that IR peaks around 1150–1180 cm^{-1} assignable to carbon-sulfur stretching vibrations in N,N-substituted 2-imidazolethione derivatives shifted to lower frequencies upon complexation [31]. Due to their structural resemblance, the absorption at 1204 cm^{-1} for the Imt ligand may be assigned to the C=S stretching vibration, which shifted to lower frequencies (maximum of 17 cm^{-1}) when bonded with platinum. On the other hand, the moderate to strong absorption bands in the region 1464–1516 cm^{-1} for free Imt shifted slightly to higher frequencies because these bands involve carbon-nitrogen C–N vibrations [30]. The opposite shifts in the two regions reveal a decrease in C=S bond and an increase in C–N bond, as observed in other thiourea compounds [31, 32]. When there is a lack of X-ray structural data, Pt–Cl stretching vibrations in far-IR regions may be used as a criterion to determine if a platinum complex possesses a *cis* or *trans* geometry [33, 34]. In the present far-IR investigation of $[PtCl_2(Imt)_2]$, a broad band at 310 cm^{-1} with an unresolved weak peak at 322 cm^{-1} were observed and may be attributed to $\nu_{Pt\text{-}Cl}$ and $\nu_{Pt\text{-}S}$, respectively, on the basis of a similar far-IR study on *trans*-$[PtCl_2(thiourea)_2]$ which showed two bands at 325 and 317 cm^{-1} [35]. Thus it seems reasonable to assign the complexes $[PtX_2(Imt)_2]$ ($X = Cl^-$ or I^-) with a *trans* configuration although far-IR spectra may not be very indicative in some cases [33, 34].

^1H NMR spectra of the complexes and free Imt were recorded in DMSO-d_6 and the spectroscopic data are listed in section 2. The ^1H NMR spectrum of free Imt exhibited singlets at 3.45 and 7.96 ppm, assignable to ethylene CH_2 and imido NH resonances, respectively. Being highly symmetric arrangements in the coordination core, the coordinated Imt ligand in $[Pt(Imt)_4]I_2$ also showed two singlets at 3.70 (CH_2) and 9.03 (NH), respectively. Both the CH_2 and NH protons of the coordinated Imt in the other two complexes are shifted downfield with respect to the free Imt. In all three complexes the shifts for the NH protons are much larger than those for the CH_2 protons, which are comparable to other metal complexes with thiourea or thiourea derivatives [36, 37].

Large deshielding of the NH protons is attributed to the increase in π electron density in the C–N bond upon coordination. Contrary to ^{1}H NMR, ^{13}C NMR signals for the ethylene carbons and thiocarbonyl carbons were shifted upfield with respect to free Imt whose absorptions were at 44.59 and 183.97 ppm, respectively. A 9-ppm shift for the C=S carbon in coordinated Imt ligands in $[Pt(Imt)_4]I_2$ (174.77 ppm) is indicative of bonding being between sulfur and platinum, contrary to the claimed platinum-nitrogen bonds in $[Pt(Imt)_4]Cl_2$ [33]. It has been suggested that the bond order of the C=S is lowered somewhat while the bond order of the C–N is increased upon complexation, leading to the chemical shifts in opposite direction in ^{1}H and ^{13}C NMR signals [36, 37], in accord with the conclusion from IR measurements.

3.4. *X-ray crystal structure*

The asymmetric unit includes two halves of independent $[Pt(Imt)_4]^{2+}$ cations, each residing on a center of symmetry, with iodides approximately in the axial positions. One DMSO and one water molecule are in general positions in the unit cell. The atom numbering scheme and the molecular packing in crystals of $[Pt(Imt)_4]I_2 \cdot DMSO \cdot H_2O$ are depicted in figures 2 and 3, respectively. Selected bond lengths and angles are listed in table 3. The platinum in each $[Pt(Imt)_4]^{2+}$ unit is in an essentially square-planar environment, lying exactly within the plane defined by the four sulfur atoms. The entire $[Pt(Imt)_4]^{2+}$ cation possesses approximate C_{2h} symmetry. The iodides occupy distorted axial positions, above and below the PtS_4 planes; the Pt–I distances are 3.8734(7) Å for Pt1–I1 and 4.1169(7) Å for Pt2–I2. Although the four unique Pt-S distances average 2.328(2) Å and are in agreement with the average values reported for similar complexes such as $[Pt(Hmimt)_4]Cl_2$ (2.324 Å) [16] and $[Pt(Hmimt)_4](NO_3)_2$ (2.321 Å) [17] (where Hmimt is 1-methyl-2(3H)-imidazolinethione), there are some differences among the three complexes. In $[Pt(Hmimt)_4]Cl_2$, the four Pt–S distances are completely different from one another and vary from 2.291(5) Å to 2.357(5) Å. In $[Pt(Hmimt)_4](NO_3)_2$, the two unique Pt–S distances also differ significantly from each other (2.307(4) Å *versus* 2.339(4) Å). As can be seen in table 2, the largest difference in Pt–S bond lengths in $[Pt(Imt)_4]I_2 \cdot DMSO \cdot H_2O$ is 0.03 Å. Significant differences in S–Pt–S bond angles are also observed for these complexes. In $[Pt(Imt)_4]I_2 \cdot DMSO \cdot H_2O$ the four unique S–Pt–S bond angles are 88.7(1)°, 91.3(1)°, 87.2(1)° and 92.8(1)°, similar to those found in $[Pt(Hmimt)_4]Cl_2$ (92.7(2)° and 87.3(2)°) but those in $[Pt(Hmimt)_4](NO_3)_2$ cover a larger range of 85.2(3) to 94.8(3)°. The difference in bond lengths and bond angles between $[Pt(Imt)_4]^{2+}$ and $[Pt(Hmimt)_4]^{2+}$ can be accounted for by the unsymmetrical substitution of one of the two secondary amine hydrogens with a methyl. The average C–S bond distance of 1.707 Å in $[Pt(Imt)_4]I_2 \cdot DMSO \cdot H_2O$ is slightly longer than 1.692(1) in the free Imt ligand [38] and 1.6832(2) in 1-(2-aminoethyl)-2-imidazolinethione [39], indicating coordination via the thione sulfur, demonstrating that the bonding has limited effect on the double-bond character of C=S bond in terms of changes in bond lengths.

Another similar feature in the structures of $[Pt(Imt)_4]^{2+}$ and $[Pt(Hmimt)_4]^{2+}$ is the orientation of the coordinated ligands. Unlike $[Pt(Hmimt)_4](NO_3)_2$, both $[Pt(Imt)_4]I_2$ and $[Pt(Hmimt)_4]Cl_2$ have two mutually *cis*-ligands arranged above and below the PtS_4 plane [16, 17]. This arrangement in $[Pt(Hmimt)_4]Cl_2$ was suggested as a result of formation of hydrogen-bonds between the chlorides and imido hydrogen atoms.

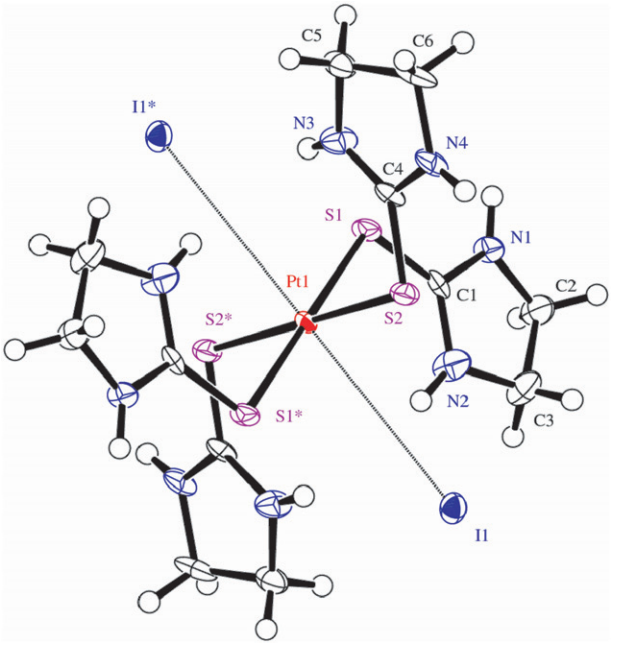


Figure 2. A view of one of the two independent complexes, showing the unique and the symmetry-related atoms. Non-hydrogen atoms are drawn with 50% displacement ellipsoids. The Pt1–I1 vector makes a 63.6 degree angle with the PtS4 plane.

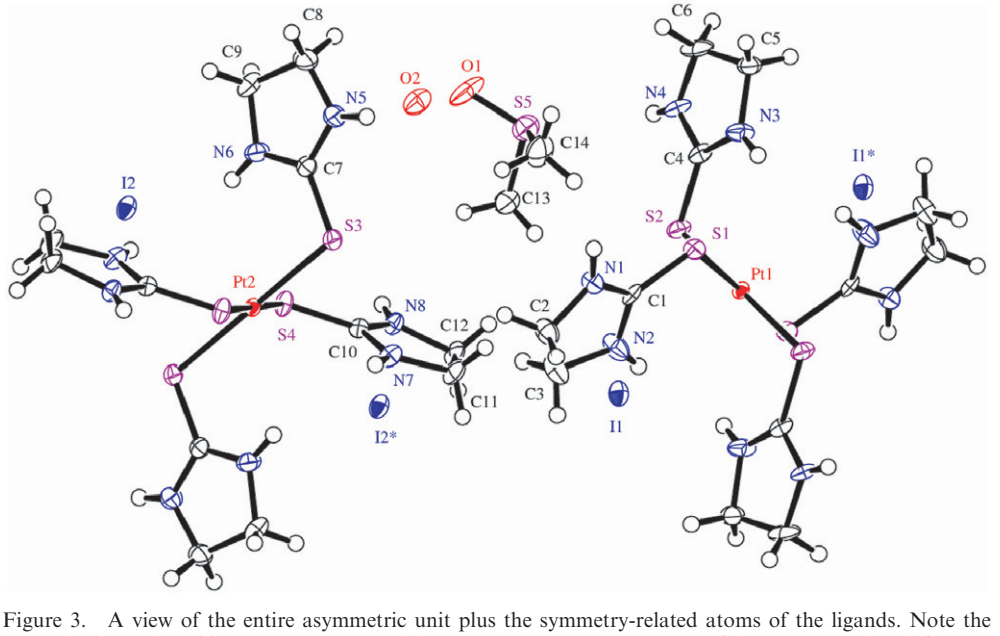


Figure 3. A view of the entire asymmetric unit plus the symmetry-related atoms of the ligands. Note the strong hydrogen bond between N5–H27 and the water oxygen (O2); atom O1 of the DMSO molecule forms a hydrogen bond with a symmetry-related position of N4–H26 (see text).

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

Bond lengths			
Pt(1)–S(1)	2.333(2)	Pt(1)–S(2)	2.324(2)
Pt(2)–S(3)	2.353(2)	Pt(2)–S(4)	2.322(2)
S(1)–C(1)	1.695(10)	S(2)–C(4)	1.716(11)
S(3)–C(7)	1.719(10)	S(4)–C(10)	1.697(11)
Bond angles			
S(1)–Pt(1)–S(1)′	180.00	S(1)–Pt(1)–S(2)	91.30(10)
S(1)–Pt(1)–S(2)′	88.70(10)	S(1)′–Pt(1)–S(2)	88.70(10)
S(1)′–Pt(1)–S(2)′	91.30(10)	S(2)–Pt(1)–S(2)′	180.00
Pt(1)–S(1)–C(1)	106.4(4)	Pt(1)–S(2)–C(4)	107.9(3)
S(1)–C(1)–N(1)	122.4(9)	S(1)–C(1)–N(2)	127.2(8)
S(2)–C(4)–N(3)	125.9(6)	S(2)–C(4)–N(4)	121.6(9)
Torsion angles			
S(1)–Pt(1)–S(2)–C(4)	67.6(4)	S(2)–Pt(1)–S(1)–C(1)	88.6(3)
S(1)–Pt(1)–S(2)′–C(4)′	112.4(4)	S(2)′–Pt(1)–S(1)–C(1)	−91.4(3)
Pt(1)–S(1)–C(1)–N(1)	−175.8(6)	Pt(1)–S(1)–C(1)–N(2)	7.4(9)
Pt(1)–S(2)–C(4)–N(3)	−6.9(11)	Pt(1)–S(2)–C(4)–N(4)	172.9(8)

Schiessl *et al*. have recently performed theoretical calculations on four different limiting molecular conformations for the homoleptic tetra(thiourea)platinum(II) complexes, $[Pt(TU)_4]X_n$ (where TU=thiourea, X=counter ions), and found that there were moderate energy differences among these conformers [40]. Thus, whether $[Pt(TU)_4]^{2+}$ takes a specific conformation depends on the hydrogen bonding between the dication and the counter ions. Although intermolecular N–H···I hydrogen bonds have been observed in $[Pt(TU)_4]X_n$ [40], they are not present in $[Pt(Imt)_4]I_2$. Therefore, the driving force for adopting the geometry in $[Pt(Imt)_4]I_2$ is not due to the presence of counter anions but the maximization of hydrogen-bonds between solvent molecules and the ligands in the dication. Intermolecular hydrogen bonds such as the N–H···O(water), N–H···O(DMSO) and C–H···O(DMSO) observed in $[Pt(Imt)_4]I_2$ stabilize the structure. Interactions occur between N5 and O2 (water, N···O, 2.926(13) Å; N–H···O, 158.1°), and between N4 and O1 (DMSO, N···O, 2.759(14) Å; N–H···O 164.0°).

It is also of interest to compare the crystal structures of $[Pt(Imt)_4]I_2 \cdot DMSO \cdot H_2O$ and $[Pt(Mi)_4]Cl_2 \cdot 2H_2O$ where Mi=2-mercaptoimidazole [41]. Although the free Mi may be in the thiol form, the coordinated Mi is present in the thione form with coordination taking place via the sulfur. Thus, both coordinated Imt and Mi are structurally the same except that the latter has slightly longer C–S bonds but shorter Pt–S bonds and a double bond C=C in the imidazole ring. Due to the similarity of the ligands, it is not surprising that both complexes crystallize in the same space group.

4. Conclusions

Three new platinum(II) complexes with 2-imidazolidinethione were prepared in aqueous solutions and characterized by elemental analysis, thermal analysis, and IR and NMR spectroscopy. Two of the three complexes are neutral compounds with two Imt molecules and two chlorides or iodides in their coordination cores and are insoluble

in water. The third complex contains four Imt molecules in its coordination core with two iodide ions as counter ions in the structure and was obtained as an unexpected product from recrystallization of *trans*-$[PtI_2(Imt)_2]$ in $DMSO/H_2O$. $[Pt(Imt)_4]I_2$ was also studied by X-ray crystallography revealing that the platinum is in an essentially square planar environment and two pairs of two mutually *cis* Imt ligands are arranged above and below the PtS_4 plane. All physical measurements are mutually supportive and indicate bonding of Imt to platinum(II) via the thione sulfurs. Spectroscopic data have shown that a decrease in C=S bond and an increase in C–N bond order occur for the Imt ligand upon complexation.

Supplementary material

Crystallographic data has been deposited with the Cambridge Crystallographic Data Center. CCDC No. 657102. 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).

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