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ORIGINAL PAPER

cis–trans Isomerism at Square-Planar MN_2S_2 Centers (M = Pd, Pt): Crystal Structures of *N*-Phenyl-*N*-(2-thiazoyl)thiourea Complexes *trans*-$Pd(S_2N_3C_{10}H_8)_2$ and *cis*-$Pt(S_2N_3C_{10}H_8)_2$ and Density Functional Calculations

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Abstract Simple palladium(II) and platinum(II) complexes, ML_2 (**1**–**2**), of *N*-phenyl-(2-thiazoyl)thiourea have been prepared and fully characterized. The structure of $Pd(S_2N_3C_{10}H_8)_2$ (**1**) is monoclinic $P2_1/c$, a = 12.510(2), b = 5.6963(6), c = 15.322(2) Å, b = 90.07(2)° and $Pt(S_2N_3C_{10}H_8)_2$ (**2**) is orthorhombic $P2_12_12_1$, a = 7.3021(5), b = 11.8025(9), c = 25.628(2) Å. In both complexes the ligands bind in a chelate fashion through the nitrogen atom of the thiazole ring and the sulfur atom of the thiourea to give six-membered chelate rings. In **1** the metal ion sits on an inversion center and the two ligands adopt a relative *trans*-disposition of like atoms, while in **2** all atoms are unique and the ligands are in a relative *cis*-disposition. DFT calculations on the *cis* and *trans* isomers based on **1** and **2** reveal that each pair of isomers is isoenergetic in the gas phase.

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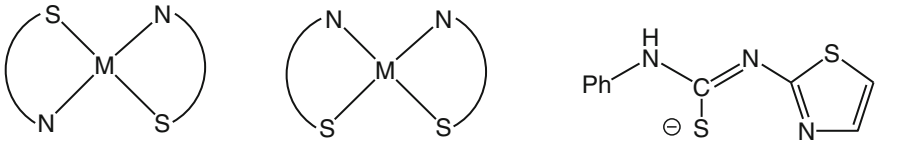
Introduction

The thiazole ring is found in a wide range of living organisms [1, 2] and common foodstuffs [3, 4], while several antibiotics [5, 6] also contain this simple organic group. Recently thiazole-containing compounds called epothilones have been identified as a new class of anti-cancer drugs, working by preventing cancer cells from dividing by interfering with tubulin [7]. A range of platinum-containing complexes as exemplified by cisplatin [8, 9], carboplatin [9] and oxaliplatin [10] also find widespread use as anti-cancer drugs, reacting in vivo with DNA resulting in cross-linking which ultimately triggers programmed cell death. Cytotoxic palladium(II) complexes are less well-developed [11–17] but Das and Livingstone [17] have reported that the palladium(II) complex of *S*-methyldithiobarbazate and related derivatives which possess a $Pd(NS)_2$ core show good cytotoxic activity .

We have recently prepared a range of platinum and palladium complexes with ligands containing simple heterocyclic substituents [18–21] as such complexes are anticipated to show interesting biological activity. In seeking to further develop this approach we were drawn to an earlier report concerning the coordination chemistry of *N*-phenyl-*N*-(2-thiazole)thiourea (LH) [22], which is easily prepared from commercially available 2-aminothiazole and phenylisothiocyanate in a single step, as it is a monoanionic NS-chelating ligand. While a number of complexes of *N*-phenyl-*N*-(2-thiazoyl)thiourea (L) (Chart 1) have been reported [22–27], a search of the literature revealed that none had been crystallographically characterized. Thus in

Chart 1 Possible *trans* and *cis* $[M(NS)_2]$ isomers of N-phenyl-(2-thiazoyl) thiourea (NS)



trans *cis* N-phenyl-N-(2-thiazoyl)thiourea

order to confirm the assumed coordination mode of this ligand, namely in a chelate fashion through the nitrogen of the thiazole ring and the sulfur of the thiourea, we have prepared and carried out single crystal X-ray diffraction studies on $M(S_2N_3C_{10}H_8)_2$ (M = Pd, Pt) (**1**–**2**). These show that the relative coordination geometry at the metal center is a function of the metal type as found for *trans*-$Pd(S_2N_3C_{10}H_8)_2$ (**1**) but *cis*-$Pt(S_2N_3C_{10}H_8)_2$ (**2**). As far as we are aware this is the first crystallographically established example of *cis*–*trans* isomers (Chart 1) based on a $M(NS)_2$ core (M = Pd, Pt), and in order to probe this further we have carried out a series of density functional calculations on all four possible isomers.

Experimental

Materials and Methods

^{1}H NMR spectra were recorded at the Institut für Chemie, Martin-Luther-Universität, Halle-Wittenberg, Germany on a Varian Unity 500 spectrometer with $CDCl_3$, DMF-d_7 or DMSO-d_6 as solvent and internal reference. IR spectra were recorded on a Shimadzu FT-IR 8400 spectrophotometer in the 400–4,000 cm^{-1} range using KBr discs. Elemental analysis was carried out at Martin-Luther-Universität. Melting points were measured on a Gallenkamp melting point apparatus and were uncorrected. Na_2PdCl_4, K_2PtCl_4, and other commercial products were used as supplied.

Preparation of *N*-Phenyl-*N*-(2-thiazole)thiourea

Phenylisothiocyanate (6 cm^3, 0.50 mol) was added to a solution of 2-aminothiazole (5.00 g, 0.50 mmol) in benzene (20 cm^3). The mixture was refluxed for 6 h. The resulting precipitate was filtered off, dried and recrystallized from benzene–hexane to afford a white crystalline solid (8.50 g, 70 %). Anal. Calc. for $C_{10}H_9N_3S_2$: C, 51.0; H, 3.9; N, 17.7. Found: C, 51.2; H, 3.8; N, 18.0 %. IR (KBr): 3170m, 3020m, 2945m, 1625s, 1575s, 1504s, 1375s, 1180s, 754m, 721m, 605w, 435w cm^{-1}. ^{1}H NMR ($CDCl_3$): δ 7.56 (bs, 1H, NH), 7.54 (bs, 1H, NH), 7.73, 7.35, 7.33, 7.22, 7.21 (individual multiplets each integrating for 1H, Ph), 7.30 (d, *J* 3.6 Hz, 1H, thiazole), 6.81 (d, *J* 3.6 Hz, 1H, thiazole). Melting point: 168–170 °C.

Preparation of $M(S_2N_3C_{10}H_8)_2$ (**1**, M = Pd, **2**, M = Pt)

A solution of *N*-phenyl-*N*-(2-thiazole)thiourea (0.15 g, 0.64 mol) in acetone (5 cm^3) was added to a warm solution of Na_2PdCl_4 (0.10 g, 0.32 mol) in acetone (10 cm^3). An orange yellow solid was formed directly. The mixture was stirred for 3 h and then chloroform (10 cm^3) was added and the mixture was refluxed for a further 3 h. The yellow precipitate was collected by filtration, washed with cold $CHCl_3$, and dried under vacuum to give yellow crystals of $Pd(S_2N_3C_{10}H_8)_2$ (**1**) (0.18 g, 97 %). Single crystals suitable for X-ray diffraction were grown upon slow evaporation of a DMF and ethanol mixture containing **1**. Anal. Calc. for $C_{20}H_{16}N_6PdS_4$: C, 41.5; H, 3.5; N, 14.5. Found: C, 41.6; H, 3.2; N, 14.3 %. IR (KBr): 3300m, 3120w, 3099w, 2923w, 1594m, 1535s, 1490s, 1443s, 1311m, 1173m, 882m, 754m, 539w, 495w cm^{-1}. ^{1}H NMR (DMF-d_7): δ 10.47 (s, 1H, NH), 7.98 (d, *J* 7.6 Hz, 2H, Ph), 7.52 (m, 3H, 2Ph+thiazole), 7.26 (t, *J* 7.2 Hz, 1H, Ph), 7.23 (d, *J* 4.0 Hz, 1H, thiazole). Melting point: 200–202 °C.

A solution of *N*-phenyl-*N*-(2-thiazole)thiourea (0.10 g, 0.43 mol) in warm MeOH (10 cm^3) was added to a solution of K_2PtCl_4 (0.10 g, 0.206 mol) in water (2 cm^3). A yellow solid was formed directly. The mixture was stirred for 3 h and then chloroform (10 cm^3) was added and the mixture was refluxed for 8 h. The resulting yellow precipitate was collected by filtration, washed with water, and dried under vacuum to give $Pt(S_2N_3C_{10}H_8)_2$ (**2**) (0.11 g, 70 %). Crystals suitable for X-ray diffraction were grown upon slow evaporation of an acetone/ethanol mixture containing **2**. Anal. Calc. for $C_{20}H_{16}N_6PtS_4$: C, 36.0; H, 3.0; N, 12.6. Found: C, 36.3; H, 3.1; N, 12.9 %. IR (KBr): 3367s, 332m, 3106w, 2924w, 1595m, 1535s, 1480s, 1445s, 1313m, 1168m, 881m, 756m, 546w, 536w, 505w, 476w cm^{-1}. ^{1}H NMR (DMSO-d_6): δ 10.22 (s, 1H, NH), 7.65 (d, *J* 7.6 Hz, 2H, Ph), 7.30 (dd, *J* 7.5 Hz, 2H, Ph), 7.06 (t, *J* 7.6 Hz, 1H, Ph), 7.25 (d, 1H, *J* 4.0 Hz, thiazole), 7.11 (d, *J* 4.0 Hz, 1H, thiazole). Melting point: 256–258 °C.

Table 1 Crystallographic data and structure refinement details for **1–2**

Compound	**1**	**2**
Empirical formula	$C_{20}H_{16}S_4H_{16}Pd$	$C_{20}H_{16}S_4H_{16}Pt$
Formula weight (Å)	575.03	663.73
Temperature (K)	220(2)	220(2)
Wavelength (Å)	0.71073	0.71073
Crystal system	Monoclinic	Orthorhombic
Space group	$P2_1/c$	$P2_12_12_1$
Unit cell dimensions		
a (Å)	12.510(2)	7.3021(5)
B (Å)	5.6963(6)	11.8025(9)
c (Å)	15.322(2)	25.628(2)
α (°)	90	90
β (°)	90.07(2)	90
γ (°)	90	90
Volume ($Å^3$)	1091.9(3)	2208.7(3)
Z	2	4
Density (calculated) (Mg/m^3)	1.749	1.996
Absorption coefficient (mm^{-1})	1.254	6.752
F(000)	576	1280
Crystal size (mm)	0.38 × 0.07 × 0.02	0.22 × 0.15 × 0.11
θ Range for data collection (°)	2.66–26.13	2.35–26.10
Index ranges	$-14 \le h \ge 15$	$-8 \le h \ge 8$
	$-7 \le k \ge 7$	$-14 \le k \ge 14$
	$-19 \le l \ge 18$	$-31 \le l \ge 31$
Reflections collected	7970	17267
Independent reflections [R_{int}]	2127 [$R_{int} = 0.0675$]	4191 [$R_{int} = 0.0705$]
Max. and min. transmission	0.9754 and 0.6472	0.5238 and 0.3181
Data/restraints/parameters	2127/1/146	4191/0/280
Goodness-of-fit on F^2	0.967	0.894
Final R indices [I > 2σ(I)]	$R_1 = 0.0403$, $wR_2 = 0.0817$	$R_1 = 0.0275$, $wR_2 = 0.0452$
R indices (all data)	$R_1 = 0.0699$, $wR_2 = 0.0900$	$R_1 = 0.0392$, $wR_2 = 0.0475$
Largest diff. peak and hole (e. $Å^{-3}$)	1.034 and −0.396	1.059 and −0.618

Crystal Structure Determination

Table 1 gives the crystallographic data and collection parameters for **1** and **2**. Intensity data were collected on a STOE-IPDS diffractometer with Mo-K_α radiation ($\lambda = 0.7103$ Å, graphite monochromater). Absorption corrections were made using the IPDS software package [28]. All structures were solved by direct methods with SHELX-97 [29] and refined using full-matrix least-square routines against F^2 with SHELXL-97 [30]. Non-hydrogen atoms were refined with anisotropic displacement parameters. The absolute structure parameter for **2** was −0.013(8).

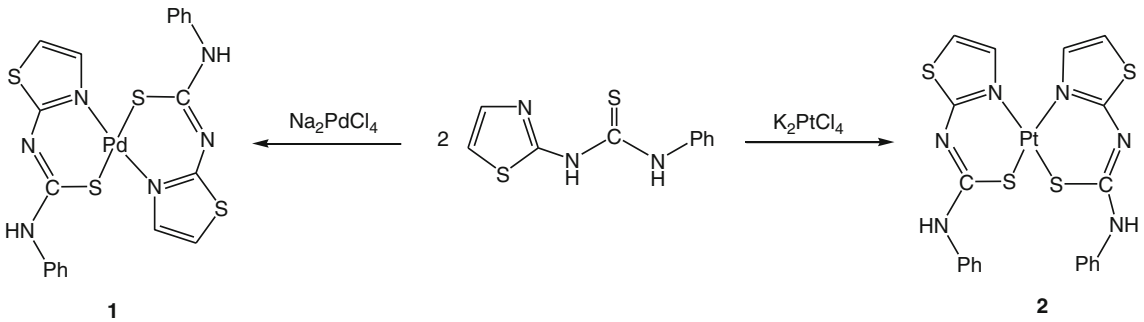
Computational Details

The DFT calculations were performed with the hybrid DFT functional B3LYP, as implemented by the Gaussian 09 program package [31]. This functional utilizes the Becke three-parameter exchange functional (B3) [32], combined with the correlation functional of Lee, Yang and Parr (LYP) [33]. The Pd and Pt atoms were described by Stuttgart–Dresden effective core potentials (ecp) and a SDD basis set, while the 6-31G(d′) basis set was employed for the remaining atoms. The geometries found for each isomeric pair of compounds based on **1** and **2** were fully optimized, and the analytical Hessian afforded only positive eigenvalues for the ground-state minima. The computed frequencies were used to make zero-point and thermal corrections to the electronic energies. The natural charges and Wiberg bond indices reported here were computed using Weinhold's natural bond orbital (NBO) program, as executed by Gaussian 09 [34, 35]. The geometry-optimized structures have been drawn with the *JIMP*2 molecular visualization and manipulation program [36, 37].

Results and Discussion

N-phenyl-*N*-(2-thiazole)thiourea (LH) was prepared by a modified literature method upon refluxing equimolar amounts of phenylisothiocyanate and 2-aminothiazole in benzene; the desired product was isolated as a white crystalline solid in 70 % yield. Addition of two equivalents to Na_2PdCl_4 in acetone, followed by heating to drive the reaction to completion, gave $Pd(S_2N_3C_{10}H_8)_2$ (**1**) as a yellow solid in 97 % yield after recrystallization from a mixture of DMF and ethanol. Likewise addition of a slight excess of *N*-phenyl-*N*-(2-thiazole)thiourea in methanol to Na_2PtCl_4 in water, followed by heating for 8 h, gave $Pt(S_2N_3C_{10}H_8)_2$ (**2**) also as a yellow solid in 70 % yield (Scheme 1). In this case crystallization was carried out using a binary solvent system composed of acetone and ethanol. While *N*-phenyl-*N*-(2-thiazole)thiourea and $Pd(S_2N_3C_{10}H_8)_2$ (**1**) [22] have previously been reported, preparation of $Pt(S_2N_3C_{10}H_8)_2$ (**2**) appears novel.

Characterization of both products was straightforward based on ^{1}H NMR and IR spectroscopy and elemental analysis. The ^{1}H NMR spectra are most informative, all showing the expected resonances for the phenyl group. For *N*-phenyl-*N*-(2-thiazoyl)thiourea (LH) there are also two



Scheme 1 Reactions of N-phenyl-(2-thiazoyl) thiourea with $[MCl_4]^{2-}$ (M = Pd, Pt)

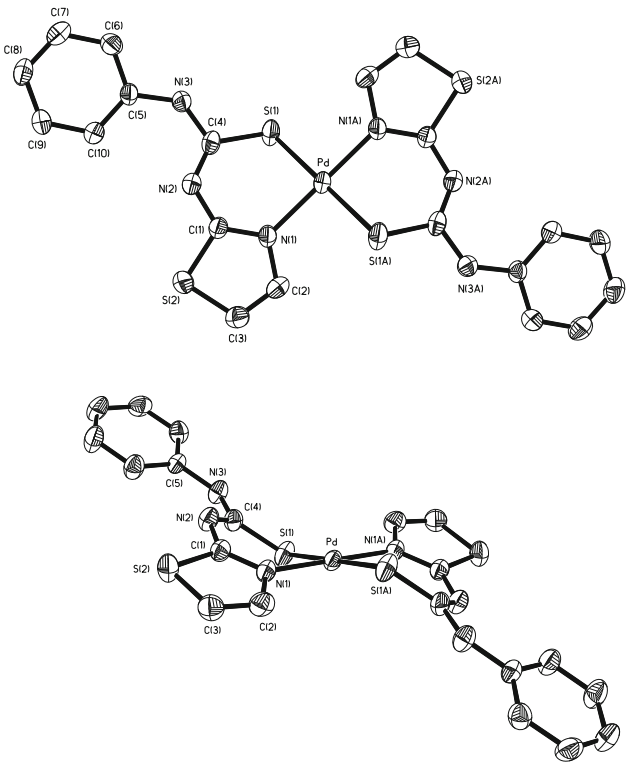


Fig. 1 Two ORTEP views of the molecular structure of **1** (hydrogen atoms omitted for clarity). Ellipsoids are drawn at 50 % probability level. Selected bond lengths (Å) and angles (°); Pd–N1 2.038(4), Pd–S1 2.312(1), N1–Pd–S1 88.2(1), N1–Pd–N1A 180.0(3), S1–Pd–S1A 180.0(7), N1–Pd–S1 91.8(1), N1–C1 1.323(6), N1–C2 1.364(6), N2–C1 1.364(6), N2–C4 1.304(6), N3–C4 1.367(6), S1–C4 1.744(5), S2–C1 1.722(5), S2–C3 1.708(5), C2–C3 1.333(7), Pd–S1–C4 104.1(2), Pd–N1–C1 125.9(3), C1–N2–C4 122.3(4), N2–C4–N3 118.7(5)

broad singlets at δ 7.56 and 7.54 assigned to the inequivalent amine protons and a pair of doublets at δ 7.30 and 6.81 ($^3J_{HH}$ 3.6 Hz) associated with the vicinal protons on the thiazole ring. For both complexes, a single broad band associated with the remaining amine proton is seen at δ 10.47 and 10.23 for **1** and **2**, respectively. The patterns of the phenyl and thiazole protons in **1** and **2** are similar. For **1** the thiazole protons appeared as a pair of doublets at δ 7.52 and 7.23 ($^3J_{HH}$ 4.0 Hz), while for **2** they are shifted upfield, slightly appearing at δ 7.25 and 7.11 ($^3J_{HH}$ 4.0 Hz).

The molecular structures of **1** and **2** are shown in Figs. 1 and 2, respectively, with selected bond lengths and angles given in the captions. The palladium complex **1** crystallizes in the monoclinic space group $P2_1/c$. The unique angle of 90.06(1)° first suggested orthorhombic symmetry, however, the merging *R*-value for the orthorhombic Laue group mmm was ca. 50 % indicating a monoclinic crystal system The molecule is centrosymmetric, the ligands thus adopting a relative *trans*-disposition (of like atoms) [N1–Pd–N1A 180.0(**3**), S1–Pd–S1A 180.0(**7**)°]. The platinum complex **2** crystallizes in the orthorhombic space group $P2_12_12_1$ and all atoms are unique. Here the ligands adopt a relative *cis*-disposition [S1–Pt–S3 87.77(8), N1–Pt–N4 92.8(2)°].

The structures confirm the supposition of Shoukry et al. [22] based on spectroscopic data that the *N*-phenyl-*N*-(2-thiazoyl)thiourea ligands bind to metal centers in a chelate fashion through ring nitrogen and thiocarbonyl sulfur atoms. This results from the selective deprotonation of the thiourea at the thiazole ring bound nitrogen atom. As seen from the metal-centered bond angles in both complexes, the metal is in a square-planar coordination environment. The bite angles of the ligands in both complexes are quite similar and close to 90°, that in **1** of 91.7(1)° being somewhat larger than those of 89.6(**1**) and 90.0(1)° in **2**. Metal-nitrogen bond lengths do not vary significantly between the two complexes [Pd–N1 2.038(4), Pt–N1 2.042(6), Pt–N4 2.033(6) Å] but there is a slight variation in the metal-sulfur distances [Pd–S1 2.3123(1), Pt–S1 2.272(2), Pt–S3 2.285(2) Å]. Bond lengths and angles within the chelate rings are fully consistent with the resonance structures shown in Scheme 1 (vide infra). Most important in this respect are the bond lengths to the central ring nitrogen atoms [N2 and N5], for example as shown in **1** [N2–C1 1.364(6), N2–C4 1.304(**6**) Å], which are clearly indicative of single and double bonds, respectively. These bond-length trends rule out any significant contributions from zwitterionic resonance structures associated with

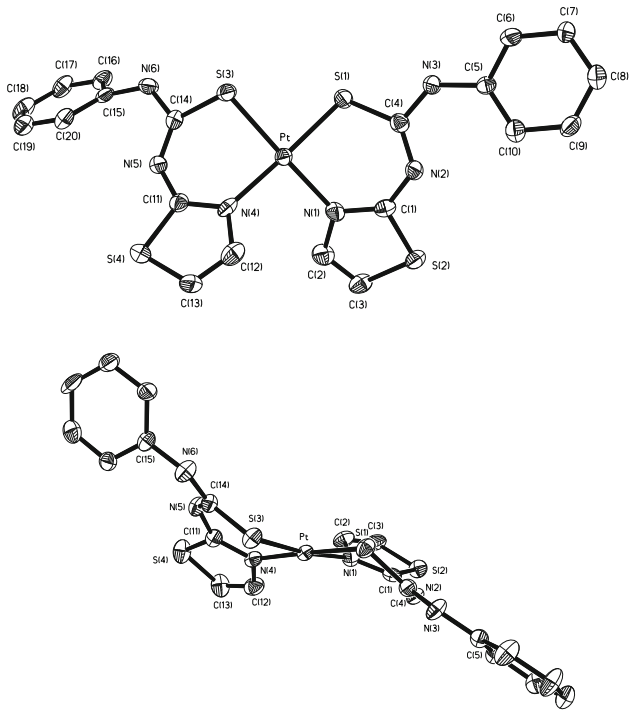


Fig. 2 Two ORTEP views of the molecular structure of **2** (hydrogen atoms omitted for clarity). Ellipsoids are drawn at 50 % probability level. Selected bond lengths (Å) and angles (°); Pt–S1 2.272(2), Pt–S3 2.285(2), Pt–N1 2.042(6), Pt–N4 2.033(6), S1–Pt–S3 87.77(8), N1–Pt–N4 92.8(2), N1–C1 1.345(8), N1–C2 1.39(1), N2–C1 1.365(9), N2–C4 1.30(1), N3–C4 1.356(9), S1–C4 1.761(6), S2–C1 1.722(8), S2–C3 1.713(7), C2–C3 1.34(1), N4–C11 1.347(8), N4–C12 1.390(9), N5–C11 1.373(8), N5–C14 1.294(8), N6–C14 1.357(8), S3–C14 1.769(7), S4–C11 1.710(7), S4–C13 1.707(9), C12–C13 1.32(1), Pt–S1–C4 104.4(2), Pt–N1–C1 126.1(5), C1–N2–C4 122.1(6), N2–C4–N3 119.7(6), Pt–S3–C14 103.0(2), Pt–N4–C11 126.3(4), C11–N5–C14 123.7(6), N5–C14–N6 118.6(6)

delocalisation of the lone-pair of electrons from the exocyclic nitrogen atom into the chelate ring.

While the MN_2S_2 subunit lies approximately in a plane, the chelate rings are far from planar. In both complexes the SN_2C_2 subunit is approximately planar, the largest deviations from planarity being of the order of 0.164 Å (C1) in **1** and 0.176 (C1)/0.164 Å(C11) in **2**, with the metal ions lying around 0.90–0.94 Å out of this plane. This then leads to an "up-down" orientation of the two ligands (as seen best by the phenyl rings) out of the MN_2S_2 plane. In each structure there are intermolecular interactions primarily between sulfur and hydrogen atoms. In **1** the shortest of these is between S1 and H3 of 2.681 Å, while the same sulfur atom also displays a longer interaction with H4 [S1···H4 2.951 Å]. In **2** the shortest intermolecular interaction is between Pt and H4 of 2.825 Å, while there are also a number of sulfur-hydrogen interactions [S1···H3 2.976, S2···H6 2.903, S3···H11 2.976 Å]. None of these appear to influence significantly the overall molecular structure or isomer type.

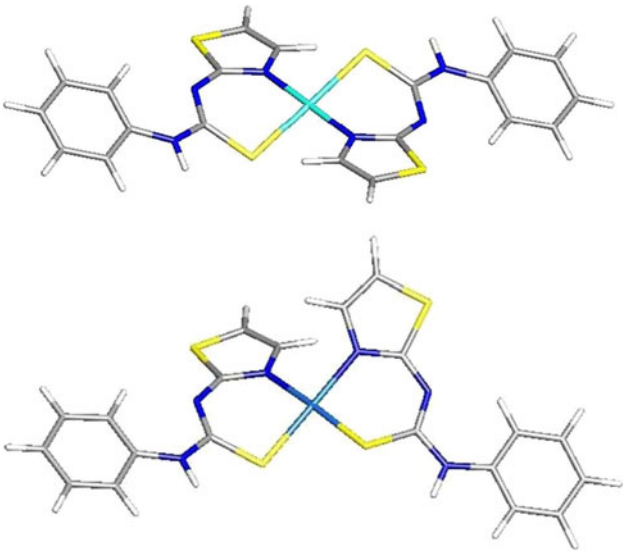


Fig. 3 Optimized structures for the ground-state minima of **1** (*top*) and **2** (*bottom*)

Since the pioneering work of Chatt and Wilkins on *cis–trans* isomerism at a square-planar platinum(II) center in the 1950s [38], a great deal of subsequent work has been carried out in this area due to the importance of this isomerism in catalysis and anti-cancer activity. Energy differences between isomers are generally found to be small with steric effects, electrostatic interactions, differences in bond energies, and solvation being key determinants [39]. Harvey and co-workers have probed the relative stabilities of isomers of MX_2L_2 complexes using density functional theory (DFT) [40]. Treating the MX_2L_2 core as five point charges interacting in a vacuum allows an electrostatic energy difference (EED) between *cis* and *trans* isomers to be determined and solvation effects can be added to this. Interesting in CH_2Cl_2 the free energy of the *cis* isomer of $PtCl_2(PMe_3)_2$ is predicted to be 4.5 kcal mol^{-1} more stable than the *trans*-derivative, while for palladium the *trans* isomer that is calculated to lie 0.6 kcal mol^{-1} lower in energy than *cis*-$PdCl_2(PMe_3)_2$. The preference for the *trans* isomer in the palladium compound is attributed to the greater importance of ionic bonding at the slightly harder Pd(II) metal. However, the present situation is more complex and a key finding of this work is that the bonding in complexes containing two *N*-phenyl-*N*-(2-thiazoyl)thiourea ligands has both ionic and covalent character, the latter resulting from σ-donation from the ligands into a metal-based sd-hydrid orbital through a three-center, three-orbital, four-electron interaction [40]. Consequently where two mutually *trans* ligands are not identical they compete as donors, and *softer* ligands higher in the *trans*-influence scale donate electrons more effectively, leading to an antisymbiotic effect whereby stronger ligands prefer to bind *trans* to weaker ligands [41].

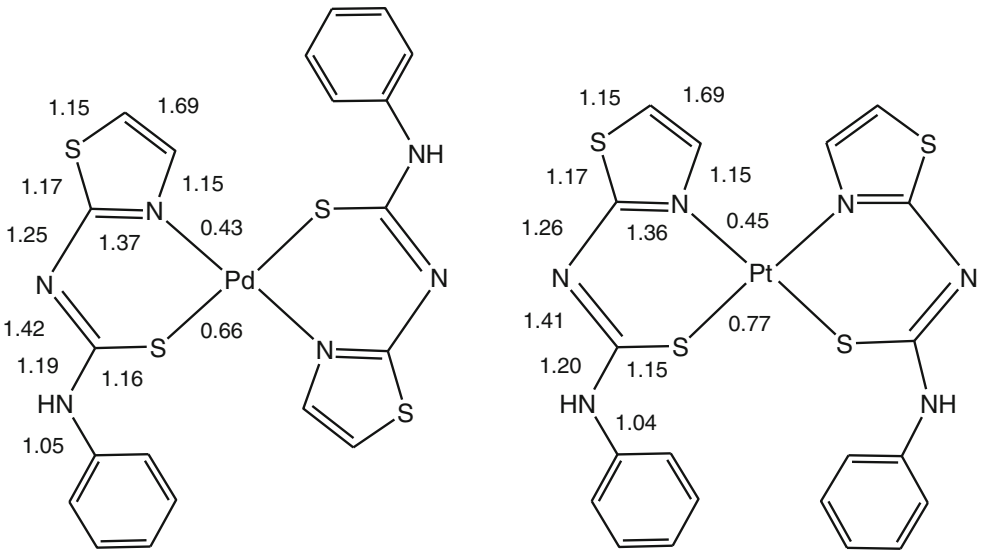


Fig. 4 Wiberg bond indices for compounds **1** and **2**. Due to the two-fold symmetry inherent in these compounds, only one half of the bond indices are displayed

Thus based on a predominance of covalent bonding, sulphur-nitrogen chelate ligands would be expected to adopt a relative *trans* arrangement as sulphur is much *softer* than nitrogen. Thus it appears that for palladium, the ionic component of the bonding outweighs the covalent contribution and a *trans* geometry is favoured, while for platinum the converse is true and covalency dominates the metal–ligand bonding, affording the observed *cis* structure.

In order to probe this further we have carried out DFT calculations on all four possible isomeric arrangements of the *N*-phenyl-*N*-(2-thiazoyl)thiourea complexes $M(S_2N_3C_{10}H_8)_2$. The DFT computed geometries for both observed compounds closely match the X-ray diffraction data. Figure 3 shows the DFT-optimized structures for *trans*-**1** and *cis*-**2** and Fig. 4 shows the Wiberg bond indices for **1** and **2**, where the bond-length trends are in excellent agreement with the principal resonance contributor of each compound. Here theory is again fully consistent with the resonance structures shown in Scheme 1 and a natural bond order (NBO) analysis provides additional support for the bonding within each diffraction structure. The corresponding isomer of each of these complexes (*cis*-**1** and *trans*-**2**) was also investigated computationally, and the energy difference between the respective pairs of isomers was found to be isoenergtic ($\Delta G < 1.0$ kcal mol^{-1}). Given the small calculated energy differences between the *cis* and *trans* isomers we considered that the crystallographic characterization of *trans*-$Pd(S_2N_3C_{10}H_8)_2$ (**1**) and *cis*-$Pt(S_2N_3C_{10}H_8)_2$ (**2**) may simply be a solid-state effect, with both isomers co-existing in solution as has been found to be the case for related amino-phenolate complexes [42]. Careful inspection of the ^{1}H NMR spectra of both **1** and **2** did not, however, reveal the presence of a second isomer and thus we conclude that if this is the case the second isomer as only an extremely minor component.

There are crystallographically characterized examples of $Pd(NS)_2$ complexes in both *trans* [43–45] and *cis* [45–52] arrangements, although the latter is more prevalent. Thus the preferential formation of *trans*-$Pd(S_2N_3C_{10}H_8)_2$ (**1**) is somewhat unexpected. Of the three examples we found in the literature containing a *trans*-$Pd(NS)_2$ core, two [43, 44] might be rationalised on the basis of the minimisation of adverse steric effects between ligand substituents, but in the third [45] no such effects can exist as both nitrogen and sulphur atoms bear no other substituents. Interestingly, Yoda et al. [52] have reported crystal structures of three palladium 1,1-dimethyl-3-(2-thiazolyl)thiourea complexes all found in the *cis* form. There are fewer examples of crystallographically characterized complexes containing a $Pt(NS)_2$ core and the majority contain a *trans* arrangement [42, 53–58]. The *cis*-$Pt(NS)_2$ core geometry has been shown [42] or postulated [58] to exist in solution but the

Chart 2 A comparison of the metal binding of N-phenyl-(2-thiazoyl) thiourea and methyl-2-amino-cyclopentenedithi ocarboxylate

N-phenyl-N-(2-thiazoyl)thiourea methyl-2-amino-cyclopentenedithiocarboxylate

only previously crystallographically characterized example is that of the platinum(II) complex of methyl-2-amino-cyclopentenedithiocarboxylate [51]. This complex is quite similar to **2**, both supporting six-membered chelate rings containing two double and four single element–element bonds (Chart 2). Thus, there may be something special about this chelate ligand type which results in selective isolation of *trans* structures. It is noteworthy also that in contrast to the *N*-phenyl-*N*-(2-thiazoyl)thiourea chemistry reported herein, the palladium complex of methyl-2-amino-cyclopentenedithiocarboxylate has also been shown crystallographically to adopt the *cis* conformation, although the analogous nickel complex is *trans* [51].

In conclusion, we believe that we have herein confirmed crystallographically for the first time that *N*-phenyl-*N*-(2-thiazoyl)thiourea acts as an NS chelate ligand binding to metals via the nitrogen atom of the thienyl ring and the sulfur of the thiourea moiety. This appears to be the first example of a pair of crystallographically characterized $M(NS)_2$ complexes (M = Pd, Pt) which differ in the relative arrangement of the chelating ligands. The adoption of a *trans* geometry at palladium and *cis* at platinum are unusual, although not unprecedented. This likely results from a number of factors, especially important being the degree of ionic and covalent nature of the metal–ligand bonding [40], with ionicity dominating for palladium and covalency for platinum. Thus, 60 years on from Chatt and Wilkin's seminal work [38] on *cis–trans* isomerism at a square-planar d^8 metal center there remains much to be understood before gross stereochemical generalizations can be made with certainty. This is especially true with new and novel ligand systems where geometry surprises are likely given the complex interplay of bonding interactions between the ligand(s) and the class b metal ion.

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