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# Quantum Chemical Analysis of the Enantiomerisation Mechanism of Complexes of the Type $[M^{II}(XU)_4]F^+$ (M = Pt, Pd, Ni; X = S, Se, Te; U = urea)

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The enantiomerisation pathway for $\{[Pt(thiourea)_4]\}F^+$ [a model for the $C_4$-symmetric $[Pt(SU)_4]SiF_6$ (SU = thiourea) complex] and derivatives is explored by density functional theory (B3LYP/LANL2DZp) und the activation barrier for the one-step process from $C_4$ to $C_4'$ via a $C_4$ transition state is computed. The substitution of $Pt^{2+}$ by $Pd^{2+}$ and $Ni^{2+}$ and the exchange of selenourea and tellurourea increase the barrier. ($\{[Pt(thiourea)_4]\}F^+$: 4.2 kcal/mol, $\{[Pd(thiourea)_4]\}F^+$: 4.5 kcal/mol, $\{[Ni(thiourea)_4]\}F^+$: 7.6 kcal/mol, $\{[Pt(selenourea)_4]\}F^+$: 5.3 kcal/mol, $\{[Pt(tellurourea)_4]\}F^+$: 8.8 kcal/mol).



## Introduction

Besides the common use of platinum complexes as catalysts in industrial processes,[1–4] $Pt^{II}$ complexes deliver the most common anti-tumour drugs for certain types of cancer.[5] Intracellular thiols are known to play an important role in the metabolism of Pt anti-tumour drugs because of their participation in trapping the drug.[6] Also, thiols can influence renal toxicity and can be involved in other side-effects.[7] Thiourea (SU) is one of the best-known nucleophiles for $Pt^{II}$ complexes[8,9] and is commonly used in the investigation of ligand-substitution reactions in coordination chemistry. Hence, thiourea can very easily displace other ligands from the metal centre in $Pt^{II}$ complexes, including S-bonded ligands such as L-cysteine in $[Pt(terpy)(S\text{-}cys)]^+$.[10] The strong binding ability of S-donor nucleophiles can also be applied to reverse unwanted side-effects in chemotherapy.[11,12] It has been demonstrated that thiourea could restore the biological activity of Pt-loaded DNA.[13] Thiourea and other sulfur-containing compounds have been applied as emergency or protective agents in order to reduce the toxicity of platinum anti-tumour complexes.[14–16] The protective effect of these compounds is either to prevent or to reverse the formation of Pt–S adducts of proteins.

As shown in Figure 1, thiourea is able to coordinate in different ways to the $Pt^{II}$ centre depending on the packing forces and H-bonding networks in different solid $[Pt(SU)_4]^{2+}$ salts,[17,18] which is controlled by the selected counter anions. There is current interest in the design of selective receptors for anions,[19,20] held together by either electrostatic or hydrogen-bonding-based forces.[21,22] Even though thiourea seems to show an inherently flexible coordination of the $S{=}C(NH_2)_2$ branches to the platinum centre, the IOIO conformation has until recently been known as the only isomer of $[Pt(SU)_4]^{2+}$, based on the structure of $[Pt(SU)_4]Cl_2$.[17,18,23] In contrast, $[Pd(SU)_4]Cl_2$ and $[Pd(SU)_4]I_2$ show the IIOO conformer.[23,24] While investigating the effects of solvent[25] and dicarboxylates[26] on the structure of $[Pt(SU)_4]^{2+}$, Gale et al. isolated IIOO as a new conformer. By serendipity they were able to build a molecular capsule from two $[Pt(SU)_4]^{2+}$ moieties in the OOOO conformer complexing endohedrally to a $Cl^-$ ion. This molecular capsule is stabilised by a hydrogen-bonded corset of croconates. In a recent study, we were able to show that all

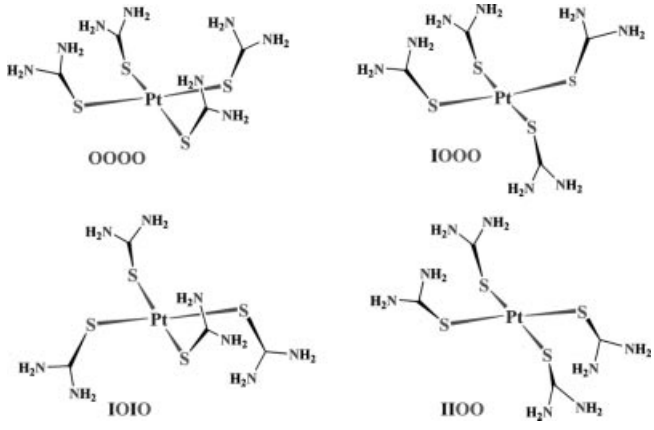


Figure 1. The four possible conformers of $[Pt(SU)_4]^{2+}$.

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four possible conformers (see Figure 1) of the $[Pt(SU)_4]^{2+}$ unit can be realised in the solid state by nothing more than a systematic tuning of the molecular structure by the hydrogen-bonding ability of the counter anion.[27] The chiral $C_4$-symmetric (four SU moieties up) was realised in $[Pt(SU)_4]SiF_6$, where four $NH_2$ groups interact with the $SiF_6^{2-}$ ion (see Figure 2).

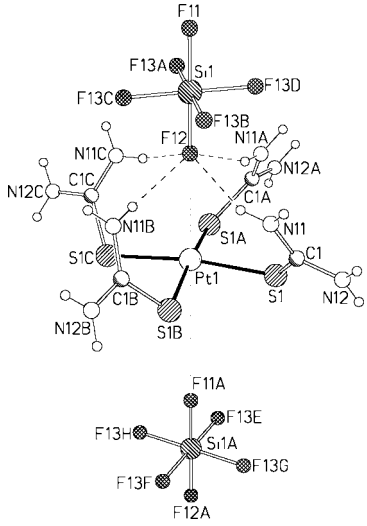
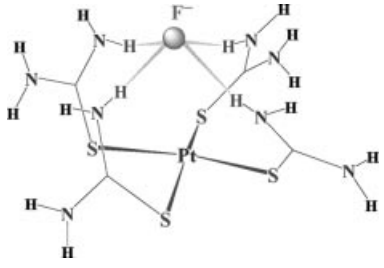



Figure 2. Conformation and H-bonding in $[Pt(SU)_4]SiF_6$ (OOOO).[27]

The H-bonds of the $NH_2$ protons formed with adjacent acceptors usually lead to the formation of clusters bearing interesting host–guest motifs.[28] The H-bonds formed by the $NH_2$ protons are especially important in terms of the motivation for the current study. We recently studied a larger number of $[Pt(SU)_4]X_2$ salts (X = $S_2O_6^{2-}$, $SiF_6^{2-}$, $ClO_4^-$, $CF_3SO_3^-$, $I^-$, $BPh_4^-$, etc.),[29] and found that the relatively strong N–H···X interactions in the case of X = one $F^-$ of the $SiF_6^{2-}$ anion in $[Pt(SU)_4]SiF_6 \cdot 0.25H_2O$ drives the $[Pt(SU)_4]^{2+}$ cation into the OOOO conformation (see Scheme 1). An analogous arrangement to that shown in Scheme 1 was recently also found by Gale et al. for the salt where X = $Cl^-$.[30,31]




Scheme 1. View of the N–H···$F^-$ interactions in the $\{[Pt(SU)_4]F\}^+$ unit of $[Pt(SU)_4]SiF_6 \cdot 0.25H_2O$.

In these $[Pt(SU)_4]X$ units, six-membered proton chelate rings of the type Pt–S–C–N–H···X are formed. As found so far,[30] these four rings give rise (in the solid state) to either λλλλ or δδδδ chiral patterns (cf. Scheme 2).


Scheme 2. Enantiomers of the $\{[Pt(SU)_4]F\}^+$ unit based on the difference in ring chirality.

The question that we want to answer in the present study concerns the mechanistic details of the interconversion between the enantiomers shown in Scheme 2. On the basis of the well-known flexibility of the Pt–S bond, one would expect a nondissociative enantiomerisation mechanism, but the nature of this pathway is so far completely unknown. In order to simplify our computational studies, the $SiF_6^{2-}$ counterion was replaced by a simple $F^-$ ion leading to the $C_4$ model units $\{[Pt(SU)_4]F\}^+$ (see Scheme 2). In order to learn more about the influence of the metal centre and the donor atoms coordinated to the metal ion, we extended our investigation of the enantiomerisation mechanism to $[Ni(SU)_4]F^+$ and $[Pd(SU)_4]F^+$, and also to the $Pt^{II}$ complexes of the heavier analogue, viz. selenourea (SeU) and tellurourea (TeU).

## Results and Discussion

Two alternative pathways seem to be possible for the enantiomerisation of the $\{[Pt(SU)_4]F\}^+$ entity shown in Scheme 2, viz. a dissociative or a nondissociative mechanism. Bond breakage would imply either cleavage of the Pt–S bond or rupture of the N–H···F H-bond. The nondissociative alternative is ruled out based on the strength of both the Pt–S bond and the N–H···F interactions.

The $\{[Pt(SU)_4]F\}^+$ unit can be considered to be a {3}-cryptand consisting of one metal bridgehead, one fluorine bridgehead and four *pseudo bidentate* SU ligands (one S-donor and one NH-hydrogen-bond donor, see Figure 3). Therefore, $\{[Pt(SU)_4]F\}^+$ can be regarded as a special cryptand, viz. a mixed {3}-metalla-halide-cryptand.

The nondissociative enantiomerisation can either proceed by a fully chiral pathway, in line with Mislow's paradoxon,[29,30] or via a nonchiral transition state of higher symmetry. In the present study, our DFT calculations clearly show that the twisted quadratic prismatic enantiomers with $C_4$ symmetry, containing four puckered semi-chelate rings of opposite chirality (λλλλ vs. δδδδ), are linked by a single-step, all-chiral enantiomerisation path (see Figure 4). In contrast to other enantiomerisation processes,[31] all ground and transition states have the same point group $C_4$.

The complexes in the present study contain ligands with puckered six-membered pseudo-chelate rings, where enantiomerisation involves flipping of these rings (cf. Figure 5).

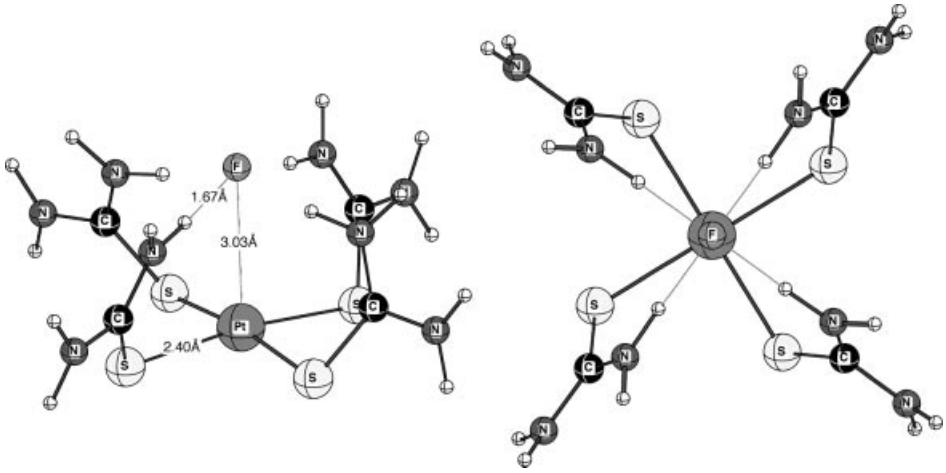



Figure 3. Calculated (RB3LYP/LANL2DZp) structure of $\{[Pt(SU)_4]F\}^+$.

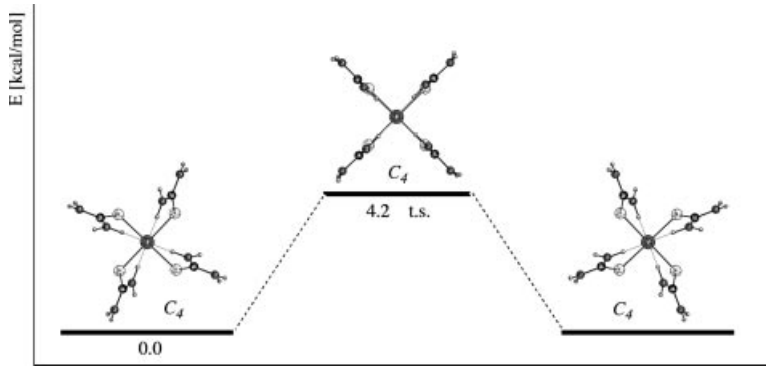



Figure 4. Calculated (RB3LYP/LANL2DZp) enantiomerisation pathway for $[Pt(SU)_4]F^+$.

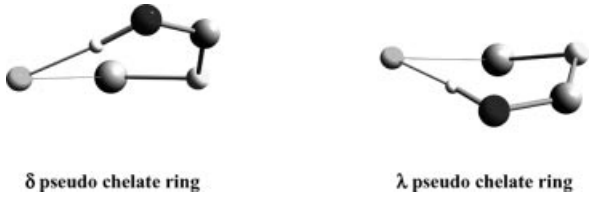



Figure 5. Comparison of the enantiomeric pseudo proton chelate rings belonging to the enantiomers shown in Scheme 2.

It is well known that the six-membered all-$sp^3$ carbon ring of cyclohexane can undergo ring inversion in a three-step process at room temperature. In contrast to $C_6H_{12}$, $\{[Pt(SU)_4]F\}^+$ and related complexes contain chelate rings with atoms linked by different types of bonding interactions and a type of hybridisation that differs from cyclohexane. These features seem to account for the unexpected single-step isomerisation pathway found in the present case. Despite extensive searches, no alternative isomerisation pathways could be found.

On the basis of planar six-membered rings in the transition state, one would expect an achiral $C_{4v}$ structure. This was computed to be a higher order saddle point (five imaginary frequencies), since the symmetry in the transition is diminished by the slightly pyramidal $NH_2$ groups of the XU ligands.

The activation barrier for enantiomerisation of the three $\{[M(SU)_4]F\}^+$ (M = $Ni^{2+}$, $Pd^{2+}$, $Pt^{2+}$) cations decreases from $Ni^{2+}$ to $Pd^{2+}$ and $Pt^{2+}$ to ca. 60% (see Table 1). Except for the obvious differences in the $M^{II}$–S bonds, the structural parameters of the three complexes, describing the ground and transition states, are essentially the same. On going from the ground state to the transition state, the $M^{II}$–S bonds are elongated somewhat, while the $M^{2+}\cdots F$ distances are slightly shortened and the twist angles [M–S···N–F] are reduced to a tenth of the value (see Table 2). The elongation of the $M^{II}$–S bond is most pronounced in the case of $Ni^{2+}$; we expect this to be the main reason for the higher activation barrier.

Table 1. Calculated (RB3LYP/LANL2DZp) energy barriers for the enantiomerisation of complexes of the type $[M(XU)_4]F^+$.[a]

| $[M(XU)_4]F^+$ | $[Ni(SU)_4]F^+$ | $[Pd(SU)_4]F^+$ | $[Pt(SU)_4]F^+$ | $[Pt(SeU)_4]F^+$ | $[Pt(TeU)_4]F^+$ |
|---|---|---|---|---|---|
| [kcal/mol] | 7.6 | 4.5 | 4.2 | 5.3 | 8.8 |

[a] SU = thiourea, SeU = selenourea, TeU = tellurourea.

In contrast to the straightforward results for $[M(SU)_4]F^+$, a variation of the donor atom type in the thiourea ligands from S to Se and Te reveals a more complex picture. Here the activation barrier increases on going to the heavier chalcogens. Whereas the transition from SU to SeU is ac-

Table 2. Calculated (RB3LYP/LANL2DZp) data for $[M(XU)_4]F^+$.[a]

| $[M(XU)_4]F^+$ | Ground state | | | | | Transition state | | | | |
|---|---|---|---|---|---|---|---|---|---|---|
| | PG | M–donor [Å] | F–$H_{NH2}$ [Å] | F···M [Å] | [F–D···N–M] [°] | PG | M–donor [Å] | F–$H_{NH2}$ [Å] | F···M [Å] | [M–D···N–M] [°] |
| $[Ni(SU)_4]F^+$ | $C_4$ | 2.30 | 1.69 | 2.60 | 24.6 | $C_4$ | 2.33 | 1.67 | 2.55 | 2.3 |
| $[Pd(SU)_4]F^+$ | $C_4$ | 2.42 | 1.68 | 2.85 | 24.5 | $C_4$ | 2.43 | 1.67 | 2.79 | 2.3 |
| $[Pt(SU)_4]F^+$ | $C_4$ | 2.40 | 1.67 | 3.03 | 25.2 | $C_4$ | 2.41 | 1.66 | 3.01 | 2.5 |
| $[Pt(SeU)_4]F^+$ | $C_4$ | 2.51 | 1.67 | 3.05 | 26.3 | $C_4$ | 2.53 | 1.66 | 3.03 | 1.0 |
| $[Pt(TeU)_4]F^+$ | $C_4$ | 2.67 | 1.69 | 3.13 | 27.4 | $C_1$ | 2.70 | 1.68 | 3.07 | –5.3, 9.3, 7.4, –10.2 |

[a] SU = thiourea, SeU = selenourea, TeU = tellurourea.

companied by only a moderate increase in the barrier (4.2 and 5.3 kcal/mol, respectively), the barrier for TeU is almost twice as high (8.8 kcal/mol) compared to that for SU. This can obviously be attributed to the metalloid character of Te, as shown by the change in the Natural Population Analysis (NPA) charges for the platinum centre and the S, Se and Te atoms, respectively (see Table 3).[32]

Table 3. Calculated NPA charges (RB3LYP/LANL2DZp) for $Pt^{2+}$ and the coordinating donor atom of XU.[a]

| $[Pt(XU)_4]F^+$ | $[Pt(SU)_4]F^+$ | $[Pt(SeU)_4]F^+$ | $[Pt(TeU)_4]F^+$ |
|---|---|---|---|
| NPA charge of $Pt^{2+}$ | +0.2 | ±0.0 | –0.2 |
| NPA charge of donor (X) | –0.1 | ±0.0 | +0.2 |

[a] SU = thiourea, SeU = selenourea, TeU = tellurourea.

The $Pt^{2+}$–X bond lengths and the Pt···F distances increase in the expected range. The F···$H_{NH2}$ distances show no significant differences, neither in the ground state, nor in the transition state. The constant F···$H_{NH2}$ distances lead in the case of $\{[Pt(TeU)_4]F\}^+$ to a $C_1$ transition state, since the arms of the tellurourea cage have to be more twisted than in all other cases. Again, the $M^{2+}$–chalcogen bonds are slightly extended in the transition state, whereas the Pt···F distance is now somewhat reduced.

## Conclusions

We have shown that the enantiomerisation of $[M(TU)_4F]^+$ and related model complexes of this type do not require cleavage of the $M^{2+}$–chalcogen bonds nor the rupture of the N–H···X bond. Instead, a pathway with a chiral transition structure with four planar rings was found. The activation barrier is lowered by 60% along the series $[Ni(SU)_4]F^+$, $[Pd(SU)_4]F^+$ and $[Pt(SU)_4]F^+$. In the series $[Pt(SU)_4]F^+$, $[Pt(SeU)_4]F^+$ and $[Pt(TeU)_4]F^+$, the activation barrier increases slightly on going from the SU to the SeU derivatives, but doubles in the case of $[Pt(TeU)_4]F^+$.

## Quantum Chemical Methods

We performed hybrid density functional calculations using the B3LYP functional[33a–33c] and the LANL2DZ basis set with effective core potentials,[33d–33g] augmented with polarisation functions on non-hydrogen atoms.[33h] The performance of this level (denoted as B3LYP/LANL2DZp) has been documented by us and others.[34] Structures were characterised as minima, transition structures, or higher-order saddle points by computation of vibrational frequencies. Relative energies were corrected for zero point vibrational energy. The GAUSSIAN suite of programs was used.[35]

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