ChemPhysChem

Communications
doi.org/10.1002/cphc.202100468

**Chemistry
Europe**
European Chemical
Societies Publishing

Noncovalent Axial I⋯Pt⋯I Interactions in Platinum(II) Complexes Strengthen in the Excited State

Evgeny Bulatov,[a] Toni Eskelinen,[b] Alexander Yu. Ivanov,[c] Peter M. Tolstoy,[c] Elina Kalenius,[a] Pipsa Hirva,[b] and Matti Haukka*[a]

Coordination compounds of platinum(II) participate in various noncovalent axial interactions involving metal center. Weakly bound axial ligands can be electrophilic or nucleophilic; however, interactions with nucleophiles are compromised by electron density clashing. Consequently, simultaneous axial interaction of platinum(II) with two nucleophilic ligands is almost unprecedented. Herein, we report structural and computational study of a platinum(II) complex possessing such intramolecular noncovalent I⋯Pt⋯I interactions. Structural analysis indicates that the two iodine atoms approach the platinum (II) center in a "side-on" fashion and act as nucleophilic ligands. According to computational studies, the interactions are dispersive, weak and anti-cooperative in the ground electronic state, but strengthen substantially and become partially covalent and cooperative in the lowest excited state. Strengthening of I⋯Pt⋯I contacts in the excited state is also predicted for the sole previously reported complex with analogous axial interactions.

In the last decades, the scope of noncovalent interactions in the chemistry of coordination compounds[1–5] has been augmented with the discoveries of new types of interactions involving metal centers.[6] Square planar complexes of d8 transition metals are particularly interesting in this aspect due to sterically exposed open axial positions of the metal, which allow metal-lophilic stacking[7,8] and axial interactions with various ligands.[9–11] Thus, the nucleophilic role of d8 metal centers in

axial noncovalent interactions with electron-deficient π-systems[12] and hydrogen[13–15] or halogen[16–21] bond donors has been recognized. On the other hand, axial interactions with nucleophilic ligands are known but less abundant,[9] due to the clashing of the ligand electron lone pair with the filled d_z^2 orbital and high energy of the vacant p_z orbital of the metal.[22] For this reason, the interaction of platinum(II) center simultaneously with two nucleophilic ligands above and below the plane is particularly unlikely. To date, the sole example of such interaction has been reported by Stephenson in arsine platinum (II)[23] and palladium(II)[24] complexes, but no studies on the underlying interactions followed. Lately, the field has been revoked with several publications on interaction of square planar nickel(II) complexes with both electrophilic and nucleophilic ligands in axial positions, the latter referred to as pseudo-[25] or semi-coordination.[26] In this communication, we report our investigations on intramolecular noncovalent axial I⋯Pt⋯I bonding in platinum(II) complex [1]2+ (Scheme 1), which represents a rare example of platinum(II) interacting simultaneously with two nucleophilic ligands above and below the coordination plane.

We previously reported synthesis, structures, and photophysical properties of cationic bis(2-iodobenzyldi(2-pyridyl) amine)platinum(II) complex [1]2+ and analogue [2]2+ with non-substituted phenyl rings (Scheme 1).[27]

Crystallizations of [1](OTf)2 consistently resulted in the disordered structure, in which two conformations were present simultaneously with the iodine atoms oriented towards or away from the platinum center, denoted as conformations [1-in]2+ and [1-out]2+ accordingly (Figure 1). Due to the disorder, the interatomic Pt⋯I distances for [1-in]2+ could not be measured reliably.

In order to get reliable crystal structures of each conformation, the anion was changed, and crystallizations of [1]Br2 under various conditions (section 1 in the SI) afforded solvates [1-in] Br2·3.5H2O and [1-out]Br2·4CH3CN (Figure 2),[28] which were used for structural analysis and computational studies. In
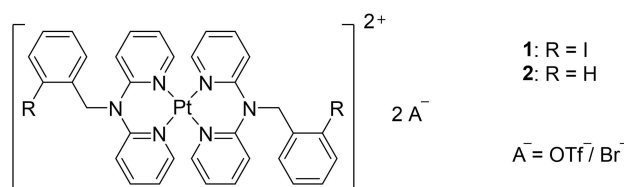
[a] E. Bulatov, E. Kalenius, Prof. M. Haukka
     Department of Chemistry
     University of Jyväskylä
     P.O. Box 35, 40014 Jyväskylä, Finland
     E-mail: matti.o.haukka@jyu.fi
[b] T. Eskelinen, P. Hirva
     Department of Chemistry
     University of Eastern Finland
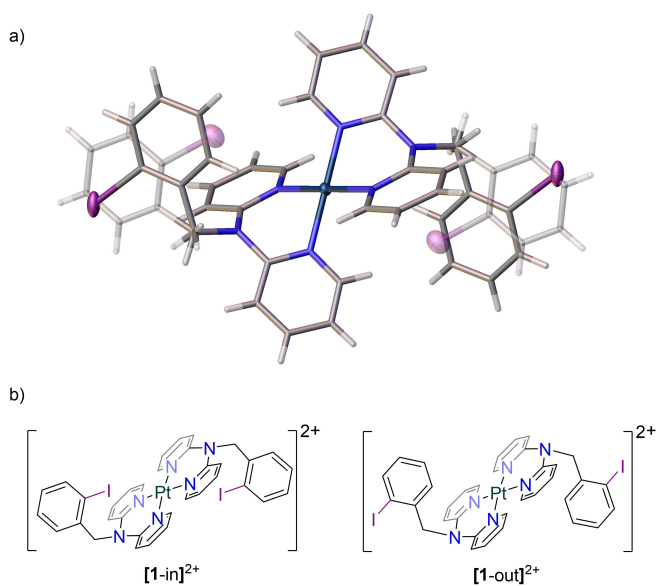   P.O. Box 111, 80101 Joensuu, Finland
[c] A. Y. Ivanov, Prof. P. M. Tolstoy
     Center for Magnetic Resonance
     St. Petersburg State University
     198504 St. Petersburg, Russia

1: R = I
2: R = H

A⁻ = OTf⁻/ Br⁻

Scheme 1. Structures of [1]2+ and [2]2+ studied in the previous work.[27]

ChemPhysChem

Communications
doi.org/10.1002/cphc.202100468

Chemistry Europe
European Chemical
Societies Publishing

Figure 1. a) Disordered crystal structure of **[1](OTf)₂** (the minor "in"-conformation is presented semi-transparent; triflate counterions are omitted for clarity), b) schematic drawing of **[1-in]²⁺** and **[1-out]²⁺**.[28]
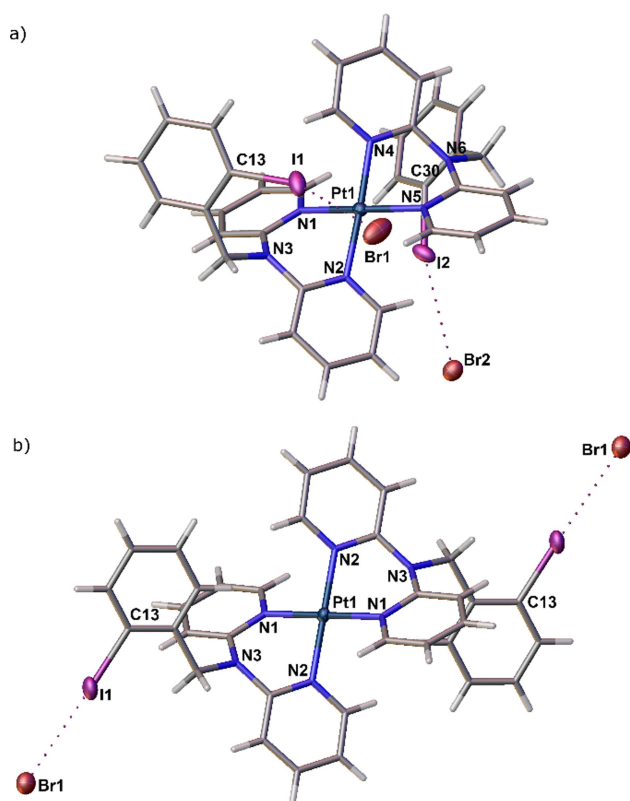
Figure 2. Crystal structures of a) **[1-in]Br₂·3.5H₂O**, b) **[1-out]Br₂·4CH₃CN** (solvent molecules are omitted for clarity).

addition, "in"- and "out"-forms of **[1]I₂** and **[1](NO₃)₂** were crystallized, in which similar structural parameters were found (section 2 in the SI).

All crystal structures of **[1-in]²⁺** feature Pt···I distances of 3.65–3.72 Å (Tables 1 and S2), which are less than sum of the corresponding atomic van der Waals radii (3.73 Å),[29] suggesting that a weak attractive interaction may take place between the atoms. Nearly straight C–I···Pt angles (Tables 1 and S3) indicate that the iodine atoms in **[1-in]²⁺** are oriented toward the metal center with their nucleophilic regions ("electronic belts" around the C–I bond axis)[18] in a "side-on" fashion.[30] Such orientation is contrary to the Pt···I halogen bonding, in which the iodine atoms would be oriented towards platinum with their electron-deficient areas (σ-holes, located along the C–I bond axis) in an "end-on" fashion, and the C–I···Pt angle would be close to 180°.[16,18,19]

Analysis of various types of previously reported axial interactions of platinum(II) complexes (for overview and discussion of axial interactions see section 3 in the SI and Ref. [9]) reveals that Pt···I interactions in **[1-in]²⁺**, where the iodine atoms act as nucleophiles, belong to a rare kind of interactions for platinum(II) complexes. Indeed, while axial interactions with electrophilic ligands are rather abundant,[9] the cases where platinum center would interact with nucleophilic ligands, while remaining in clearly defined oxidation state +2, are limited to compounds containing S-donor ligands[31–33] and iodide anions.[23,34–36] Moreover, the I···Pt···I bonding situation in **[1-in]²⁺**, in which two nucleophilic ligands simultaneously approach the metal center from above and below the square plane, is only encountered in one literature example **[3]I₂** (see Figure 5 below).[23] Rarity of axial interaction of platinum(II) with simultaneously two nucleophilic ligands prompted us to further study the observed Pt···I contacts.

To verify the presence of Pt···I interactions and address their nature, the obtained crystal structures of **[1]Br₂** were studied computationally using DFT and QTAIM[37] approaches. The detailed description of computational studies is presented in section 4 of the SI.

The optimized structures of **[1-in]²⁺** and **[1-out]²⁺** possessed similar geometrical parameters to the corresponding experimental ones, and revealed 34.4 kJ/mol lower calculated potential energy for **[1-in]²⁺** (Table 1), which was attributed to primarily dispersive Pt···I interactions. Dispersive interactions are important in noncovalent interactions involving iodine,[38,39] and trial optimizations of **[1-in]²⁺** without correction for dispersion and in methanol environment (polarizable solvents are known to attenuate dispersion interactions[40]) afforded structures with significantly elongated Pt···I distances and lower energy differences between the "in"- and "out"-conformers (Table S4).

Topological analysis of electron density[37] revealed the Pt···I bond critical points (BCPs) in the structure of **[1-in]²⁺**, and the values of electron and energy densities at the BCPs indicated weak attractive noncovalent Pt···I interactions (Figure S9 and Table S10). Furthermore, calculated electrostatic surface potentials revealed the entire surface of the cation being positively charged, and the close Pt···I contact being present despite the electrostatic repulsion (Figure S8).

To reveal possible (anti-)cooperativity of the two Pt···I interactions, additional conformation **[1-inout]²⁺** was optimized, in which one of the iodine atoms is oriented towards and the

other away from the platinum center. While such form was not explicitly observed in the crystal structures, it can be expected to exist in gas phase and solution. The calculated energy and geometric parameters (Tables 1 and S9), as well as the topological properties of electron density (Table S10) in [1-inout]$^{2+}$ indicate small but significant strengthening of the Pt⋯I interaction compared to [1-in]$^{2+}$. Therefore, the two Pt⋯I interactions can be considered anti-cooperative in agreement with the general trends of axial interactions in platinum(II) complexes (section 3 in the SI and Ref. [9]).

Analysis of Kohn-Sham molecular orbitals (MOs) generated from DFT calculations of [1-in]$^{2+}$ revealed HOMO-13 and HOMO, representing σ(I⋯Pt⋯I) and σ*(I⋯Pt⋯I) accordingly. The MOs are formed primarily from p_z orbitals of the iodine atoms and d_{z^2} orbital of the platinum atom (Figure 3). Therefore, from the MO point of view the Pt⋯I interactions in [1-in]$^{2+}$ appear similar to metallophilic interactions, where filled d_{z^2} atomic orbitals of metals overlap to form filled bonding and anti-bonding MOs. The net attractive nature of such metallophilic interactions is usually attributed to the strong dispersive component and configuration interaction with the vacant p_z orbitals of the metals.[7,8] Since iodine atoms in [1-in]$^{2+}$ do not possess vacant orbitals sufficiently close in energy, the dispersive component accounts for the weak attractive interaction between the atoms. However, the MO interaction can provide bonding contribution in the excited electronic state:

since σ*(I⋯Pt⋯I) in [1-in]$^{2+}$ is the HOMO, its population in the excited state would decrease, whereas the bonding orbital would remain fully occupied. Such strengthening in the excited state is a known feature of metallophilic interactions.[41,42] Accordingly, computational studies were further conducted to investigate changes in the Pt⋯I interactions in the excited electronic state.

Since [1]Br$_2$ does not possess luminescence in solution at ambient temperature, but reveals phosphorescence upon cooling to 78 K,[27] it was concluded that [1]$^{2+}$ undergoes fast intersystem crossing to the triplet state upon photoexcitation. Accordingly, optimizations of excited triplet T1 states of all conformations of [1]$^{2+}$ were preformed using Tamm-Damcoff approximation to time-dependent DFT[43] (section 4.3 in the SI). The optimized structure of [1-in]$^{2+}$ in T1 state possesses Pt⋯I distances 0.8 Å shorter than in the ground electronic state (Table 1), and according to the topological analysis of electron density the Pt⋯I interactions gain significant covalent character (Table S10).

To prove that the strengthening of Pt⋯I interactions in the excited state is due to depopulation of the σ*(I⋯Pt⋯I) orbital, analysis of the lowest single-occupied MO (LSOMO) of [1]$^{2+}$ in the T1 state was performed. Indeed, in the case of [1-in]$^{2+}$ the LSOMO is the σ*(I⋯Pt⋯I) orbital (Figure 4a). On the other hand, the LSOMO of [1-out]$^{2+}$ in T1 state is localized within one of the phenyl rings (Figure 4c). In the case of [1-inout]$^{2+}$, the proximity

**Table 1.** Selected bond lengths (*l*, Å), angles (∠, °), and relative energies (ΔE, kJ/mol)[a] for different conformations of [1]$^{2+}$ in crystal structures and DFT optimized structures in S0 and T1 electronic states.

| Conformation of [1]$^{2+}$	*l*(Pt⋯I)	∠(I⋯Pt—N)	∠(C—I⋯Pt)	ΔE[a]
in (XRD)[b]	3.6523(5), 3.6615(5)	85.02(12)–97.35(13)	90.46(16), 96.90(15)	–
in (DFT, S0)[c]	3.753	84.7, 95.1	95.8	0
in (DFT, T1)[c]	2.934	88.6–93.9	107.4	189.9
inout (DFT, S0)[c,d]	3.701	87.6–92.3	100.1	17.0
inout (DFT, T1)[c,d]	3.658	84.5–96.1	97.8	305.7
out (DFT, S0)[c]	–	–	–	34.4
out (DFT, T1)[c]	–	–	–	320.7

[a] Relative to the energy of [1-in]$^{2+}$ in S0 state in vacuum. [b] From the crystal structure of [1-in]Br$_2$·3.5H$_2$O. [c] From the optimized structures of [1]$^{2+}$ in vacuum. [d] Specifically "symmetric" conformation [1-sym-inout]$^{2+}$ (Table S9).
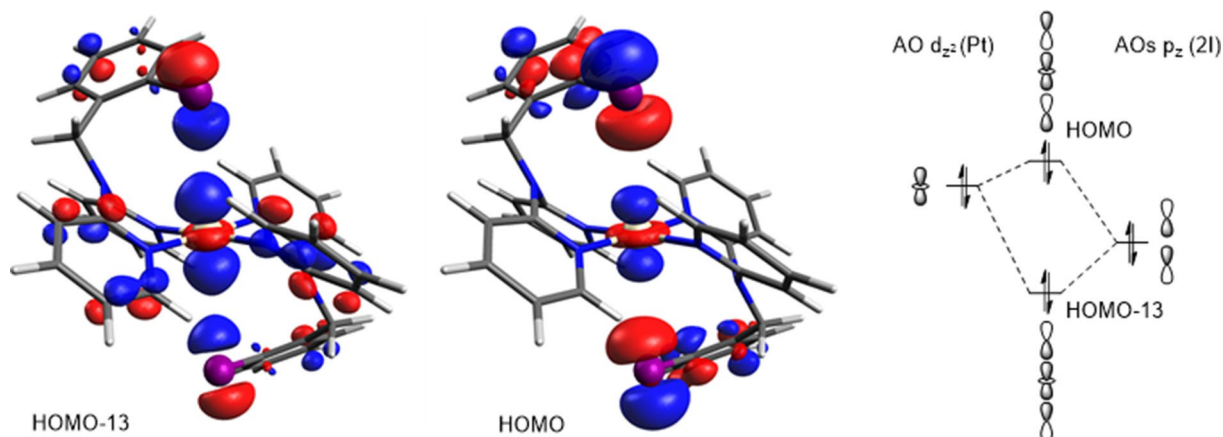
Figure 3. Calculated I⋯Pt⋯I bonding and anti-bonding Kohn-Sham MOs of [1-in]$^{2+}$ in vacuum (the orbitals are displayed with isosurface value of 0.045 a.u.) and schematic representation their formation from the parenting d_{z^2} (Pt) and p_z (I) atomic orbitals (AO).
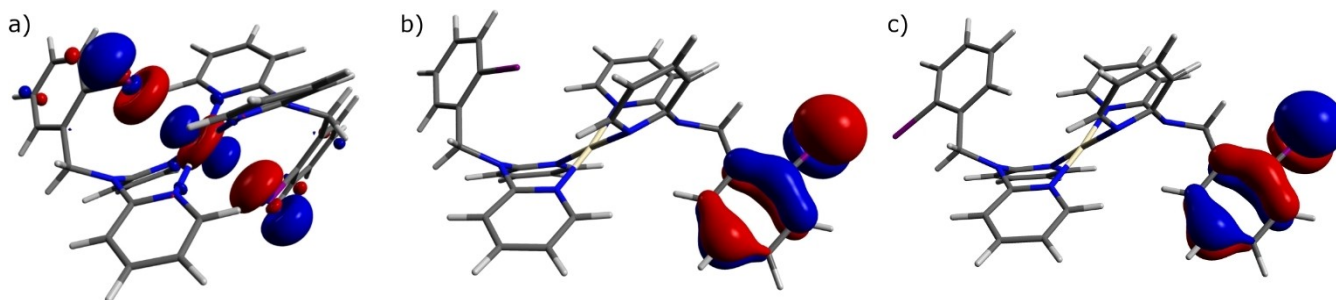
Figure 4. Calculated LSOMOs of a) [1-in]$^{2+}$, b) [1-inout]$^{2+}$, and c) [1-out]$^{2+}$ in vacuum in the T1 state (the orbitals are displayed with isosurface value of 0.045 a.u.)
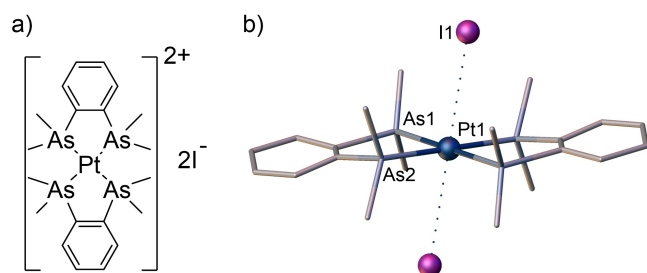
Figure 5. a) Chemical structure and b) the original crystal structure[23] of Stephenson's complex [3]I$_2$.

of only one iodine atom to the metal center is not sufficiently destabilizing σ*(Pt⋯I) MO to promote it to HOMO level. Thus, the LSOMO of [1-inout]$^{2+}$ in excited T1 state is also localized on phenyl ring, similarly to [1-out]$^{2+}$ (Figure 4b). Consequently, the Pt⋯I interaction is not strengthened in the excited T1 state of [1-inout]$^{2+}$ (Table 1), allowing to conclude, that the two Pt⋯I interactions possess cooperativity in the excited T1 state of [1-in]$^{2+}$.

While sufficient structural and computational evidence was acquired that [1-in]$^{2+}$ is stabilized by weak Pt⋯I interactions, the energy difference of 34.4 kJ/mol is too low to affect equilibria in the gas phase or solution. Accordingly, several spectroscopic experiments probing the conformational equilibrium in the gas phase (IM-MS) and solution (UV-Vis and NMR spectroscopy) using [2]Br$_2$ as a reference compound without the Pt⋯I interactions indicated the presence of a mixture of [1]$^{2+}$ conformers. Since the excitation of [1-in]$^{2+}$ leads to a non-emissive MC state (Tables S11 and S12), the luminescence spectroscopy could not provide reliable data on the conformational equilibria of [1]$^{2+}$ in the excited state. The details on spectroscopic experiments and their interpretation are presented in section 5 of the SI.

The sole another published example of I⋯Pt⋯I bonding situation, in which two nucleophilic iodine atoms simultaneously approach the metal center from above and below the square plane, is Stephenson's complex [3]I$_2$ (Figure 5).[23]

The unusual nature of the bonding between the iodide anions and platinum(II) center was noticed by the authors,[23,44] but no further studies were conducted on this subject to date.

We therefore decided to revisit the structure of complex [3]I$_2$ and perform analogous structural and computational analysis to compare it with [1-in]$^{2+}$ (section 4.4 in the SI). In this case, shorter Pt⋯I distances (3.50 Å, Table 2) compared to [1-in]$^{2+}$ were found in the crystal structure, and even shorter distances were observed in the optimized structure (3.40 Å).

The shorter Pt⋯I distances in [3]I$_2$ compared to [1-in]$^{2+}$ are attributed to the electrostatic attraction between the positively charged complex and negatively charged iodide anions, assisted by strong π-accepting properties of the arsine ligands and weak C−H⋯I hydrogen bonds. Topological analysis of electron density revealed overall similarity between the Pt⋯I interactions in [3]I$_2$ and [1-in]$^{2+}$, the former being noticeably stronger (Table S14). Furthermore, the optimized structure of ([3]I)$^+$ possesses even shorter Pt⋯I distance (2.89 Å), indicating pronounced anti-cooperativity of the two Pt⋯I interactions in [3]I$_2$. This conclusion is in agreement with the existence of stable ([3]I)$^+$ single-charged species in solution, for which square pyramidal geometry has been proposed.[44,45]

Analysis of the optimized T1 state revealed contraction of Pt⋯I bonds (3.40 to 2.96 Å, Table 2) associated with depopulation of the anti-bonding σ*(I⋯Pt⋯I) orbital in [3]I$_2$ (Figure 6a), whereas much smaller contraction (2.89 to 2.78 Å) was observed for ([3]I)$^+$. Nonetheless, the shorter Pt⋯I distance in the excited state of ([3]I)$^+$ compared to [3]I$_2$ indicates anti-cooperative interactions, in contrast with [1-in]$^{2+}$. The difference is attributed to the stronger Pt⋯I interaction in ([3]I)$^+$ in the ground state, which is sufficient to rise the σ*(Pt⋯I) orbital to HOMO (as supported by the assignment of the LSOMO in ([3]I)$^+$ in T1 state to σ*(I⋯Pt⋯I), Figure 6b), whereas the presence of both interactions in [1-in]$^{2+}$ is necessary to achieve the depopulation of the σ*(I⋯Pt⋯I) upon excitation.

Table 2. Selected bond lengths (*l*, Å) and angles (∠, °) for [3]I$_2$ and ([3]I)$^+$ in the crystal and DFT optimized structures in S0 and T1 electronic states in vacuum.

Molecule	*l*(Pt⋯I)	∠(I⋯Pt As)
[3]I$_2$ (XRD)[23]	3.50	84.4–95.6
[3]I$_2$ (DFT, S0)	3.40	90
[3]I$_2$ (DFT, T1)	2.96	90
([3]I)$^+$ (DFT, S0)	2.89	95.9
([3]I)$^+$ (DFT, T1)	2.78	93.3, 94.5
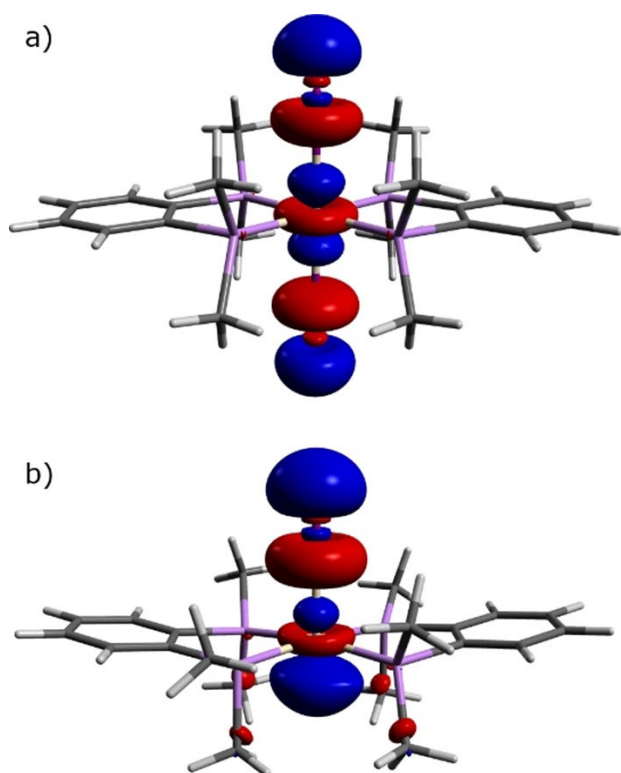
Figure 6. Calculated LSOMOs of [3]I$_2$ and ([3]I)$^+$ in vacuum in the T1 state (the orbitals are displayed with isosurface value of 0.045 a.u.)

Therefore, [1-in]$^{2+}$ and [3]I$_2$ are examples of rare I···Pt···I interactions, in which platinum(II) interacts simultaneously with two nucleophilic ligands. The interactions are principally similar in the two compounds, and possess similar feature of substantial strengthening in the excited state, with the main differences being stronger interactions and their anti-cooperativity in the excited state in the case of [3]I$_2$. Based on the similarities between [1-in]$^{2+}$ and [3]I$_2$, we expect that other systems of this kind can be designed for applications in e.g. luminescence, molecular photoswitches, and photosensitive redox systems.

Acknowledgements

Conflict of Interest

The authors declare no conflict of interest.

[1] A. M. Maharramov, K. T. Mahmudov, M. N. Kopylovich, A. J. Pombeiro, *Non-covalent Interactions in the Synthesis and Design of New Compounds*, Wiley, **2016**.
[2] R. Bertani, P. Sgarbossa, A. Venzo, F. Lelj, M. Amati, G. Resnati, T. Pilati, P. Metrangolo, G. Terraneo, *Coord. Chem. Rev.* **2010**, *254*, 677–695.
[3] J. Reedijk, *Chem. Soc. Rev.* **2013**, *42*, 1776–1783.
[4] B. Li, S.-Q. Zang, L.-Y. Wang, T. C. W. Mak, *Coord. Chem. Rev.* **2016**, *308*, 1–21.
[5] K. T. Mahmudov, M. N. Kopylovich, M. F. C. Guedes da Silva, A. J. L. Pombeiro, *Coord. Chem. Rev.* **2017**, *345*, 54–72.
[6] E. R. T. Tiekink, *Coord. Chem. Rev.* **2017**, *345*, 209–228.
[7] K. Krogmann, *Angew. Chem. Int. Ed. Engl.* **1969**, *8*, 35–42.
[8] L. H. Doerrer, *Dalton Trans.* **2010**, *39*, 3543–3553.
[9] G. Aullón, S. Alvarez, *Inorg. Chem.* **1996**, *35*, 3137–3144.
[10] A. Amgoune, D. Bourissou, *Chem. Commun.* **2011**, *47*, 859–871.
[11] D. M. P. Mingos, *J. Organomet. Chem.* **2014**, *751*, 153–173.
[12] A. V. Rozhkov, M. A. Krykova, D. M. Ivanov, A. S. Novikov, A. A. Sinelshchikova, M. V. Volostnykh, M. A. Konovalov, M. S. Grigoriev, Y. G. Gorbunova, V. Y. Kukushkin, *Angew. Chem. Int. Ed.* **2019**, *58*, 4164–4168; *Angew. Chem.* **2019**, *131*, 4208–4212.
[13] L. Brammer, J. M. Charnock, P. L. Goggin, R. J. Goodfellow, A. G. Orpen, T. F. Koetzle, *J. Chem. Soc. Dalton Trans.* **1991**, 1789–1798.
[14] S. Rizzato, J. Bergès, S. A. Mason, A. Albinati, J. Kozelka, *Angew. Chem. Int. Ed.* **2010**, *49*, 7440–7443; *Angew. Chem.* **2010**, *122*, 7602–7605.
[15] R. Sánchez-de-Armas, M. S. G. Ahlquist, *Phys. Chem. Chem. Phys.* **2015**, *17*, 812–816.
[16] R. A. Gossage, A. D. Ryabov, A. L. Spek, D. J. Stufkens, J. A. M. van Beek, R. van Eldik, G. van Koten, *J. Am. Chem. Soc.* **1999**, *121*, 2488–2497.
[17] D. W. Shaffer, S. A. Ryken, R. A. Zarkesh, A. F. Heyduk, *Inorg. Chem.* **2012**, *51*, 12122–12131.
[18] D. M. Ivanov, A. S. Novikov, I. V. Ananyev, Y. V. Kirina, V. Y. Kukushkin, *Chem. Commun.* **2016**, *52*, 5565–5568.
[19] V. Oliveira, D. Cremer, *Chem. Phys. Lett.* **2017**, *681*, 56–63.
[20] L. E. Zelenkov, A. A. Eliseeva, S. V. Baykov, V. V. Suslonov, B. Galmés, A. Frontera, V. Y. Kukushkin, D. M. Ivanov, N. A. Bokach, *Inorg. Chem. Front.* **2021**, *8*, 2505–2517.
[21] M. Bulatova, D. M. Ivanov, M. J. Rautiainen, M. A. Kinzhalov, K.-N. Truong, M. Lahtinen, M. Haukka, *Inorg. Chem.* **2021**, DOI: 10.1021/acs.inorg-chem.1c01591.
[22] A. Y. Rogachev, R. Hoffmann, *J. Am. Chem. Soc.* **2013**, *135*, 3262–3275.
[23] N. C. Stephenson, *J. Inorg. Nucl. Chem.* **1962**, *24*, 791–795.
[24] N. C. Stephenson, *J. Inorg. Nucl. Chem.* **1962**, *24*, 797–800.
[25] S. N. Melnikov, K. A. Lyssenko, I. V. Ananyev, I. L. Eremenko, *Russ. Chem. Bull.* **2017**, *66*, 1550–1556.
[26] Z. M. Bikbaeva, D. M. Ivanov, A. S. Novikov, I. V. Ananyev, N. A. Bokach, V. Y. Kukushkin, *Inorg. Chem.* **2017**, *56*, 13562–13578.
[27] E. Bulatov, M. Haukka, *Dalton Trans.* **2019**, *48*, 3369–3379.
[28] The conformations differ not only in orientation of the iodine atoms ("in" and "out") but also in tilting of the phenyl rings towards different sides of the molecule ("symmetric", "sym"-conformation) or the same side ("asymmetric", "asym"-conformation). From here onwards in this communication [1-in]$^{2+}$ and [1-out]$^{2+}$ denote [1-asym-in]$^{2+}$ and [1-sym-out]$^{2+}$ accordingly, which were the only conformations observed in the non-disordered crystal structures. Details on conformational analysis are presented in section 4.2 of the SI.
[29] A. Bondi, *J. Phys. Chem.* **1964**, *68*, 441–451.
[30] R. Trokowski, S. Akine, T. Nabeshima, *Chem. Eur. J.* **2011**, *17*, 14420–14428.
[31] R. Colton, M. F. Mackay, V. Tedesco, *Inorg. Chim. Acta* **1993**, *207*, 227–232.
[32] G. J. Grant, *Dalton Trans.* **2012**, *41*, 8745–8761.
[33] A. J. Blake, R. O. Gould, A. J. Holder, T. I. Hyde, A. J. Lavery, M. O. Odulate, M. Schröder, *J. Chem. Soc. Chem. Commun.* **1987**, 118–120.
[34] R. Makiura, I. Nagasawa, N. Kimura, S. Ishimaru, H. Kitagawa, R. Ikeda, *Chem. Commun.* **2001**, 1642–1643.
[35] S. Otto, A. Roodt, *Inorg. Chem. Commun.* **2001**, *4*, 49–52.
[36] R. Contreras, M. Valderrama, A. Nettle, D. Boys, *J. Organomet. Chem.* **1997**, *527*, 125–132.
[37] R. F. W. Bader, R. F. Bader, *Atoms in Molecules: A Quantum Theory*, Clarendon Press, **1990**.

[38] A. Bauzá, A. Frontera, *ChemPhysChem* **2015**, *16*, 3108–3113.

[39] S. Tsuzuki, T. Uchimaru, A. Wakisaka, T. Ono, *J. Phys. Chem. A* **2016**, *120*, 7020–7029.

[40] L. Yang, C. Adam, G. S. Nichol, S. L. Cockroft, *Nat. Chem.* **2013**, *5*, 1006.

[41] P. Coppens, O. Gerlits, I. I. Vorontsov, A. Y. Kovalevsky, Y.-S. Chen, T. Graber, M. Gembicky, I. V. Novozhilova, *Chem. Commun.* **2004**, 2144–2145.

[42] J. Romanova, M. R. Ranga Prabhath, P. D. Jarowski, *J. Phys. Chem. C* **2016**, *120*, 2002–2012.

[43] S. Hirata, M. Head-Gordon, *Chem. Phys. Lett.* **1999**, *314*, 291–299.

[44] C. M. Harris, R. S. Nyholm, N. C. Stephenson, *Nature* **1956**, *177*, 1127.

[45] R. Ros, E. Tondello, *J. Inorg. Nucl. Chem.* **1971**, *33*, 245–251.