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

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1 Experimental procedures

1.1 Syntheses

All chemicals and solvents were purchased from Sigma-Aldrich, except for K₂PtCl₆ (Strem Chemicals and Alfa Aesar) and used as received without further purification unless mentioned otherwise. Preparation of complexes [1·2]Br₂ and free ligands L1 and L2 has been reported previously. [1]

[1]NO₃Br: Platinum(II) bis(2,2′-dipyridylamide) (53.6 mg, 0.1 mmol, prepared according to previously published procedure[2]), 2-iodobenzyl bromide (59.4 mg, 0.2 mmol), and silver nitrate (34 mg, 0.2 mmol) were suspended in acetonitrile (20 ml) and stirred at 60 °C for 48 h in darkness. The obtained mixture was filtered from yellow precipitate, filtrate concentrated on rotary evaporator, and yellow residue was recrystallized from methanol and dried under vacuum to afford the product as colorless crystalline material (68 mg, 62% yield). ¹H NMR spectrum of [1]NO₃Br was identical to that of [1]Br₂.

[1]I₂: Sodium iodide (33 mg, 0.22 mmol) and 2-iodobenzyl bromide (59.4 mg, 0.2 mmol) were refluxed in acetone (15 ml) for 6 h, and resulting yellowish solution was filtered from colorless precipitate into suspension of platinum(II) bis(2,2′-dipyridylamide) (53.6 mg, 0.1 mmol) in acetonitrile (20 ml). The obtained mixture was stirred at 70 °C for 48 h, and cooled to room temperature. Next day, formed precipitate was filtered, recrystallized from acetonitrile/methanol (3/1) solution, and dried under vacuum to afford the product as colorless crystals (37.5 mg, 31% yield).

L1 HCl: Concentrated HCl (110 µl, 1.35 mmol) was added to suspension of L1 (52.2 mg, 0.135 mmol) in methanol (10 ml), and the mixture was stirred until complete dissolution of the solids was achieved. The obtained solution was evaporated on air, and residual yellowish oil was recrystallized from acetonitrile/acetone (1/1) mixture to afford the product after drying under vacuum as colorless crystals (27.9 mg, 49% yield). ¹H NMR (CD₂OD, 400 MHz): δ 8.52 (ddd, J = 5.6, 1.8, 0.6 Hz, 2H), 8.12 (ddd, J = 9.0, 7.4, 1.8 Hz, 2H), 8.03 (dd, J = 7.8, 1.1 Hz, 1H), 7.42 (ddd, J = 7.4, 5.6, 0.7 Hz, 2H), 7.34 (ddd, J = 7.8, 7.8 1.1 Hz, 1H), 7.28 – 7.24 (m, 2H), 7.22 (dd, J = 6.6, 1.2 Hz, 1H), 7.11 (ddd, J = 7.8, 1.5, 0.7 Hz, 1H), 5.35 (s, 2H).

L2 HCl: Concentrated HCl (12 µl, 0.14 mmol) was added to suspension of L2 (37 mg, 0.14 mmol) in methanol (8 ml). The obtained solution was evaporated on air, yellow oily residue was washed with acetone (3 x 1 ml), recrystallized from acetonitrile and dried under vacuum to afford the product as colorless crystals (21.4 mg, 38% yield). ¹H NMR (CD₂OD, 400 MHz): 8.51 (ddd, J = 5.5, 1.9, 0.8 Hz, 2H), 8.12 (ddd, J = 9.1, 7.4, 1.9 Hz, 2H), 7.47 – 7.28 (m, 9H), 5.51 (s, 2H).

1.2 Crystallization experiments

Throughout the crystallizations, structures containing [1·in]Br₂ were more consistently obtained, whereas crystallizations of [1·out]Br₂ were challenging and less reproducible, indicating that “in”-conformation is more preferable in the crystalline state. [1·in]Br₂: Colorless rectangular crystals were obtained by slow evaporation of undried methanol or acetonitrile solution of [1]Br₂ under ambient conditions. The best quality crystals were obtained from methanol. In addition, [1·in]Br₂·CH₃CN was obtained from dry acetonitrile (molecular sieves 4Å), but strong disorder of the solvent molecules within the structure deterred us from further investigation of this structure.

[1·out]Br₂·4CH₃CN: Colorless elongated crystals were obtained by slow evaporation of acetonitrile/methanol (1/1) solution of [1]Br₂ with equimolar amount of pyrazine added. However, consequent recrystallizations always resulted in structures of 1·in, and crystallization of [1·out]Br₂·4CH₃CN could not be reproduced. Nevertheless, the obtained structure was of sufficient quality for further investigations.

[1·in]NO₃Br·3H₂O: Colorless cubic crystals were obtained by slow evaporation of undried methanol/DCM (1/2) solution of [1]NO₃Br·3H₂O under ambient conditions. The obtained crystals were consistently of small size and possessed twinning (short crystallization time afforded too small crystals and longer crystallization time resulted in severe twinning).

[1·out]NO₃Br: Colorless needle crystals were obtained by dissolving [1]NO₃Br in a small amount of hot methanol, diluting the solution with large volume of DCM and slow crystallization under ambient conditions.

[1·in]Br₂·2H₂O: Colorless cubic crystals were obtained by slow evaporation of undried acetonitrile/methanol (3/1) solution of [1]Br₂ under ambient conditions.

[1·out]Br₂·2CH₃CN: Colorless elongated rectangular crystals were obtained by slow evaporation of dry acetonitrile/methanol (1/1) solution of [1]Br₂·2CH₃CN under ambient conditions.

2 X-ray diffraction analysis

2.1 Crystal structure data

The obtained crystals of various forms of 1 were immersed in cryo-oil, mounted in a MiTeGen loop and measured at 120 K on a Rigaku Oxford Diffraction Supernova diffractometer using Mo Kα (λ = 0.71073) or Cu Kα (λ = 1.54184) radiation or at 170 K on a Bruker Axs...
Kappa Apex II diffractometer using Mo Kα (λ = 0.71073) radiation. The CrysAlisPro[3] or Denzo-Scalepack[4] program packages were used for cell refinements and data reductions. Multi-scan/Gaussian/Analytical absorption correction (CrysAlisPro,[3] SADABS[5]) was applied to the intensities before structure solution. The structures were solved by intrinsic phasing (SHELXT)[6] or charge flipping (SQUEEZE). Structural refinements were carried out using ShelXL[8] software and Olex2[9] graphical user interface. Intrinsic disorder of NO₂− anions was modelled in structures [1-in-][NO₂]₂·3H₂O and [1-out][NO₂]₂. C–H and O–H hydrogen atoms were positioned geometrically and constrained to ride on their parent atoms, with C–H = 0.95 - 1.00 Å, O–H = 0.85 Å, and Ueq = 1.2 - 1.5 Ueq (parent atom). The obtained crystal structures are presented in Figures S1-S6, and selected bond lengths, angles, and torsions are listed in Tables S2 and S3. CCDC 2084774 - 2084779 contain the supplementary crystallographic data.

Table S1. Crystal data and refinement parameters.

|                      | [1-in][Br₂]·3H₂O | [1-in][H₂O] | [1-in][NO₂]₂·3H₂O | [1-out][Br₂·4CH₃CN] | [1-out][2·2CH₃CN] | [1-out][NO₂]₂ |
|----------------------|------------------|-------------|-------------------|----------------------|------------------|--------------|
| CCDC number          | 2084776          | 2084778     | 2084777           | 2084775              | 2084774          | 2084779      |
| empirical formula     | C₂₅H₂₂Br₂N₂O₂₆Pt| C₂₅H₂₂NO₂₆Pt| C₂₅H₂₂NO₂₆Pt      | C₂₅H₂₂Br₂N₂O₂₆Pt     | C₂₅H₂₂NO₂₆Pt     | C₂₅H₂₂NO₂₆Pt |
| formula weight        | 1192.39          | 1241.33     | 1147.58           | 1293.55              | 1305.42          | 1093.53      |
| temp (K)              | 120.01(10)       | 120.0       | 170.0             | 120                  | 119.98(11)       | 120.01(10)   |
| λ (Å)                 | 1.54184          | 0.71073     | 0.71073           | 0.71073              | 0.71073          | 1.54184      |
| crystal system        | monoclinic       | othorhombic | monoclinic        | monoclinic           | monoclinic       | monoclinic   |
| space group           | P2₁/c            | Pccn        | P2₁/c             | P2₁/c                | P-1              | I2/a         |
| a (Å)                 | 14.3139(3)       | 14.0828(6)  | 15.041            | 10.7530(2)           | 7.8090(3)        | 15.0827(7)   |
| b (Å)                 | 14.0584(3)       | 14.7499(5)  | 13.893            | 12.4851(2)           | 10.8104(4)       | 15.2214(5)   |
| c (Å)                 | 18.2872(4)       | 18.5946(9)  | 18.283            | 16.8707(4)           | 12.6926(5)       | 16.4052(8)   |
| α (°)                 | 90               | 90          | 90                | 90                   | 73.405(3)        | 90           |
| β (°)                 | 91.5880(19)      | 90          | 90.19             | 103.0590(10)         | 73.607(3)        | 114.744(6)   |
| γ (°)                 | 90               | 90          | 90                | 90                   | 78.510(3)        | 90           |
| V (Å³)                | 3678.53(13)      | 3862.5(3)   | 3820.6            | 2206.35(8)           | 976.89(7)        | 3420.5(3)    |
| Z                     | 4                | 4           | 4                 | 4                    | 2                | 4            |
| ρcalc (g/cm³)         | 2.153            | 2.135       | 1.995             | 1.947                | 2.219            | 2.123        |
| μ(Kα) (mm⁻¹)          | 23.225           | 6.864       | 5.352             | 6.433                | 6.790            | 22.346       |
| No. refin.            | 29186            | 32884       | 32266             | 21774                | 14469            | 7858         |
| Unique refin.         | 7736             | 3803        | 7454              | 5045                 | 5081             | 3559         |
| GOOF (F²)             | 1.037            | 1.023       | 1.086             | 1.082                | 1.030            | 1.061        |
| Rdiff (I > 2σ(I))     | 0.0424           | 0.0824      | 0.0616            | 0.0287               | 0.0237           | 0.0399       |
| R(II) (I > 2σ(I))     | 0.0369           | 0.0523      | 0.0796            | 0.0221               | 0.0213           | 0.0469       |
| wR2(II) (I > 2σ(I))   | 0.0887           | 0.1363      | 0.2044            | 0.0475               | 0.0431           | 0.1134       |

[a] R1 = Σ||Fo|| - |Fo||)|Fo|| / Σ||Fo|| |Fo||, [b] wR2 = Σ[w(Fo² - Fc²)²] / Σ[w(Fc²)], [c] Fc = Fo - 2Fo². [4]
Figure S1. Crystal structure [1-in]Br₂·3.5H₂O. Atom O2 has occupancy 0.5. Anisotropic displacement parameters are drawn at 50% probability level.

Figure S2. Crystal structure [1-in]I₂·H₂O. The second half of the molecule is generated by symmetry operations. Anisotropic displacement parameters are drawn at 30% probability level.

Figure S3. Crystal structure [1-in](NO₃)₂·3H₂O. Atoms O4-O6 and O4A-O6A have occupancies 0.5. Anisotropic displacement parameters are drawn at 30% probability level.
Figure S4. Crystal structure [1-out]Br₂·4CH₃CN. The second half of the molecule is generated by symmetry operations. Anisotropic displacement parameters are drawn at 50% probability level.

Figure S5. Crystal structure [1-out]I₂·2CH₃CN. The second half of the molecule is generated by symmetry operations. Anisotropic displacement parameters are drawn at 50% probability level.

Figure S6. Crystal structure [1-out][NO₃]₃. The second half of the molecule is generated by symmetry operations. Anisotropic displacement parameters are drawn at 50% probability level.
Table S2. Selected bond lengths (Å).

|                  | [1-in]Br₂3.5H₂O | [1-in]I₂-H₂O | [1-in]([NO₃]₂)3H₂O<sup>a</sup> | [1-out]Br₂-4CH₃CN | [1-out]I₂-2CH₃CN | [1-out]([NO₃]₂)3H₂O<sup>a</sup> |
|------------------|------------------|--------------|-------------------------------|-------------------|------------------|-------------------------------|
| Pt₁–I₁           | 3.6523(5)        | 3.7177(7)    | –                             | –                 | –                | –                             |
| Pt₁–I₂           | 3.6615(5)        | –            | 3.7134(16)                    | –                 | –                | –                             |
| Pt₁–N₁           | 2.006(4)         | 2.002(7)     | –                             | 2.016(2)          | 2.023(2)         | 2.014(5)                      |
| Pt₁–N₂           | 2.034(4)         | 2.027(7)     | –                             | 2.008(2)          | 2.013(2)         | 2.012(5)                      |
| Pt₁–N₄           | 2.013(4)         | –            | –                             | –                 | –                | –                             |
| Pt₁–N₅           | 2.032(4)         | –            | –                             | –                 | –                | –                             |
| N₃–C₁            | 1.396(7)         | 1.395(11)    | –                             | 1.406(3)          | 1.403(4)         | 1.412(8)                      |
| N₃–C₆            | 1.403(7)         | 1.392(11)    | –                             | 1.406(3)          | 1.401(4)         | 1.405(8)                      |
| N₃–C₁₁           | 1.475(6)         | 1.496(11)    | –                             | 1.473(3)          | 1.474(4)         | 1.470(7)                      |
| N₆–C₁₈           | 1.395(7)         | –            | –                             | –                 | –                | –                             |
| N₆–C₂₃           | 1.392(7)         | –            | –                             | –                 | –                | –                             |
| N₆–C₂₈           | 1.491(7)         | –            | –                             | –                 | –                | –                             |
| I₁–C₁₃           | 2.109(6)         | 2.113(11)    | –                             | 2.120(3)          | 2.118(3)         | 2.099(7)                      |
| I₂–C₃₀           | 2.111(6)         | –            | –                             | –                 | –                | –                             |
| I₁–Br₁ (or I₁–I₂) | 3.6065(10)       | 3.7202(13)   | –                             | 3.4313(5)         | 3.5665(3)        | –                             |
| I₂–Br₂           | 3.5117(8)        | –            | –                             | –                 | –                | –                             |

<sup>a</sup>The low quality of crystal structure due to small twinned crystals afforded low bond length and angle precisions. Therefore, only the distances and angles involving the heaviest atoms Pt and I were extracted.
2.2 Discussion of crystal structures

Almost all of the obtained crystal structures of 1 contain half of the complex in asymmetric unit, whereas in [1-in]Br₂·3.5H₂O and [1-in][NO₃]₂·3H₂O asymmetric unit contains full molecule of [1]²⁺ with the two ligands being not symmetrically equivalent. Depending on counter-ion and crystallization conditions, [1]²⁺ adopts two conformations [1-in]²⁺ and [1-out]²⁺. The principal difference between which is the orientation of phenyl rings with the iodine atoms oriented towards or away from the platinum center. In addition, all obtained structures of [1-out]²⁺ possessed two phenyl rings tilted towards different sides of the molecule ("symmetric", [1-out-sym]²⁺), whereas each obtained structure of [1-in]²⁺ featured orientation of phenyl rings towards the same side of the molecule ("anti-symmetric", [1-in-asy]²⁺).

From comparison of the relevant bond lengths and angles of the structures (Tables S2 and S3) as well as from the overlaid pairs of structures (Figure S7) it can be concluded, that [1-in]²⁺ and [1-out]²⁺ cations in all structures possess similar coordination geometry of the platinum atom and conformation of di(2-pyridyl)amine moieties. The main differences are associated with rotation of the phenyl rings (dihedral angles between N₃–C₁₁ bond and phenyl ring are about 60° in [1-in]²⁺ and about 25 - 30° in [1-out]²⁺, Table S3).
Halogen bonding interactions between the halide anions and the iodine atoms of the ligands in the structures of [1]Br₂ and [1]I₂ are weaker in the structures of [1]Br₂ and [1]I₂ are weaker in the structures of [1]Br₂, which is attributed to the steric hindrance of the iodine atoms in this conformation. The Pt⋯I distances in the structures of [1]Br₂ (3.65 – 3.72 Å, Table S2) are just below the sum of the corresponding atomic van der Waals radii (3.73 Å), indicating weak noncovalent axial interactions of the platinum center. Almost straight C⋯Pt angles (Table S3) in the structures of [1]Br₂ indicate that the iodine atoms in [1]Br₂ are oriented toward the metal center with their nucleophilic regions. The similarity of the I⋯Pt⋯I contacts in all three structures of [1]Br₂ allows to rule out the packing effects as the reason for the close contact.

3 Overview of axial interactions of platinum(II) complexes

This overview is intended as illustrative rather than comprehensive, and largely based on the work by G. Aullón and S. Alvarez on axial bonding of square planar d⁶ complexes, complemented with some recent additions in the field. Platinum(II) compounds presented here are classified based on the coordination number and geometry, as well as type of axial interaction with loosely bound ligands. The following notation is used: regular nucleophilic ligands, or Lewis bases, are denoted B, and electrophilic Z-type ligands, or Lewis acids, are denoted as A. Regular coordinate bonds are presented by dashes, and relatively weak axial interactions between metal center and loosely bound ligands are presented by arrows pointing in direction of electron donation.

3.1 Five-coordinate platinum(II) complexes

When a platinum center is strongly bound with five ligands, the complexes adopt trigonal bipyramidal (TBP) geometry (Chart S1a). Examples include complexes containing alkene or alkyne ligands and a bis-nitrogen chelating ligand (for example, 4). Complexes containing tripod-like tris(phosphinoethyl)amine ligands (for example, 5) possesing exceptionally symmetric trigonal bipyramidal geometry have been reported. In other reported compounds, bonding to one nucleophilic ligand is significantly weaker compared to the other four. In such cases square pyramidal (SPy) compounds with elongated apical bond are formed. These compounds are ascribed to B⋯[Pt(II)B₄] type (Chart S1b). Examples of such compounds include complexes with sulfur apical ligands, such as dithiocarbamate complex 7. Series of thiocrown complexes 8 and bis(thiacrown) complex 9 in all of which one sulfur atom is weakly bound to platinum center and located at the apex of the pyramid with elongated Pt–S distance. Another group of B⋯[Pt(II)B₄] type complexes possess weakly bound iodide anions in the apical position, such as phosphane complex 10 and dinuclear complex 11.

Five-coordinate species containing one Z-type electrophilic ligand (Lewis acid) typically adopt SPy geometry, in which the acceptor ligand occupies apical position, thus belonging to [Pt(II)B₄]⋯A type (Chart S1c). In particular, molecular iodine in 12 plays role of Lewis acid coordinating to platinum(II) complexes in “end-on” mode in the apical position, with platinum center playing a role of halogen bond acceptor. Another representatives of this type are hydrogen bonded compounds (co-crystal 13 being among the first reported examples) in which platinum(II) center plays a role of hydrogen bond acceptor.
3.2 Six-coordinate platinum(II) complexes

Similarly to [Pt(II)B₄]→A compounds, interaction of square planar platinum(II) compounds with two Lewis acids above and below the square plane, resulting in octahedral (Oh) A←[Pt(II)B₄]→A type compounds (Chart S2a), is possible, albeit weaker.\textsuperscript{[12]} The examples of this type of six-coordinate compounds include associates with two positively charged cations \textsuperscript{[29]} and \textsuperscript{[30]} double hydrogen bonded complexes (for example, \textsuperscript{[31]}) and “reversed sandwiches” like \textsuperscript{[32]} in which the electron deficient aromatic system acts as a Lewis acid. Upon interaction with a Lewis acid, platinum(II) center in SPy compounds of [Pt(II)B₄]→A type become a better acceptor of an additional nucleophilic ligand compared to the parent [Pt(II)B₄] compound.\textsuperscript{[12]} As the result, Oh compounds of B→[PtB₄]→A type (Chart S2b) can be obtained. However, the formal oxidation state of platinum center can be ascribed to 2+ or 4+, depending on the amount of electron transfer from platinum to the Lewis acid.\textsuperscript{[33,34]} Nevertheless, boratrane complex \textsuperscript{[35,36]} and complex \textsuperscript{[37]} containing I₂ molecule as Lewis acid and iodide as Lewis base represent examples of platinum(II) compounds of B→[PtB₄]→A type. Formation of six-coordinate compounds of B→[Pt(II)B₄]→B type is expected to be unfavorable. A good illustration of this is provided by the aforementioned complex \textsuperscript{[38]}. In which only one sulfur atom is coordinated weakly bound to the metal center, whereas the second pendant sulfur atom is not bonded.\textsuperscript{[21]} To the best of our knowledge, only bis(diarsine)platinum(II) diiodide \textsuperscript{[3]I₂} (Chart S2c) reported by Stephenson, in crystal structure of which the iodide counterions approach platinum center to distance of 3.5 Å from above and below the square plane, can be considered as six-coordinate platinum(II) compound of this type.\textsuperscript{[38]}
3.3 What is unusual in the intramolecular I⋯Pt⋯I interaction in [1-in]²⁺?

From the overview presented above it can be concluded, that the individual interactions of platinum(II) center with the iodine atoms in [1-in]²⁺ themselves, in which the iodine atoms act as nucleophiles (Lewis bases), belong to a known, albeit rare, kind of interactions for platinum(II) complexes. The double bonding I⋯Pt⋯I situation in the case of [1-in]²⁺, in which two donor ligands are simultaneously approaching the metal center from above and below the square plane, is however very unusual. Thus, [1-in]²⁺ can be viewed as a six-coordinate complex of B→[Pt(II)B₄]←B type.

To the best of our knowledge, the only other known example with such bonding situation is the Stephenson’s complex [3]₂. The unusual nature of the bonding between the iodide anions and platinum(II) center (3.50 Å) was noticed by the authors themselves,[38,39] and analogous bonding was also observed in the corresponding palladium(II) congener,[40] however, no further studies were conducted on this subject to date. It could be argued that the position of the iodide anions in proximity to the metal center in [3]₂ is purely due to electrostatic attraction to the positively charged cation. However, in analogous compound bis(diarsine)platinum(II) dichloride [3]Cl₂ (Chart S3) the chloride anions, possessing the same charge as iodides, are found at significantly longer distance of 4.16 Å from the platinum(II) center,[41] despite the shorter van der Waals radii. Based on this comparison it can be suggested, that the Pt⋯I interaction in [3]₂ is more than a mere electrostatic attraction between the oppositely charged ions. On the other hand, in the oxidized Oh complex 20, possessing regular coordinate bonds to the iodide ligands, the Pt–I distance is 2.67 Å,[42] indicating rather weak interaction in the case of [3]₂ and supporting its assignment to a six-coordinate complex of B→[Pt(II)B₄]←B type. We therefore decided to include complex [3]₂ into computational studies to compare it with [1-in]²⁺.
Chart S3. Different platinum complexes with two o-phenylenebisdimethylarsine ligands and reported metal–halide distances in their crystal structures.

4 Computational studies

4.1 Computational methods

Structure optimizations of $[1]^{2+}$, $[3]I_2$, and $([3]I)^+$ were performed at DFT level of theory using PBE0-D3 functional,[43,44] which has been shown to yield accurate results for third row transition metal complexes,[45–47] and def2-TZVPPD (Pt, I)[48] and 6-31G(d) (other atoms)[49] basis sets with the Gaussian 16 program package.[50] In addition, some trial optimizations without dispersion correction were performed. The corresponding crystal structures of $[1]Br_2$ and $[3]I_2$ were used as starting points for the optimizations. In case of $[3]I_2$ and $([3]I)^+$ hydrogen atoms, missing from the crystal structure, were added to the most probable locations prior to optimization. Frequency calculations with no scaling were conducted to ensure optimization to local minima. Topological electron density analysis and visualization were performed within the QTAIM (Quantum Theory of Atoms in Molecules) framework[51] using AIMAll program.[52]

Electrostatic potential surfaces were calculated and mapped in the range from 0.00 (blue) to 0.26 (red) a.u. to cover the entire range of values using Jmol program.

Potential energy surface scan for $[1]^{2+}$ was performed in a two-step formalism, first rotating around the first benzyl C–C single bond, while the second benzyl C–C single bond was scanned in the second step. 360-degree scans with 10-degree increments were performed in both steps. The located minima were consequently optimized to achieve the structures of all six conformations of $[1]^{2+}$. Absorption properties of the optimized $[1]^{-}$ and $[1]^{2+}$ and excited triplet state optimizations were performed using the Tamm-Dancoff Approximation (TDA) to TD-DFT.[53] Emission properties were estimated with a scalar-relativistic ZORA Hamiltonian with perturbative inclusion of SOC effects,[54,55] using the ADF program package.[56,57] A TZP all-electron basis set was used in the ADF calculations.

All ground state analyses were performed for both vacuum and methanol solution environments to mimic the crystalline and solution states accordingly. In the latter case conductor-like polarizable continuum (C-PCM) solvent model was used.[58,59] For the excited state studies, vacuum environment was used due to SCF convergence issues.

4.2 Ground state structure optimizations and analysis for $[1]^{2+}$

Structures of $[1]^{-}$ and $[1]^{2+}$ were optimized starting from the corresponding crystal structures $[1]^{-}$Br$_2$-3.5H$_2$O and $[1]^{-}$Br$_2$-4CH$_3$CN using dispersion corrected functional in vacuum and methanol. Optimization without correction for dispersion was also performed to reveal the influence of dispersion on the Pt···I interactions. Key structural parameters of the obtained models are summarized in Table S4.
The Pt∙∙∙I BCPs in points (BCPs) are presented in Figure S1. The optimized structures were further analyzed using the approach of quantum theory of atoms in molecules (QTAIM) to investigate the intramolecular interactions. The fully optimized structures of the two conformations with located bond paths (BPs) and bond critical points (BCPs) are presented in Figure S9, and selected parameters of electron density at BCPs are presented in Table S10. QTAIM analysis revealed the Pt–I BCPs in [1-in]2+ and [1-out]2+ and the calculated total energy differences (ΔE, kJ/mol) between the optimized structures of [1-in]2+ and [1-out]2+.

| Parameter | [1-in]2+ (XRD)[a] | [1-in]2+ (PBE0-D3-vac)[b] | [1-in]2+ (PBE0-D3-MeOH)[c] | [1-out]2+ (PBE0) | [1-out]2+ (PBE0-D3-vac)[d] | [1-out]2+ (PBE0-D3-MeOH)[e] |
|------------|------------------|------------------------|------------------------|----------------|------------------------|------------------------|
| l(Pt–N)    | 2.006(4) – 2.034(4) | 2.014, 2.027 | 2.012, 2.027 | 2.022, 2.023 | 2.008(2), 2.016(2) | 2.019, 2.020 |
| l(Cpy–Nout) | 1.392(7) – 1.402(7) | 1.395, 1.398 | 1.395, 1.400 | 1.397, 1.399 | 1.406(3) | 1.393, 1.399 |
| l(I–Pt)    | 3.6523(5), 3.6615(5) | 3.753 | 3.901 | 3.894 | – | – |
| l(I–C)     | 2.109(6), 2.112(6) | 2.097 | 2.096 | 2.096 | 2.120(3) | 2.095 |
| θ(Cpy–Nout–Cpy) | 118.5(4), 112.3(4) | 118.7 | 118.3 | 118.1 | 118.5(2) | 119.2 |
| θ(l–l–Pt–N) | 85.02(12) – 97.35(13) | 84.7 – 95.1 | 82.1 – 95.7 | 85.5 – 94.5 | – | – |
| θ(C–l–Pt)  | 90.46(16), 96.90(15) | 95.8 | 91.2 | 100.4 | – | – |
| ΔE–E(Etot) | – | -34.4 | -19.6 | -13.6 | 0 | 0 |

[a] From the crystal structure of [1-in]Br2-3.5H2O. [b] From the optimized structures of [1]2+ in vacuum using dispersion corrected functional. [c] From the optimized structures of [1]2+ in methanol using dispersion corrected functional. [d] From the optimized structures of [1]2+ in vacuum without dispersion correction. [e] From the crystal structure of [1-out]Br2-4CH3CN.

Analysis of the obtained optimized structures reveals good agreement with the experimental ones, apart from the 0.1 Å longer Pt–I distances. When methanol solvent environment was included in the optimization, Pt–I distances elongated further, whereas the rest of the structure was not affected by that change. The implication of the same functional without dispersion correction had similar effect. These observations suggest that dispersion plays major role in the Pt–I interactions.

Electrostatic potential surfaces (EPS) of the obtained structures were analyzed to evaluate whether the close Pt–I contacts are associated with electrostatic attraction. The calculated EPS are presented in Figure S8. The cations possess positive potentials throughout the entire surfaces, and the interactions appear to take place despite the electrostatic repulsion.

The optimized structures were further analyzed using the approach of quantum theory of atoms in molecules (QTAIM) to investigate the intramolecular interactions. The fully optimized structures of the two conformations with located bond paths (BPs) and bond critical points (BCPs) are presented in Figure S9, and selected parameters of electron density at BCPs are presented in Table S10. QTAIM analysis revealed the Pt–I BCPs in [1-in]2+, and according to the calculated properties of electron density at these points, the Pt–I interactions are rather weak and dispersive in nature, as indicated by the low electron density and predominant kinetic energy density at the BCP (|V/G| < 1) and lack of electron sharing between the platinum and iodine atoms (delocalization index δ(Pt–I) = 0.13)[63–65] in [1-out]2+. I–H hydrogen bonding interactions of similar character with methylene and pyridine hydrogen atoms are present instead.
Absorption spectra of the optimized [1-in]$^{2+}$ and [1-out]$^{2+}$ were calculated using the TDA-TD-DFT approach. The orbital contributions to the lowest calculated excitations for both conformations and involved MOs are presented in Tables S6 and S7 accordingly, and the simulated absorption spectra are presented in Figure S10. The lowest energy absorptions can be attributed to σ*(I⋯Pt⋯I)→π* metal-to-ligand charge transfer (MLCT) in [1-in]$^{2+}$ and π→π* intraligand charge transfer (ILCT) in [1-out]$^{2+}$. While the introduction of methanol environment causes blue shift of absorption, the transitions remain essentially the same in vacuum and methanol.

Table S6. The lowest calculated singlet-singlet vertical excitations of [1-in]$^{2+}$ and [1-out]$^{2+}$ in vacuum and methanol solvent.

| Transition          | λ, nm | f  | Contributions     | λ, nm | f  | Contributions     |
|---------------------|-------|----|-------------------|-------|----|-------------------|
| S0 → S1 (vacuum)   | 353   | 0.024 | 97 % HOMO→LUMO | 352   | 0.006 | 73 % H-1→LUMO    |
|                     |       |     |                   |       |     | 19 % H-1→L+1     |
| S0 → S2 (vacuum)   | 348   | 0   | 97 % HOMO→L+1   | 352   | 0   | 73 % HOMO→LUMO   |
|                     |       |     |                   |       |     | 19 % HOMO→L+1    |
| S0 → S3 (vacuum)   | 324   | 0   | 81 % HOMO→L+2   | 343   | 0.010 | 68 % H-1→L+1    |
|                     |       |     |                   |       |     | 25 % H-1→LUMO    |
| S0 → S4 (vacuum)   | 321   | 0.001 | 87 % HOMO→L+3  | 343   | 0   | 69 % HOMO→L+1   |
|                     |       |     |                   |       |     | 24 % HOMO→LUMO   |
| S0 → S1 (methanol) | 325   | 0.013 | 93 % HOMO→LUMO | 303   | 0.052 | 61 % HOMO→L+1   |
|                     |       |     |                   |       |     | 16 % HOMO→LUMO   |
| S0 → S2 (methanol) | 317   | 0.001 | 93 % HOMO→L+1  | 300   | 0.125 | 61 % HOMO→LUMO   |
|                     |       |     |                   |       |     | 15 % HOMO→L+1    |
| S0 → S3 (methanol) | 299   | 0   | 89 % HOMO→L+2   | 296   | 0   | 43 % H-3→L+1    |
|                     |       |     |                   |       |     | 30 % HOMO→L+3    |
| S0 → S4 (methanol) | 298   | 0.004 | 52 % HOMO→L+3  | 287   | 0   | 53 % H-3→LUMO   |
|                     |       |     |                   |       |     | 11 % H-3→L+1    |
|                     |       |     |                   |       |     | 28 % HOMO→L+2    |
| MO        | [1-in]$^1$ (vacuum) | [1-in]$^1$ (methanol) | [1-out]$^1$ (vacuum) | [1-out]$^1$ (methanol) |
|-----------|----------------------|-----------------------|----------------------|-----------------------|
| H-3       | ![H-3](image1)       | ![H-3](image2)       | ![H-3](image3)       | ![H-3](image4)       |
| H-1       | ![H-1](image5)       | ![H-1](image6)       | ![H-1](image7)       | ![H-1](image8)       |
| HOMO      | ![HOMO](image9)      | ![HOMO](image10)     | ![HOMO](image11)     | ![HOMO](image12)     |
| LUMO      | ![LUMO](image13)     | ![LUMO](image14)     | ![LUMO](image15)     | ![LUMO](image16)     |
| L+1       | ![L+1](image17)      | ![L+1](image18)      | ![L+1](image19)      | ![L+1](image20)      |
| L+2       | ![L+2](image21)      | ![L+2](image22)      | ![L+2](image23)      | ![L+2](image24)      |
| L+3       | ![L+3](image25)      | ![L+3](image26)      | ![L+3](image27)      | ![L+3](image28)      |

[a] The orbitals are displayed with isosurface value of 0.045 a.u.
Analysis of potential energy surface for \([1]^2+\) was performed to locate other possible conformations and the corresponding rotational barriers. The located conformations differ not only in orientation of the iodine atoms ("in", "out", and "inout", the latter corresponding to one iodine atom oriented towards platinum center and the other away from it), but also in tilting of the phenyl rings towards different sides of the molecule ("symmetric", "sym"-conformation) or the same side ("asymmetric", "asym"-conformation). The six local minima corresponding to different conformations were located (selected geometric parameters are listed in Table S9); the potential surfaces calculated in vacuum and methanol are presented in Figure S11, and the energies of the minima and transition states are listed in Table S8. The obtained values indicate stabilizing effect of "in"-orientation of the iodine atoms, which is additive: each "in"-oriented ligand reduces calculated total energy by about 17 kJ/mol in vacuum (10 kJ/mol in methanol). The calculated difference between "asymmetric" and the corresponding "symmetric" conformations of about 1 kJ/mol is considered negligible, and throughout this paper \([1\text{-in}]^2+\) and \([1\text{-out}]^2+\) denote \([1\text{-asym-in}]^2+\) and \([1\text{-sym-out}]^2+\) accordingly (the only conformations observed in the crystal structures) for conciseness.

Overall, the obtained results suggest that the Pt\(\cdots\)I interactions stabilize the two conformations of \([1\text{-in}]^2+\). However, the small energy differences between the conformations combined with low rotational barriers predict mixture of co-existing conformers of \([1]^2+\) in gas phase and methanol solution.
Table S8. Relative energies (E, kJ/mol) of calculated conformations and corresponding transition states for [1]2+ in vacuum and methanol.

| Conformations | E(vac) | E(MeOH) | Transition states | E(vac) | E(MeOH) |
|---------------|--------|---------|-------------------|--------|---------|
| [1-asym-in]2+ | 0.0    | 0.0     | [1-asym-in]2+ ↔ [1-sym-in]2+ | 64[a] | 64[a] |
| [1-sym-in]2+  | 0.8    | 1.8     | [1-sym-in]2+ ↔ [1-sym-inout]2+ | 17[b] | 13[b] |
| [1-asym-inout]2+ | 16.4  | 10.1    | [1-asym-inout]2+ ↔ [1-sym-inout]2+ | 36[b] | 21[b] |
| [1-sym-inout]2+ | 17.0  | 10.0    | [1-sym-inout]2+ ↔ [1-asym-in]2+ | 36[b] | 21[b] |
| [1-asym-out]2+ | 33.5  | 18.6    | [1-asym-inout]2+ ↔ [1-sym-out]2+ | 52.1  | 37.0   |
| [1-sym-out]2+  | 34.4  | 19.6    | [1-sym-out]2+ ↔ [1-asym-out]2+ | 34[b] | 21[b] |

[a] Crude estimation based on the PES scan. [b] Barrier associated with flipping of out-oriented ring. [c] Barrier associated with flipping of in-oriented ring.

4.3 Excited state structure optimizations and analysis for [1]2+

All six conformations were re-optimized in the lowest triplet T1 state in vacuum, and the key structural properties are compared in S0 and T1 electronic states in Table S9. The two conformations of [1-in]2+ undergo the most pronounced structural changes in the excited state, associated with significant (0.7-0.8 Å) contraction of Pt–I distances, indicating strengthening of these interactions. On the other hand, in [1-inout]2+ the contraction of Pt–I distance is only minor (0.04 - 0.07 Å). The changes in parameters of electron density at Pt–I BCPs (Table S10) further indicate strengthening of Pt–I interactions in the two forms of [1-in]2+, which gain partial covalent character, as evidenced by the shifts in potential and kinetic energy density ratio at the BCP from 0.98 to 1.28 and the electron delocalization index from 0.13 to 0.43, compared to the ground state systems. However, Pt–I BCPs in [1-inout]2+ are practically unaffected by the excitation.

The I–H hydrogen bonds, found in the ground states of [1-in]2+ and [1-out]2+, weaken or vanish completely in T1 state, indicating negligible impact on the conformation in excited state compared to the strengthened Pt–I interactions.

Severe elongation of Pt-N bonds takes place in [1-sym-in]2+ and [1-asym-in]2+ upon excitation. In combination with changes at the corresponding BCPs, it indicates weakening of the bonds, characteristic for metal-centered (MC) excited states in complexes of platinum(II).

Table S9. Selected bond lengths (l, Å) and angles (ϕ, °) in the structures of [1]2+ in S0 and T1 electronic states optimized in vacuum.

| conformations | l(–I–Pt) | l(Pt–N) | l(–I–H(CH3))| l(–I–H(py)) | ϕ(C–I–Pt) | ϕ(C–I–Pt) |
|---------------|---------|--------|-------------|-------------|-----------|-----------|
| [1-asym-in]2+ | 3.753   | 2.934  | 2.014, 2.027| 2.203, 2.228| –         | –         |
| [1-sym-in]2+  | 3.744   | 2.936  | 2.020, 2.021| 2.212, 2.217| –         | –         |
| [1-asym-inout]2+ | 3.714 | 3.644 | 2.014 - 2.027| 2.021 - 2.055| 2.774 | 2.993 | 3.044 | 4.389 | 97.3 | 99.9 |
| [1-sym-inout]2+ | 3.701 | 3.658 | 2.020, 2.021| 2.025 - 2.045| 2.774 | 2.952 | 3.047 | 4.655 | 100.1 | 97.8 |
| [1-asym-out]2+ | –       | –      | 2.015, 2.019| 2.054 | 2.797 | 2.769, 2.949 | 3.147 | 3.109, 4.642 | – | – |
| [1-sym-out]2+  | –       | –      | 2.020, 2.019| 2.022 - 2.048| 2.775 | 2.781, 2.953 | 3.038 | 3.059, 4.650 | – | – |

[a] Hydrogen atom of methylene group, nearest to the iodine atom (H11a, H11b, H28a, or H28b in the crystal structures). [b] Hydrogen atom of pyridine ring, nearest to the iodine atom (H2, H7, H19, or H24 in the crystal structures).
Table S10. QTAIM analysis of electron density at the Pt···I and Pt···N BCPs of [1]²⁻ in S0 and T1 electronic states optimized in vacuum (p = local electron density, |V|/G = ratio of potential energy density and kinetic energy density; H = total energy; δ(A,B) = delocalization index between two atoms).

| conformations       | BCP            | p [eÅ⁻³] | Laplacian [eÅ⁻⁵] | |V|/G | H [a.u.] | δ(A,B) |
|---------------------|----------------|----------|-------------------|-----|---------|--------|
|                     | S0  | T1  | S0  | T1  | S0  | T1  | S0  | T1  | S0  | T1  |
| [1-asym-in]²⁻       | Pt-N | 0.897 | 0.601 | 10.374 | 7.086 | 1.35 | 1.24 | -0.0565 | -0.0232 | 0.79 | 0.53 |
|                     | Pt-N | 0.868 | 0.570 | 10.151 | 6.698 | 1.33 | 1.23 | -0.0527 | -0.0205 | 0.77 | 0.51 |
|                     | Pt-I | 0.078 | 0.298 | 0.593 | 1.756 | 0.98 | 1.29 | 0.0001 | -0.0073 | 0.13 | 0.43 |
| [1-sym-in]²⁻        | Pt-N | 0.883 | 0.590 | 10.282 | 6.923 | 1.34 | 1.24 | -0.0546 | -0.0223 | 0.78 | 0.52 |
|                     | Pt-N | 0.882 | 0.583 | 10.259 | 6.882 | 1.34 | 1.23 | -0.0545 | -0.0216 | 0.78 | 0.52 |
|                     | Pt-I | 0.080 | 0.297 | 0.601 | 1.750 | 0.98 | 1.28 | 0.0001 | -0.0072 | 0.13 | 0.43 |
| [1-asym-inout]²⁻    | Pt-N | 0.899 | 0.836 | 10.262 | 10.108 | 1.35 | 1.32 | -0.0568 | -0.0485 | 0.79 | 0.76 |
|                     | Pt-N | 0.871 | 0.915 | 10.123 | 8.180 | 1.34 | 1.42 | -0.0530 | -0.0606 | 0.78 | 0.85 |
|                     | Pt-N | 0.870 | 0.860 | 10.187 | 10.206 | 1.34 | 1.33 | -0.0530 | -0.0516 | 0.78 | 0.76 |
|                     | Pt-N | 0.896 | 0.805 | 10.336 | 10.210 | 1.35 | 1.30 | -0.0563 | -0.0445 | 0.79 | 0.73 |
|                     | Pt-I | 0.083 | 0.091 | 0.624 | 0.691 | 0.99 | 1.01 | 0.0001 | 0.0000 | 0.14 | 0.15 |
| I--H(CH₂)²⁻         | 0.100 | –     | 1.045 | –     | 0.90 | –   | 0.0010 | –     | 0.07 | –   |
| I--H(py)²⁻          | 0.032 | –     | 0.360 | –     | 0.70 | –   | 0.0009 | –     | 0.02 | –   |
| [1-sym-inout]²⁻     | Pt-N | 0.882 | 0.853 | 10.212 | 10.139 | 1.34 | 1.33 | -0.0546 | -0.0507 | 0.79 | 0.77 |
|                     | Pt-N | 0.885 | 0.903 | 10.169 | 8.388 | 1.34 | 1.40 | -0.0549 | -0.0588 | 0.79 | 0.84 |
|                     | Pt-N | 0.884 | 0.848 | 10.259 | 10.184 | 1.34 | 1.32 | -0.0547 | -0.0500 | 0.79 | 0.75 |
|                     | Pt-N | 0.884 | 0.825 | 10.280 | 10.357 | 1.34 | 1.31 | -0.0547 | -0.0470 | 0.79 | 0.74 |
|                     | Pt-I | 0.084 | 0.089 | 0.637 | 0.678 | 0.99 | 1.00 | 0.0001 | 0.0000 | 0.14 | 0.14 |
| I--H(CH₂)²⁻         | 0.100 | –     | 1.045 | –     | 0.90 | –   | 0.0010 | –     | 0.07 | –   |
| I--H(py)²⁻          | 0.033 | –     | 0.369 | –     | 0.70 | –   | 0.0009 | –     | 0.03 | –   |
| [1-asym-out]²⁻      | Pt-N | 0.872 | 0.808 | 10.148 | 10.114 | 1.34 | 1.30 | -0.0532 | -0.0450 | 0.79 | 0.74 |
|                     | Pt-N | 0.899 | 0.858 | 10.235 | 10.166 | 1.35 | 1.33 | -0.0568 | -0.0514 | 0.80 | 0.76 |
|                     | Pt-N | 0.899 | 0.916 | 10.235 | 8.410 | 1.35 | 1.41 | -0.0568 | -0.0604 | 0.80 | 0.86 |
|                     | Pt-N | 0.872 | 0.844 | 10.148 | 10.096 | 1.34 | 1.32 | -0.0532 | -0.0495 | 0.79 | 0.77 |
|                     | I--H(CH₂)²⁻ | 0.100 | 0.101 | 1.041 | 1.050 | 0.90 | 0.90 | 0.0010 | 0.0010 | 0.07 | 0.07 |
|                     | I--H(py)²⁻  | 0.056 | 0.049 | 0.593 | 0.534 | 0.81 | 0.78 | 0.0010 | 0.0010 | 0.05 | 0.04 |
| [1-sym-out]²⁻       | Pt-N | 0.885 | 0.854 | 10.214 | 10.118 | 1.34 | 1.33 | -0.0548 | -0.0508 | 0.79 | 0.77 |
|                     | Pt-N | 0.888 | 0.909 | 10.206 | 8.415 | 1.34 | 1.41 | -0.0553 | -0.0594 | 0.79 | 0.85 |
|                     | Pt-N | 0.885 | 0.847 | 10.214 | 10.158 | 1.34 | 1.32 | -0.0548 | -0.0499 | 0.79 | 0.76 |
|                     | Pt-N | 0.888 | 0.820 | 10.206 | 10.220 | 1.34 | 1.31 | -0.0553 | -0.0464 | 0.79 | 0.74 |
|                     | I--H(CH₂)²⁻ | 0.100 | 0.099 | 1.044 | 1.035 | 0.90 | 0.89 | 0.0010 | 0.0010 | 0.07 | 0.07 |
|                     | I--H(py)²⁻  | 0.056 | 0.054 | 0.593 | 0.576 | 0.81 | 0.80 | 0.0010 | 0.0010 | 0.05 | 0.05 |

[a] Hydrogen atom of methylene group, nearest to the iodine atom (H11a, H11b, H28a, or H28b in the crystal structures). [b] Hydrogen atom of pyridine ring, nearest to the iodine atom (H2, H7, H19, or H24 in the crystal structures).
Different impact of excitation to T1 state for different conformations suggests different nature of the excited states. The assignments of the excited states were done according to localization of the calculated single-occupied molecular orbitals (SOMOs), presented in Table S11. Furthermore, calculated emission properties of the excited states are listed in Table S12. “In”-orientation of both iodine atoms in $[1]^2$ causes involvement of the metal center in the metal-centered (MC) excited state for $[1$-asym-in]$^2$ and $[1$-sym-in]$^2$, whereas for the remaining four conformations the intraligand charge transfer (ILCT) excited states are predicted. Further discussion on the interpretation and assignments of the theoretically and experimentally obtained phosphorescence spectra is presented in section 5.

Table S11. SOMOs of $[1]^2$ in T1 electronic state calculated in vacuum.

| conformations | LSOMO | HSOMO | T1 assignment |
|---------------|-------|-------|---------------|
| $[1$-asym-in]$^2$ | ![Figure 1](image1.png) | ![Figure 2](image2.png) | MC |
| $[1$-sym-in]$^2$ | ![Figure 3](image3.png) | ![Figure 4](image4.png) | MC |
| $[1$-asym-inout]$^2$ | ![Figure 5](image5.png) | ![Figure 6](image6.png) | ILCT |
| $[1$-sym-inout]$^2$ | ![Figure 7](image7.png) | ![Figure 8](image8.png) | ILCT |
| $[1$-asym-out]$^2$ | ![Figure 9](image9.png) | ![Figure 10](image10.png) | ILCT |
Table S12. Calculated emission wavelengths ($\lambda$), individual radiative rates for each triplet substate ($k_i$) and average radiative rates ($k_{r,avg}$) and lifetimes ($\tau_{avg}$) for [1]$^{2+}$ in T1 electronic state in vacuum.

| conformation        | $\lambda$ [nm] | $k_i$ [s$^{-1}$] | $k_{r,i}$ [s$^{-1}$] | $k_{r,avg}$ [s$^{-1}$] | $\tau_{avg}$ |
|---------------------|----------------|------------------|----------------------|------------------------|--------------|
| [1-sym-out]$^{2+}$  | 4499           | –                | –                    | –                      | –            |
| [1-sym-in]$^{2+}$   | 4319           | –                | –                    | –                      | –            |
| [1-asym-inout]$^{2+}$| 577            | 1.15E+2          | 2.46E+2              | 4.19E+4                | 1.41E+4      | 71 us        |
| [1-asym-out]$^{2+}$ | 571            | 4.86E+1          | 2.69E+2              | 2.74E+4                | 9.25E+3      | 108 us       |
| [1-asym-inout]$^{2+}$| 573            | 5.55E+1          | 9.55E+1              | 1.07E+4                | 3.60E+3      | 278 us       |
| [1-asym-out]$^{2+}$ | 575            | 1.86E+1          | 1.61E+2              | 1.02E+4                | 3.47E+3      | 288 us       |

In summary, calculations indicate clear trend of strengthening Pt⋯I interactions in the two forms of [1-in]$^{2+}$ in the excited state, caused by the removal of one electron from $\sigma^*$(I⋯Pt⋯I) orbital. It is important to notice that such effects take place only when both iodine atoms of [1]$^{2+}$ are “in”-oriented, and no significant strengthening of Pt⋯I interaction is predicted for [1-inout]$^{2+}$. In other words, the two Pt⋯I interactions possess cooperativity in the excited state, in contrast with their weak anti-cooperativity in the ground state.

4.4 Computational studies of [3]$\text{I}_2$

In order to verify the presence of Pt⋯I interactions in the crystal structure of [3]$\text{I}_2$, further structure analysis and computational studies were undertaken. Since the published crystal structure lacks hydrogen atoms and possesses some distortions and bond length discrepancies (Figure S12, left and Table S13, row 1), it was used as a starting point for geometry optimization calculation after adding hydrogen atoms at their standard calculated positions. In the DFT optimized structure, planarity of the aromatic rings and [PtAs$_4$] fragment were restored, and 0.1 Å shorter Pt⋯I distances were observed (Figure S12, right and Table S13, row 2) in contrast with [1-in]$^{2+}$, for which DFT optimized Pt⋯I distances were slightly longer than obtained from the crystal structures (Table S4). Stronger bonding in [3]$\text{I}_2$ compared to [1-in]$^{2+}$ can be attributed to electrostatic attraction between the negatively charged iodides and positively charged complex in the former case, assisted by strong π-accepting properties of the arsine ligands and additional C–H⋯I interactions.

Figure S12. Crystal (left)$^{[35]}$ and optimized (right) structures of complex [3]$\text{I}_2$. In both cases, the two halves of the molecule are symmetrically equivalent.

Table S13. Selected bond lengths (Å) and angles (°) in the crystal structure of [3]$\text{I}_2$ and structures of [3]$\text{I}_2$ and ([3]$\text{I}$)$^+$ in S0 and T1 electronic states optimized in vacuum.

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In order to investigate, whether the two Pt⋯I interactions in [3]I₂ feature cooperativity or anti-cooperativity, additional optimization of [(3)I]⁺ was performed, in which one of the iodides was removed. The obtained structure possessed significantly contracted Pt–I bond (2.89 Å) with SPy coordination environment. Therefore, the two Pt⋯I interactions are anti-cooperative, and the elongated Pt⋯I distances are due to the interference of the two B-type ligands.

Like in the case of [1-sym]-in²⁺, [3]I₂ possess HOMO anti-bonding σ*(I⋯Pt⋯I), which undergoes depopulation upon excitation, resulting in strengthening of the I⋯Pt⋯I bonding. Analysis of single-occupied MOs (Figure S13) indicate 3MC T1 state for [3]I₂, similarly to [1-sym]-in²⁺. The T1 state for [(3)I]⁺ also appears to be of 3MC nature, however, in this case only minor contraction of Pt–I bond takes place as the σ*(Pt⋯I) is only weakly anti-bonding in the ground state.

![Figure S13. LSOMO (left) and HSOMO (right) of [3]I₂ (top) and [(3)I]⁺ (bottom) in T1 electronic state. The orbitals are displayed with isosurface value of 0.045 a.u.](image-url)

Finally, topological analysis of calculated electron density revealed bond paths and BCPs corresponding to the Pt⋯I interactions in [3]I₂. Analysis of properties of electron density in BCPs (Pt⋯I) revealed similar, albeit slightly stronger interaction compared to that in both conformations of [1-sym]-in²⁺ in both ground and excited electronic states. (Table S14).
Table S1. QTAIM analysis of electron density at the Pt⋯I BCPs of [3]I₂ and two conformations of [1-in]²⁺ in S0 and T1 electronic states optimized in vacuum (ρ = local electron density, |V|/G = ratio of potential energy density and kinetic energy density; H = total energy; δ(A,B) = delocalization index between two atoms).

| conformations     | ρ [e/Å³] | Laplacian [e/Å³] | |V|/G | H [a.u.] | δ(A,B) |
|-------------------|----------|------------------|-----|-------|--------|
| [3]I₂             | 0.143    | 0.290            | 1.023 | 1.562 | 1.08 | 1.29 | -0.0010 | -0.0067 | 0.32 | 0.51 |
| [1-asym-in]²⁺     | 0.078    | 0.246            | 0.593 | 1.422 | 0.98 | 1.24 | 0.0001 | -0.0046 | 0.13 | 0.35 |
| [1-sym-in]²⁺      | 0.080    | 0.297            | 0.601 | 1.750 | 0.98 | 1.28 | 0.0001 | -0.0072 | 0.13 | 0.43 |

In summary, both Pt⋯I distances and QTAIM descriptors of electron density at the corresponding BCPs indicate stronger Pt⋯I interactions in [3]I₂ than in [1-in]²⁺. Furthermore, the two Pt⋯I interactions in [1-in]²⁺ and [3]I₂ are anti-cooperative, and removal of one iodide leads to substantial strengthening of the remaining Pt⋯I interaction. Nevertheless, both compounds share the property of strengthening I⋯Pt⋯I bonding upon excitation due to depopulation of HOMO σ*(I⋯Pt⋯I).

5 Discussion of spectroscopic experiments to study conformational equilibria

5.1 UV-Vis spectroscopy

The absorption spectrum of [1]Br₂ in methanol solution has been reported previously. The calculated absorption spectra of the two conformers in methanol (section 4.2) appear rather similar between each other, and are in a reasonable agreement with the experimental spectrum (Figure S14). Therefore, the absorption spectrum of [1]Br₂ doesn’t allow differentiating between different conformations of [1-in]²⁺ in solution.

Figure S14. Experimental absorption spectrum of [1]Br₂ in methanol (C = 20 µM) and calculated absorption spectra for [1-in]²⁺ and [1-out]²⁺ in methanol.

5.2 NMR spectroscopy

NMR spectra were recorded with Bruker Avance III 400 MHz spectrometer (400.13 MHz for ¹H and 85.78 MHz for ¹⁹⁵Pt) at 25 °C (expect for variable temperature experiments) using CD₃OD (Sigma-Aldrich, 99.8% D) as solvent. NMR spectra were referenced using solvent lock (²H) signal according to IUPAC recommended secondary referencing method and the spectrometer manufacturer’s protocols. For the measurement of long-range J(C,H) coupling constants ¹H-selective HSQMB-TOCSY IPAP method was employed. As in this experiment we have used an isolated spin system of the methylene group of benzyl substituent, the TOCSY block of the pulse sequence was switched off. The desired selectivity was achieved by using Gaussian shaped pulses 40 ms in duration. All other NMR experiments were carried out using standard pulse sequences from Bruker’s library. In selective TOCSY experiments the TOCSY mixing time was 80 ms in all cases, the Gaussian shaped pulse duration was 40 ms or 80 ms, depending on the desired selectivity. Correlation methods (COSY, HSQC, HMBC) were used for to assign signals in ¹H NMR spectra of compounds [1]Br₂ and [2]Br₂, as well as the corresponding free ligands L₁ and L₂ and their hydrochlorides L₁·HCl and L₂·HCl. Atom labeling scheme for all studied compounds is presented in Scheme S1 and matches labeling scheme in the crystal structures (section 2.1). Chemical shifts are expressed in ppm. The spectra are presented in Figure S15.
Scheme S1. Atom labelling for the ligands L1 and L2, their hydrochlorides L1·HCl and L2·HCl and platinum(II) complexes [1]Br2 = [Pt(L1)2Br2] and [2]Br2 = [Pt(L2)2Br2] in the NMR spectroscopy studies.

[1]Br2 1H NMR (CD3OD, 400 MHz): δ 8.27 (ddd, J = 8.8, 7.3, 1.5 Hz, 2H, Hαβγδ), 8.00 – 7.94 (m, 4H, Hα7, Hγ′, and Hγ′′), 7.82 (dd, J = 6.0, 1.5 Hz, 2H, Hγδ′), 7.49 (ddd, J = 7.7, 1.1 Hz, 1H, Hα′), 7.32 (ddd, J = 7.3, 6.0, 1.2 Hz, 2H, Hαδ′), 7.14 (ddd, J = 7.7, 1.4 Hz, 1H, Hα′′), 5.63 (s, 2H, H11); 195Pt NMR (CD3OD, 86 MHz): δ -2546.0.

[2]Br2 1H NMR (CD3OD, 400 MHz): δ 8.22 (ddd, J = 7.4, 7.3, 1.4 Hz, 2H, Hαβγδ), 7.96 – 7.86 (m, 6H, Hαβ′, Hγ′δ′, and Hγ′′δ′), 7.43 (ddd, J = 7.5, 7.4 Hz, 2H, H14′16′), 7.39 – 7.27 (m, 3H, Hαδ′ and Hα′′δ′), 5.65 (s, 2H, H11); 195Pt NMR (CD3OD, 86 MHz): δ -2699.3.

L1 1H NMR (CD3OD, 400 MHz): δ 8.35 – 8.21 (m, 2H, Hαβγδ), 7.86 (dd, J = 7.7, 1.0 Hz, 1H, Hα′), 7.68 (ddd, J = 9.2, 7.3, 2.0 Hz, 2H, Hα′′β′′), 7.33 – 7.13 (m, 4H, Hα7, Hγ′, and Hγ′′), 7.07 – 6.91 (m, 3H, Hαδ′ and Hα′′δ′), 5.35 (s, 2H, H11).

L2 1H NMR (CD3OD, 400 MHz): δ 8.25 (ddd, J = 5.0, 1.9, 0.8 Hz, 2H, Hαβγδ), 7.62 (ddd, J = 8.5, 7.2, 1.9 Hz, 2H, Hαβ′γδ′), 7.35 – 7.31 (m, 2H, H14′16′), 7.27 – 7.21 (m, 2H, H14′16′), 7.19 – 7.14 (m, 3H, Hαβ′γ and Hγ′′), 6.95 (ddd, J = 7.2, 5.0, 0.8 Hz, 2H, Hαβ′γ), 5.43 (s, 2H, H11).

L1·HCl 1H NMR (CD3OD, 400 MHz): δ 8.52 (ddd, J = 5.6, 1.8, 0.6 Hz, 2H, Hαβ′γ′δ′), 8.12 (ddd, J = 9.0, 7.4, 1.8 Hz, 2H, Hαβ′γδ′), 8.03 (ddd, J = 7.8, 1.0 Hz, 1H, Hα′), 7.42 (ddd, J = 7.4, 5.6, 0.7 Hz, 2H, Hα′γ′), 7.34 (ddd, J = 7.8, 7.8, 1.1 Hz, 1H, Hα′′), 7.28 – 7.24 (m, 2H, Hα′′β′′), 7.22 (dd, J = 8.0, 1.1 Hz, 1H, Hα′′), 7.11 (ddd, J = 8.0, 7.8, 1.0 Hz, 1H, Hα′′), 5.35 (s, 2H, H11).

L2·HCl 1H NMR (CD3OD, 400 MHz): 8.51 (ddd, J = 5.5, 1.9, 0.8 Hz, 2H, Hαβ′γ′δ′), 8.12 (ddd, J = 9.1, 7.4, 1.9 Hz, 2H, Hαβ′γδ′), 7.47 – 7.28 (m, 9H, Hα′′β′′, Hαβ′γ′ and H14′16′), 5.51 (s, 2H, H11).
**Figure S15.** $^1$H NMR spectra of free ligands L1 and L2, their hydrochlorides L1·HCl and L2·HCl and platinum(II) complexes [1]Br$_2$ and [2]Br$_2$ in CD$_3$OD and the changes in chemical shifts of characteristic signals of H$^{5/10}$ (black arrows) and H$^{6/7}$ (purple arrows) upon protonation and coordination.

In attempts to observe dynamic conformational equilibria of [1]Br$_2^+$ in solution, various NMR spectroscopy experiments on [1]Br$_2$ in CD$_3$OD were undertaken. Analogous experiments were also performed on [2]Br$_2$ possessing hydrogens instead of iodine atoms in the phenyl rings to elucidate the role of the Pt∙∙∙I interactions in the equilibria. Unfortunately, the nuclear Overhauser effect (NOE) could not be used to observe the proximities between the methylene group (H$^{11}$) and the nearest aromatic protons (H$^{6/7}$ and H$^{17}$, Figure S16, left) due to the overlap between the signals, as supported by the signal assignment and selective 1-dimensional total correlation spectroscopy (sel. TOCSY) experiments (Figure S16, right).

**Figure S16.** Left: expected NOE signals in [1-in]Br$_2^+$ and [1-out]Br$_2^+$. Right: sel. TOCSY spectra of the phenyl (top) and pyridine (middle) rings in CD$_3$OD with the signals of interest circled.
Variable temperature $^1$H and $^{195}$Pt spectra of [1]Br$_2$ and [2]Br$_2$ (Figures S17 and S18 accordingly) revealed some rather similar changes in chemical shifts upon cooling, but no signal splitting due to the slow conformational equilibrium could be achieved, as expected from the predicted low rotational barriers (section 4.2).

Figure S17. Variable temperature $^1$H (left) and $^{195}$Pt (right) NMR spectra of [1]Br$_2$ in CD$_3$OD.

Figure S18. Variable temperature $^1$H (left) and $^{195}$Pt (right) NMR spectra of [2]Br$_2$ in CD$_3$OD.

Finally, heteronuclear $^3$J$_{CH}$ coupling constants between methylene protons H$^{11}$ and ortho-carbon atoms of the phenyl group C$^{13}$ and C$^{17}$ were measured for [1]Br$_2$ and [2]Br$_2$. To observe the effect of the Pt–I interactions, the coupling constants were then also measured for the corresponding free ligands L$_1$ and L$_2$ as well as their hydrochlorides L$_1$·HCl and L$_2$·HCl. While direct determination of structural parameters from the $^3$J$_{CH}$ values is hardly possible, differences in the $^3$J$_{CH}$ coupling constants can indicate different averaged orientations of phenyl rings in solution. Protonated ligands L$_1$·HCl and L$_2$·HCl represent model compounds in which pyridine rings are locked by the intramolecular hydrogen bond,$^{[66,67]}$ but intramolecular interactions with iodine atom are absent. In absence of any
(attractive or repulsive) Pt−I interactions in [1]2+: similar changes, associated with protonation/coordination of pyridine rings, would be expected within the series free ligands → protonated ligands → platinum(II) complexes for [1]Br2 and [2]Br2 (Chart S4). Accordingly, the measured 3JCH coupling constants (Table S15) change similarly in the two series from free to protonated ligands, but deviate significantly for complexes, indicating that Pt−I interactions in [1]2+ may take place and affect conformational equilibrium in solution. However, the attractive or repulsive nature of this interaction can't be revealed by this experiment.

Chart S4. Structures of free ligands L1 and L2, their hydrochlorides L1·HCl and L2·HCl and platinum(II) complexes [1]Br2 and [2]Br2

Table S15. Measured heteronuclear 3JCH (MHz) coupling constants in series of free ligands, protonated ligands, and platinum(II) complexes for [1]Br2 and [2]Br2

| Compound       | 3JCH(H11-C13) in L1 | 3JCH(H11-C17) in L1 | 3JCH(H11-C13/17) in L2 |
|----------------|---------------------|---------------------|------------------------|
| L              | 3.6                 | 3.2                 | 3.6                    |
| L·HCl          | 3.4                 | 3.1                 | 3.1                    |
| [Pt(L1)2]Br2   | 5.4                 | 4.2                 | 3.7                    |

5.3 Ion mobility-mass spectrometry (IM-MS)

Ion mobility mass spectrometry (IM-MS) experiments were performed using Agilent 6560 ESI-IM-QTOF mass spectrometer equipped with dual-ESI ion source and Drift Gas Upgrade Kit (Agilent Technologies, USA). Mass spectrometer was calibrated using ES Tuning mix (Agilent Technologies, USA) and N2 from nitrogen generator was used as dry and nebulizer gas. All experiments were done on IM-TOF mode and using positive polarization.

Stock solutions of [1]Br2 and [2]Br2 in MeOH (2-4 mM) were diluted with ACN to give ca. 10 µM sample concentration. The samples were injected into the ESI source with a flow rate of 5µL min⁻¹ using direct infusion with syringe pump. Dry gas temperature of 350 °C, drying gas flow rate 3 L min⁻¹, and nebulizer pressure 8 psi, were used. Capillary voltage of 4500 V and fragmentor voltage of 150 V were set as source parameters.

In IM experiments the drift tube pressure was set to 3.95 Torr and high pressure funnel to 3.80 Torr. High-purity N2 (from gas cylinder) was used as a drift gas. The drift tube entrance and exit voltages were set as 1700V and 224V, respectively. Collision cross-section (CCS) values were determined using multi-field measurements and then drift tube entrance voltage was varied from 1100 V to 1700 V with 100 V increments. Before sample introduction, ES tuning mix (Agilent Technologies) was measured as a quality control sample for CCS values. Data was analyzed using MassHunter Qualitative Navigator (B.09.00) and MassHunter IM-MS Browser (Version B.08.00) from Agilent Technologies, USA.

Both samples resulted clear ESI mass spectra showing doubly charged ions for [1]2+ and [2]2+ as base peaks. In addition peaks for singly-charged [Br+] and [2Br+] were observed with lower intensity. Characterization of ions were confirmed using mass accuracies (< 1.7 mDa) and comparing theoretical and experimental isotopic distributions (Figure S19 and Table S16).
Figure S19. ESI-MS measured from a) [1]Br₂ and b) [2]Br₂ in MeCN. Insets show fit to theoretical isotopic distribution.

Table S16. IM-MS data and predicted DTCCS₂ values for [1]²⁺ and [2]²⁺ ions

| Ion   | Formula     | m/z (exp) | m/z (theor) | Drift time, ms | Drift time FWHM, ms | Drift resolution | DTCCS₂ (exp), ±0.3 Å² | Conformation      | DTCCS₂ (theor), ±1 Å² |
|-------|-------------|-----------|-------------|----------------|---------------------|------------------|----------------------|---------------------|----------------------|
| [1]²⁺ | C₃₄H₂₈I₂N₆Pt | 484.50681 | 484.50509   | 17.3           | 0.8                 | 20.4             | 276.4                | [1-asym-in]²⁺    | 272                  |
|       |             |           |             |                |                     |                  |                      | [1-sym-in]²⁺    | 270                  |
|       |             |           |             |                |                     |                  |                      | [1-asym-out]²⁺   | 276                  |
|       |             |           |             |                |                     |                  |                      | [1-sym-out]²⁺   | 275                  |
| [2]²⁺ | C₃₄H₃₀N₆Pt  | 358.60777 | 358.60844   | 16.5           | 0.5                 | 34.6             | 266.7                | [2-asym]²⁺      | 268                  |
|       |             |           |             |                |                     |                  |                      | [2-sym]²⁺       | 266                  |

In ion-mobility arrival time distributions (ATDs) drift times 17.3 and 16.5 ms were recorded for ions for [1]²⁺ and [2]²⁺ respectively. The experimental DTCCS₂ values for [1]²⁺ and [2]²⁺ were calculated using multifield-method and are presented in Table S16. Different conformers were not resolved, but peaks were clearly wider and with lower resolution (Figure S20) than typically expected for doubly charged ions (for 1700V drift entrance voltage and N₂ drift gas, typical values are FWHM = 0.3 ms and resolution R = 50 – 60).
predicted CCS values of ions [1]$^{2+}$ and [2]$^{2+}$ were calculated using simplified trajectory method \cite{70,71} implemented in IMoS Software (v. 1.08b) \cite{72} without inclusion of Lennard-Jones potentials. Atomic coordinates from DFT (vacuum) optimized structures were used in CCS calculations (six conformations for [1]$^{2+}$ presented in Figure S10 and two conformations for [2]$^{2+}$, namely [2-sym]$^{2+}$ and [2-asym]$^{2+}$). The trajectory method parameters for N$_2$ buffer gas were used, and the accommodation parameter was adjusted to achieve match between the calculated average for the two conformations and the measured CCS value for [2]$^{2+}$. The adjusted parameters, listed in Table S17, were used to calculate theoretical CCS values of the six conformations of [1]$^{2+}$ presented in Table S16. The experimentally obtained CCS value is intermediate, suggesting the presence and fast interconversion between the various conformations in gas phase in agreement with the calculated low energy differences and rotational barriers (section 4.2). Notably, the drift peak for [1]$^{2+}$ was significantly wider than for [2]$^{2+}$ (FWHM=0.8 ms and 0.5 ms accordingly, Figure S20 and Table S16) in agreement with the narrower range of the calculated CCS values for individual conformers for [2]$^{2+}$.

Figure S20. Comparison of drift peaks in ion-mobility ATDs [1]$^{2+}$ and [2]$^{2+}$.

Table S17. Trajectory method parameters used for calculation of CCS values for [1]$^{2+}$ and [2]$^{2+}$

| Parameter                  | Value       |
|----------------------------|-------------|
| Number of rotations        | 3           |
| Number of gas molecules per rotation | 10$^6$    |
| Molecular mass of gas      | 28.00 Da    |
| Alpha polarization         | 1.76 Å$^2$  |
| Radius of gas              | 1.50 Å      |
| Temperature                | 298 K       |
| Pressure                   | 101325 Pa   |
| Accommodation coefficient  | 0.2         |
| Diffuse Scattering         | yes         |
| Mean remission velocity    | 632.77 m/s Elastic(mean) |
| Timestep                   | 300         |
| Box domain                 | 16 Å        |

5.4 Luminescence spectroscopy

Phosphorescence emission of [1]Br$_2$ solution in methanol/ethanol (1:4, v/v) mixture at 78 K possesses two emission bands with $\lambda_{\text{max}}$ = 410 and 475 nm and strikingly different lifetimes of 39 μs and 3.7 ms accordingly, which were found to be independent of concentration (Figure S21).\cite{63} The longer wavelength emission can be tentatively assigned to the organic phosphorescence associated with the phenyl ring, based on the vibronic structure, characteristic for aromatic rings, and emission lifetime, which is too long for a transition involving platinum(II) center.\cite{63} Computational results presented in section 4.3 suggest that upon excitation [1-in]$^{2+}$ falls into a distorted non-emissive MC state, which is promoted by the I−Pt−I interaction, and therefore is invisible in the phosphorescence spectrum. The shorter wavelength emission, on the other hand, can be tentatively assigned to the ILCT emissions from [1-inout]$^{2+}$ and [1-out]$^{2+}$ conformations, which are not distinguishable in practice according to Table S12, and similar phosphorescence is also observed for the
reference compound [2]Br₂. Therefore the phosphorescence emission data does not provide information on relative amounts of the conformations in the excited state.

Figure S21. Left: change of the photophosphorescence emission spectrum of [1]Br₂ in glassy methanol/ethanol matrix (C = 20 µM) at 78 K with increasing delay time after excitation (λ_{ex} = 310 nm, gate time = 5 ms). Right: normalized phosphorescence emission spectra of [1]Br₂ and [2]Br₂ under the same conditions (λ_{ex} = 320 nm, delay 20 ns, gate 30 µs for [1]Br₂ and 10 µs for [2]Br₂).
Author Contributions

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