

Isosteric $\text{Cl} \leftrightarrow \text{CH}_3$ Substitution in Cyclometallated Pt(II) Thiocyanate–Isocyanide Complexes: Polymorphism, Solvatomorphism and Supramolecular Organisation 1

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Research Article

Keywords: Cyclometalated platinum(II) complexes, Thiocyanate, Arylisocyanide, Polymorphism, Solvatomorphism, Isostructurality, Supramolecular architecture, Metallophilic interactions, Luminescence, Excimeric emission

Posted Date: September 1st, 2026

DOI: <https://doi.org/10.21203/rs.3.rs-10713799/v1>

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Additional Declarations: No competing interests reported.

Version of Record: A version of this preprint was published at Structural Chemistry on October 6th, 2026. See the published version at <https://doi.org/10.1007/s11224-026-02915-1>.

Abstract

Two new cyclometallated platinum(II) complexes bearing an isothiocyanato ligand and an arylisocyanide, $[\text{Pt}(\text{ppy})(\text{NCS})(\text{CNC}_6\text{H}_3\text{-2-Cl-6-X})]$ ($\text{X} = \text{Cl}$, **1**; $\text{X} = \text{Me}$, **2**), have been synthesised and structurally characterised. IR and NMR spectroscopy show the ambidentate SCN^- ligand to be N-bound in the solid state, whereas in CDCl_3 a dynamic N/S linkage equilibrium is established, strongly favouring the N-isomer. Complex **1** is dimorphic, giving triclinic **1**^I from CH_2Cl_2 and monoclinic **1**^{II} from CHCl_3 , while **2** yields the unsolvated triclinic form from CH_2Cl_2 and the solvate **2**· CHCl_3 from CHCl_3 . The like-for-like pair **1**^I/**2** is strictly isostructural, showing the $\text{Cl} \leftrightarrow \text{CH}_3$ replacement to be crystallochemically silent even in a metallophilically associated lattice – a direct confirmation of Kitaigorodskii's close-packing expectation for a heavy-metal system. The triclinic forms are built from extended chains combining $\text{Pt} \cdots \text{Pt}$ contacts with π -hole(isocyano group) $\cdots d_z^2$ -[Pt] interactions, whereas the monoclinic forms contain isolated $\text{Pt} \cdots \text{Pt}$ dimers. All forms luminesce at room temperature.

1. Introduction

The a priori prediction of the crystal structure of organic and organometallic compounds remains one of the most persistent unsolved problems of modern structural chemistry [1, 2]. Its difficulty stems not from the absence of a theory, but from the near-degeneracy of the energy landscape: strong directional interactions and weak, essentially isotropic dispersion forces contribute to the lattice energy on a comparable scale, so that polymorphs are typically separated by less than 2 kJ mol^{-1} , and only rarely by more than 5 kJ mol^{-1} [3–8]. Systematic experiments in which a single structural variable – most conveniently, one substituent – is deliberately altered therefore retain a value that computation cannot yet replace.

The first coherent framework for this problem was the theory of close packing of molecular crystals, formulated by A. I. Kitaigorodskii in the 1940s–1950s [9]. Treating molecules as rigid bodies bounded by intersecting van der Waals spheres, it holds that the protrusions of one molecule occupy the hollows of its neighbours, maximising the packing coefficient and thus dispersive stabilisation. Where exchange–repulsion and dispersion dominate, molecular shape and volume become decisive and electronic characteristics recede into the background. A direct corollary, which Kitaigorodskii approached in his work on the isomorphism of halogen-substituted compounds, is that non-polar substituents of similar van der Waals dimensions should be mutually replaceable without substantially changing the structure.

Its best-known embodiment is the chloro–methyl exchange rule [10]. Chlorine and the methyl group are among the most widely exploited isosteres precisely because they are sterically similar yet electronically opposed: their van der Waals volume increments (ca. 22 and ca. $25 \text{ \AA}^3$) and effective radii (1.75 and ca. $2.0 \text{ \AA}$) differ only marginally, whereas chlorine is a σ -withdrawing substituent bearing a pronounced C–Cl dipole and an electrophilic σ -hole capable of halogen bonding [11, 12], while methyl is a weak σ -donor and a source of C–H donors. This duality underlies the use of $\text{Cl} \leftrightarrow \text{CH}_3$ replacement in medicinal chemistry

[13–17], exemplified by analogues of the complex II inhibitor atpenin A5, where the exchange left activity essentially unchanged [18].

That the rule is not universal: isostructurality holds for bulky, irregular molecules with preferably a single chlorine, but fails for flatter species, where type-II Cl...Cl contacts impose directional preferences no methyl group can reproduce [10]. CSD surveys accordingly find only about one third of Cl/CH₃ pairs isostructural [19] – validating the rule as a heuristic while showing that the substitution is far from crystallochemically neutral.

Almost all of this evidence concerns organic solids. In coordination compounds the balance of interactions differs qualitatively: metal-centred contacts, polar ligands and the enhanced polarisability of heavy centres compete with the peripheral interactions that govern organic packing [20–23]. Cyclometallated Pt(II) complexes are especially informative here: their square-planar geometry permits π -stacking and Pt...Pt metallophilic association, but by no means enforces it – closely related complexes crystallise with and without short Pt...Pt contacts, and the difference translates directly into colour and emission energy [24–31]. The packing question is thus functional rather than merely structural, yet the outcome is decided by peripheral substituents whose influence remains poorly rationalised.

We therefore examine two hitherto unreported cyclometallated Pt(II) thiocyanate–isocyanide complexes differing solely in one *ortho* substituent of the aryl ring: the 2,6-dichlorophenyl derivative (**1**) and its 2-chloro-6-methylphenyl analogue (**2**). This single, site-specific Cl $\leftrightarrow$ CH₃ replacement minimises steric perturbation and largely isolates the electronic contribution of the substituent. Crystallising both from a range of solvents, we establish the conditions under which each polymorph and solvate forms, compare the resulting structures, and analyse the noncovalent interactions that direct them – thereby testing how far Kitaigorodskii's close-packing expectation survives the transition from organic to metal-containing solids

2. Experimental section

2.1. Reagents, instrumentation, and methods

Solvents and all reagents were obtained from commercial sources and used as received, with the exception of CH₂Cl₂, which was purified by the conventional distillation over CaCl₂. The [Pt(ppy)(Cl)]₂ was prepared by the known procedure [32]. Infrared spectra (4000–400 cm⁻¹) were recorded on Shimadzu IRAffinity-1 FTIR spectrophotometer in KBr or CsI pellets. NMR spectra were recorded on Bruker AVANCE III 400 spectrometers in CDCl₃ at ambient temperature (at 400 and 86 MHz for ¹H and ¹⁹⁵Pt NMR, respectively). Chemical shifts are given in δ -values [ppm] referenced to the residual signals of undeuterated solvent (CHCl₃): δ 7.27 (¹H). K₂[PtCl₄] in D₂O was used as a standard for the ¹⁹⁵Pt NMR measurements. The HRESI⁺-MS data were obtained on a “MaXis”, Bruker Daltonik GmbH (Billerica, MA, USA), spectrometer equipped with an electrospray ionization (ESI) source; MeOH was used as a solvent. All syntheses were performed under ambient conditions.

2.2. Synthesis of **1** and **2**

A screw-cap vial was charged with solid $[\text{Pt}(\text{ppy})(\mu\text{-Cl})]_2$ (30 mg, 0.04 mmol), the appropriate aryl isocyanide (0.08 mmol, 14 mg of 2,6-dichlorophenyl isocyanide or 12 mg of 2-chloro-6-methylphenyl isocyanide), and NaSCN (65 mg, 0.8 mmol). Acetone (3 mL) was added, and the resulting suspension was stirred at room temperature for 3 days in the closed vial. After this period, the mixture was diluted with CH_2Cl_2 (10 mL) and stirred until complete dissolution of the solid, which was accompanied by the disappearance of its characteristic luminescence. The solution was filtered through paper, and the filtrate was concentrated under reduced pressure at ambient temperature. The crude residue was recrystallised from a $\text{CH}_2\text{Cl}_2/n$ -hexane mixture (1:3) and dried in vacuo.

Compound 1 (X = Cl): yellow microcrystalline powder. Yield: 45 mg (97%). Anal. Calcd for $\text{C}_{19}\text{H}_{11}\text{N}_3\text{Cl}_2\text{PtS}$: 39.39; H, 1.91; N, 7.25. Found: C, 40.01; H, 2.0; N, 7.18. HRMS (ESI⁺): m/z calcd for $[\text{C}_{19}\text{H}_{11}\text{N}_3\text{Cl}_2\text{NaPtS}]^+$ 600.9591; found 600.9587. IR of crystals **1**^I (from CHCl_3): 2194, 2078, 1609. IR of crystals **1**^{II} (from CH_2Cl_2): 2194, 2075, 1610. ¹H NMR (400.13 MHz, CDCl_3 , mixture of N- and S-isomers): δ 7.11–7.15 (m, 2H), 7.16–7.20 (m, 2H), 7.35–7.39 (m, 2H), 7.42–7.46 (m, 2H), 7.49–7.53 (m, 5H), 7.55–7.57 (m, 2H), 7.61–7.63 (m, 1H), 7.72–7.74 (m, 1H), 7.79–7.81 (m, 2H), 7.95–7.99 (m, 2H), 8.97–9.27 (m, 2H, H11). ¹⁹⁵Pt{¹H} NMR (86.015 MHz, CDCl_3): δ – 3872 and – 3973 (ratio ca. 0.3:1) for S- and N-bound isomers, respectively.

Compound 2 (X = Me): yellow microcrystalline powder. Yield: 42 mg (93%). Anal. Calcd for $\text{C}_{20}\text{H}_{14}\text{N}_3\text{ClPtS}$: C, 42.98; H, 2.52; N, 7.52. Found: C, 42.30; H, 2.47; N, 7.33. HRMS (ESI⁺): m/z calcd for $[\text{C}_{20}\text{H}_{14}\text{N}_3\text{ClNaPtS}]^+$ 581.0137; found 581.0142. IR of crystals **2**· CHCl_3 (from CHCl_3): 2198, 2087, 1608. IR of microcrystalline powder **2** (from CH_2Cl_2): 2196, 2088, 1610. ¹H NMR (400.13 MHz, CDCl_3 , mixture of isomers): δ 2.65 and 2.70 (two singlets, 6H, CMe), 7.10–7.15 (m, 2H), 7.15–7.19 (m, 2H), 7.29–7.31 (m, 2H), 7.34–7.37 (m, 3H), 7.39–7.42 (m, 2H), 7.54–7.56 (m, 2H), 7.60–7.62 (m, 1H), 7.71–7.73 (m, 1H), 7.78–7.80 (m, 2H), 7.83–7.85 (m, 1H), 7.94–7.98 (m, 2H), 8.95–8.96 (m, 1H, H11), 9.21–9.22 (m, 1H, H11). ¹⁹⁵Pt{¹H} NMR (86.015 MHz, CDCl_3): δ – 3886 and – 3989 (ratio ca. 0.3:1) for S- and N-bound isomers, respectively.

2.3. X-ray diffraction

Single crystals suitable for X-ray diffraction were obtained by slow evaporation of solutions of **1** and **2** in CHCl_3 and CH_2Cl_2 at room temperature. Suitable single crystals were selected and mounted on a MiTeGen tip via crystallographic oil. Data were collected using Xcalibur, Eos diffractometer (monochromated MoK α radiation, λ = 0.71073 Å) at 100(2) K. In each case, the structure was solved with the ShelXT [33] structure solution program using Intrinsic Phasing and refined with the ShelXL [33] refinement package incorporated in the OLEX2 program package [34] using Least Squares minimization. Empirical absorption correction was applied in CrysAlisPro program complex using spherical harmonics, implemented in SCALE3 ABSPACK scaling algorithm [35]. The crystal data, data collection parameters,

and structure refinement data are given in Table 1, a selected bond lengths and angles are given in **Table S2** and **Table S3**. CCDC 2581129, 2581126, 2581133, and 2581131 contain the supplementary crystallographic data for this paper. These data are provided free of charge by The Cambridge Crystallographic Data Centre.

Table 1
Crystal data and structure refinement.

CCDC	1 ^I	1 ^{II}	2	2·CHCl ₃
	2581129	2581126	2581133	2581131
Empirical formula	C ₁₉ H ₁₁ Cl ₂ N ₃ PtS	C ₁₉ H ₁₁ Cl ₂ N ₃ PtS	C ₂₀ H ₁₄ ClN ₃ PtS	C _{16.8} H ₁₂ Cl _{3.2} N _{2.4} Pt _{0.8} S _{0.8}
Formula weight	579.36	579.36	558.94	542.65
Temperature, K	99.9(8)	9.99(10)	100.0(3)	100(1)
Crystal system	triclinic	monoclinic	triclinic	monoclinic
Space group	P-1	I2/a	P-1	I2/a
a, Å	11.2073(3)	12.9903(4)	11.2765(2)	13.3839(3)
b, Å	13.6109(4)	11.2290(3)	13.6403(3)	11.3118(3)
c, Å	13.8887(5)	24.5542(6)	14.1284(2)	30.3313(8)
α, °	66.909(3)	90	65.903(2)	90
β, °	89.814(2)	90.426(3)	89.1210(10)	99.718(2)
γ, °	69.322(2)	90	69.088(2)	90
Volume, Å ³	1800.67(11)	3581.57(17)	1831.32(7)	4526.1(2)
Z	4	8	4	10
ρ _{calc} , g/cm ³	2.137	2.149	2.027	1.991
μ, mm ⁻¹	18.456	18.558	16.805	6.779
F(000)	1096.0	2192.0	1064.0	2592.0
Crystal size, mm ³	0.06 × 0.05 × 0.03	0.06 × 0.04 × 0.03	0.06 × 0.05 × 0.03	0.09 × 0.07 × 0.03
Radiation	Cu Kα (λ = 1.54184)	Cu Kα (λ = 1.54184)	Cu Kα (λ = 1.54184)	Mo Kα (λ = 0.71073)
2θ range for data collection, °	7.006 to 134.98	7.2 to 134.998	6.936 to 153.872	5.204 to 55.988
Index ranges	-13 ≤ h ≤ 13, -16 ≤ k ≤ 16, -16 ≤ l ≤ 16	-15 ≤ h ≤ 15, -13 ≤ k ≤ 13, -29 ≤ l ≤ 22	-14 ≤ h ≤ 14, -17 ≤ k ≤ 17, -17 ≤ l ≤ 15	-17 ≤ h ≤ 17, -14 ≤ k ≤ 14, -38 ≤ l ≤ 39
Reflections collected	25021	15191	23628	19122

CCDC	1^I	1^{II}	2	2·CHCl₃
	2581129	2581126	2581133	2581131
Independent reflections	6482	3178	7429	5262
Data/restraints/-parameters	6482/0/469	3178/0/235	7429/0/473	5262/0/266
Goodness-of-fit on F^2	1.108	1.058	1.039	1.047
Final R indexes [$I \geq 2\sigma(I)$]	$R_1 = 0.0279$, $wR_2 = 0.0739$	$R_1 = 0.0282$, $wR_2 = 0.0755$	$R_1 = 0.0375$, $wR_2 = 0.0996$	$R_1 = 0.0264$, $wR_2 = 0.0627$
Final R indexes [all data]	$R_1 = 0.0307$, $wR_2 = 0.0753$	$R_1 = 0.0289$, $wR_2 = 0.0761$	$R_1 = 0.0417$, $wR_2 = 0.1025$	$R_1 = 0.0316$, $wR_2 = 0.0655$
Largest diff. peak/hole, $e \cdot \text{\AA}^{-3}$	2.52/-1.02	0.99/-2.25	1.22/-0.70	1.77/-1.68

3. Results and discussion

3.1. Synthesis and general characterization

The cyclometalated platinum(II) thiocyanate–isocyanide complexes **1** and **2** of the general formula $[\text{Pt}(\text{ppy})(\text{NCS})(\text{CNC}_6\text{H}_3\text{-2-Cl-6-X})]$ ($X = \text{Cl}$ for **1**, $X = \text{Me}$ for **2**) were obtained via a one-pot reaction of the chloro-bridged dimer $[\text{Pt}(\text{ppy})(\mu\text{-Cl})]_2$ with a stoichiometric amount of the corresponding aryl isocyanide and a tenfold excess of sodium thiocyanate (Scheme 1). The transformation involves the simultaneous cleavage of the chloride bridges, induced by isocyanide coordination, and the nucleophilic substitution of the chloride ligand by the thiocyanate anion. Compounds **1** and **2** were isolated as air-stable yellow powders. Elemental analysis (C, H, N) and high-resolution mass spectrometry (HRMS ESI⁺, $[\text{M} + \text{Na}]^+$ peaks with characteristic isotope patterns) are in full agreement with the proposed molecular formulas.

IR spectroscopy was employed to establish the coordination mode of the thiocyanate ligand in **1** and **2**. According to the generally accepted criterion [36–38], the $\nu(\text{C} \equiv \text{N})$ stretching frequency for *N*-bonded (isothiocyanato) metal complexes typically appears near 2050 cm^{-1} as a strong band, whereas *S*-bonded (thiocyanato) isomers show a weaker absorption close to 2100 cm^{-1} [38]. In the solid-state IR spectra of **1** and **2** (KBr pellets), two characteristic bands are observed in the $2100\text{--}2200 \text{ cm}^{-1}$ region. The intense absorption at $2188\text{--}2197 \text{ cm}^{-1}$ is assigned to the $\nu(\text{C} \equiv \text{N})$ stretch of the coordinated isocyanide ligand [39–43]. The second band, located at $2074\text{--}2098 \text{ cm}^{-1}$, corresponds to the $\nu(\text{C} \equiv \text{N})$ vibration of the thiocyanate group [44–48]. Although this value is somewhat higher than the typical 2050 cm^{-1} quoted for pure *N*-coordination, the unambiguous assignment to the *N*-bound form is further supported by the

presence of the $\delta(\text{NCS})$ bending mode at 450–490 cm^{-1} , which is characteristic of N-coordinated thiocyanate [44–48].

However, in CDCl_3 solution, a dynamic equilibrium between N-bound and S-bound isomers is observed, as previously reported for related cyclometalated Pt(II) systems [49, 50]. At room temperature, the ^1H and $^{195}\text{Pt}\{^1\text{H}\}$ NMR spectra exhibit two sets of signals with an intensity ratio of 0.3:1 in favour of the N-isomer, separated by approximately 100 ppm. The high-frequency resonance in the ^{195}Pt spectra ($\delta = -3872$ and -3886 ppm for **1** and **2**, respectively) is attributed to the N-isomer, whereas the low-frequency signal ($\delta = -3973$ and -3989 ppm) corresponds to the S-isomer, based on literature precedents [49, 51, 52].

3.2. Polymorphic behaviour of compound 1

Compound **1** crystallises in two distinct polymorphic modifications depending on the solvent employed. Crystallisation from CH_2Cl_2 affords the triclinic polymorph **1^I** (space group $P\bar{1}$, $\rho = 2.137 \text{ g}\cdot\text{cm}^{-3}$), which contains two crystallographically independent molecules (Pt1 and Pt2) in the asymmetric unit. These independent molecules exhibit minor conformational differences, manifested in distinct torsion angles within the chelate ring – for example, the Pt1–N1–C7–C6 torsion of $3.7(6)^\circ$ versus the Pt2–N4–C26–C25 torsion of $-3.8(9)^\circ$ for the analogous fragment in the second molecule – indicating opposite directions of chelate ring puckering. In contrast, crystallisation from CHCl_3 yields the monoclinic polymorph **1^{II}** (space group $I2/a$, $\rho = 2.149 \text{ g}\cdot\text{cm}^{-3}$), featuring a single crystallographically unique molecule related by symmetry operations. The higher density of **1^{II}** (2.149 vs. $2.137 \text{ g}\cdot\text{cm}^{-3}$) suggests that this modification represents the thermodynamically more stable packing arrangement.

3.3 Solvatomorphic behaviour of compound 2

For compound **2**, the choice of crystallisation solvent determines the formation of either a solvate or a desolvated form. Crystallisation from CHCl_3 produces the solvate **2**· CHCl_3 (monoclinic, space group $I2/a$, $\rho = 1.991 \text{ g}\cdot\text{cm}^{-3}$), in which the chloroform molecule occupies a partially disordered position with 0.8 occupancy. Crystallisation from CH_2Cl_2 , however, yields the desolvated form **2** (triclinic, space group $P\bar{1}$, $\rho = 2.027 \text{ g}\cdot\text{cm}^{-3}$), containing two independent molecules in the asymmetric unit. Notably, the volume per complex molecule in **2**· CHCl_3 ($452.6 \text{ \AA}^3$) is slightly smaller than in the desolvated structure **2** ($457.8 \text{ \AA}^3$), indicating more efficient packing of the complex in the monoclinic solvate modification despite the presence of included solvent molecules. The lower overall density of **2**· CHCl_3 compared with **2** (1.991 vs. $2.027 \text{ g}\cdot\text{cm}^{-3}$) is attributed to the intrinsically lower density of chloroform relative to the organometallic complex.

3.4. Isostructural relationships between Cl and CH_3 substituted analogues

Comparison of the crystal structures reveals an interesting pattern associated with the isosteric $\text{Cl} \leftrightarrow \text{CH}_3$ replacement. The triclinic forms **1^I** and **2**, both obtained from CH_2Cl_2 , exhibit essentially complete

isostructurality [53]: both crystallise in space group $P\bar{1}$ with two independent molecules in the asymmetric unit, and their unit cell parameters differ by less than 2% in volume (1800.7 vs. 1831.3 Å³). To quantify this similarity, we applied the isostructurality indices proposed by Kálmán [54, 55]. The cell similarity index (π), calculated using the sum of orthogonalised unit cell parameters, yields $\pi = 0.009$ for the **1**^I/**2** pair – a value very close to zero, confirming near-identical cell dimensions. Such close packing similarity is a direct consequence of the almost identical sizes of the Cl and CH₃ substituents, confirming the applicability of the chloro–methyl exchange rule to this system.

In the case of the monoclinic modifications **1**^{II} and **2**·CHCl₃, both obtained from CHCl₃, the situation is different. Despite sharing the same space group $I2/a$, their unit cells differ markedly: the presence of chloroform molecules in **2**·CHCl₃ leads to a substantial increase in the *c* parameter (from 24.55 to 30.33 Å) and in the overall cell volume (from 3581.6 to 4526.1 Å³). Accordingly, the cell similarity index for this pair is $\pi = 0.114$, reflecting the significant cell expansion induced by solvate incorporation. Thus, these forms are not isostructural; they rather represent structurally related packing arrangements in which solvate molecules are incorporated into the lattice, altering its periodicity while preserving the symmetry and general organisation of the complex molecules. This distinction emphasises that solvation can break isostructurality even when the substituents themselves remain isosteric.

3.5. Molecular geometry and coordination environment

In all four crystalline forms, the Pt(II) centre adopts a distorted square-planar geometry with a *trans* arrangement of the isocyanide carbon and the cyclometalated ligand nitrogen atom; the thiocyanate ligand is N-coordinated (Fig. 1). Pt–N = CS angles ranging from 158.1(5)° to 173.8(5)°, consistent with previously reported structural data for platinum complexes with *N*-coordinated thiocyanate ligands. The Pt–C bond lengths (Table S2 in SI) and Pt–N distances fall within the typical ranges reported for related Pt(II) complexes [49, 50, 56].

3.6. Intermolecular Interactions and Supramolecular Architecture

Analysis of intermolecular contacts reveals distinct differences between the triclinic and monoclinic structures. In the triclinic forms **1**^I and **2** (both with two independent molecules), two types of interactions are observed: Pt···Pt metallophilic contacts between molecules Pt1 and Pt2 (Fig. 2A, Table 2), and a pair of symmetric Pt···N donor–acceptor interactions between the isocyanide nitrogen of one molecule and the platinum centre of another (Fig. 2B).

The Pt···Pt distances in **1**^I and **2** are 3.5524(4) Å and 3.5035(4) Å, respectively, corresponding to 103%/78% and 102%/77% of the respective sums of van der Waals radii (3.44 Å according to Bondi [57] or 4.58 Å according to Alvarez [58]). This indicates a genuine, albeit weak, closed-shell Pt(II)···Pt(II) interaction [29]. Notably, the Pt···Pt contact in **2** is shorter by ca. 0.05 Å, suggesting that the electron-

donating methyl substituent increases the electron density at the platinum centre, thereby enhancing metallophilic attraction compared to the more electron-withdrawing chlorine in **1^I**.

The Pt...N distances, which range from 3.610(6) to 3.646(6) Å, are longer than the sum of van der Waals radii according to Bondi (3.38 Å, 111–112%), but shorter than the sum according to Alvarez (3.94 Å, 91–92%). It was previously reported that when ligated isocyanides are bound to high-oxidation state metal ions, they can be involved in π -hole... d_z^2 -[M] [59–61], π -hole... π [62], and π -hole...lone pair [63, 64] interactions. In our case, the Pt...N contacts fall within the range typically associated with π -hole... d_z^2 -[M] interactions involving the electrophilic π -hole of the coordinated aryl isocyanide and the filled d_z^2 -orbital of the adjacent Pt(II) centre. The fact that these distances are systematically shorter in **2** (3.610–3.622 Å) than in **1^I** (3.635–3.646 Å) further supports the notion that the methyl substituent not only strengthens Pt...Pt contacts but also facilitates better orbital overlap in the Pt...N donor–acceptor interaction. Consequently, the symmetric Pt...N and Pt...Pt interactions cooperate to form a supramolecular 1D architecture (Fig. 2C).

Table 2
Geometrical parameters of short contacts.

Contact		Distance, Å	$R^{a/b}$
1^I	Pt1...Pt2	3.5524(4)	1.03/0.78
	Pt1...N2	3.635(5)	1.12/0.92
	Pt2...N5	3.646(6)	1.12/0.92
2	Pt1...Pt2	3.5035(4)	1.02/0.77
	Pt1...N2	3.622(7)	1.11/0.92
	Pt2...N5	3.610(6)	1.10/0.91
1^{II}	Pt1...Pt1	3.3532(6)	0.97/0.73
2·CHCl₃	Pt1...Pt1	3.4605(8)	1.01/0.76
$R = d(X...Y)/(\sum vdW (X + Y))$, X = I, N; Y = Cl, Pt; ^a Bondi [57] and ^b Alvarez [58] van der Waals radii were used.			

In contrast, in the monoclinic forms **1^{II}** and **2·CHCl₃**, each molecule participates exclusively in symmetric dimers *via* Pt...Pt contacts (Fig. 3, Table 2), with the shortest inter-dimer Pt...Pt distances exceeding 5.0 Å. The Pt...Pt distances in the dimers are 3.3532(6) Å for **1^{II}** and 3.4605(8) Å for **2·CHCl₃**, corresponding to 97%/73% and 101%/76% of the van der Waals sums, respectively. The dimer in **1^{II}** exhibits the shortest Pt...Pt contact among all structures, and indicating significant orbital overlap between the closed-shell d^8 centres [65]. In **2·CHCl₃**, the Pt...Pt distance is slightly longer, which may be attributed to the presence of

chloroform molecules in the lattice. Importantly, in both monoclinic structures, the Pt $\cdots$ N contacts are absent (the closest Pt $\cdots$ N distances exceed 4.5 Å).

It is worth noting that the Cl $\leftrightarrow$ CH₃ substitution does not change the overall supramolecular motif within each packing family: both triclinic forms are chain-like, and both monoclinic forms are dimeric. This conservation of the primary architecture across the isosteric replacement, regardless of the electronic differences between Cl and CH₃, reinforces the crystallochemical silence of the substitution at the level of supramolecular organisation, fully consistent with Kitaigorodskii's close-packing principle. At the same time, the ability to switch between chain and dimer motifs by simply changing the crystallisation solvent demonstrates that external factors can override the intrinsic preferences of the substituent.

3.7. Photophysical properties

The UV–vis absorption spectra of **1** and **2** are essentially similar, indicating that the substituent on the arylisocyanide ligand does not significantly affect the electronic transitions (Fig. 4, **Table S1** in SI). As observed for other cyclometallated platinum(II) complexes [43, 66–70], the spectra display two distinct regions: intense high-energy bands below 340 nm assigned to spin-allowed π – π^* ligand-centered transitions, and weaker low-energy bands in the 400–450 nm region attributed to mixed ¹LC/¹MLCT character. Both complexes exhibit luminescence in solution and in the solid state at room temperature. In solution the well-resolved vibronic progression with a spacing of ca. 1300–1400 cm^{–1} indicates a predominant ³LC character for the emissive state, with a minor ³MLCT contribution, in agreement with related Pt(II) systems [43, 66–70]. The emission maxima are independent of the nature of the substituent, consistent with the absorption data. In the solid state, the luminescence spectra are red-shifted and significantly broadened compared to solution, with additional shoulders at 565–594 nm ascribed to excimeric emission arising from intermolecular Pt $\cdots$ Pt and/or π – π interactions. This assignment is corroborated by the crystallographic data, which reveal close Pt $\cdots$ Pt contacts and π -stacking in the crystal lattice, as discussed above.

4. Conclusions

Two previously unreported cyclometallated platinum(II) complexes bearing thiocyanate and arylisocyanide ligands, **1** (2,6-dichlorophenyl isocyanide) and **2** (2-chloro-6-methylphenyl isocyanide), have been synthesised and characterised. X-ray diffraction and IR spectroscopy establish that the ambidentate ligand is N-bound (isothiocyanato) in the solid state, whereas multinuclear NMR reveals a dynamic N/S linkage equilibrium in solution, strongly shifted towards the N-isomer.

Complex **1** crystallises as two polymorphs – triclinic **1^I** (CH₂Cl₂) and monoclinic **1^{II}** (CHCl₃) – while **2** gives the solvate **2**·CHCl₃ from CHCl₃ and the unsolvated triclinic form **2** from CH₂Cl₂. The like-for-like comparison, **1^I** vs. **2**, shows the two to be isostructural, so that at this site the Cl $\leftrightarrow$ CH₃ replacement is indeed crystallochemically silent, in line with Kitaigorodskii's close-packing expectation. The chloroform solvate **2**·CHCl₃, by contrast, differs from **1^I** through solvent inclusion rather than through the substituent,

and therefore does not constitute a violation of the rule. Both triclinic structures are built from chains combining Pt...Pt metallophilic contacts with π -hole(isocyano group)... d_z^2 -[Pt] interactions, whereas the monoclinic forms contain only isolated Pt...Pt dimers.

Both complexes luminesce in solution and in the solid state at room temperature. Solution spectra are essentially independent of substituent, consistent with a predominantly ligand-centred emissive state. In the solid state the emission is red-shifted and broadened.

Declarations

5. Conflicts of interest

The authors declare no competing interests.

7. Funding

The work was supported by the Russian Science Foundation (project 25-23-00345).

Author Contribution

A.E.V. performed the synthesis and crystal growth. M.V.K. carried out the X-ray diffraction experiments. M.A.K. supervised the research. All authors contributed to the writing and editing of the manuscript.

Acknowledgement

Measurements were performed at the Center for Magnetic Resonance, Center for X-ray Diffraction Studies, Center for Chemical Analysis and Materials Research, Centre for Optical and Laser Materials Research and Computing Center (all belonging to St Petersburg State University).

Data Availability

The data that support the findings of this study are fully available within the article and its supplementary information files. Crystallographic data, spectroscopic measurements, and all other experimental details are provided in the Supporting Information accompanying this manuscript.

References

1. Price SL (2014) Predicting crystal structures of organic compounds. Chem Soc Rev 43(7):2098–2111. <https://doi.org/10.1039/c3cs60279f>

2. Desiraju GR (2013) Crystal Engineering: From Molecule to Crystal. *J Am Chem Soc* 135(27):9952–9967. <https://doi.org/10.1021/ja403264c>
3. Nangia A (2008) Conformational Polymorphism in Organic Crystals. *Acc Chem Res* 41(5):595–604. <https://doi.org/10.1021/ar700203k>
4. Beran GJO (2016) Modeling Polymorphic Molecular Crystals with Electronic Structure Theory. *Chem Rev* 116(9):5567–5613. <https://doi.org/10.1021/acs.chemrev.5b00648>
5. Bernstein J (2011) Polymorphism – A Perspective: Published as part of the Crystal Growth & Design 10th Anniversary Perspective. *Cryst Growth Des* 11(3):632–650. <https://doi.org/10.1021/cg1013335>
6. Nyman J, Day GM (2015) Static and lattice vibrational energy differences between polymorphs. *CrystEngComm* 17(28):5154–5165. <https://doi.org/10.1039/c5ce00045a>
7. Saha BK, Nath NK, Thakuria R (2023) Polymorphs with Remarkably Distinct Physical and/or Chemical Properties. *Chem Rec* 23(1):e202200173. <https://doi.org/10.1002/tcr.202200173>
8. Jayant V, Yusuf M (2024) Insights into polymorphism and inclusion properties in organic compounds. *Discov Chem* 1(1):52. <https://doi.org/10.1007/s44371-024-00054-2>
9. Kitaigorodskii AI (1973) *Molecular Crystals and Molecules*. Academic, New York
10. Desiraju GR, Sarma JARP (1986) The chloro-methyl exchange rule and its violations in the packing of organic molecular solids. *J Chem Sci* 96(6):599–605. <https://doi.org/10.1007/BF02936309>
11. Cavallo G, Metrangolo P, Milani R, Pilati T, Priimagi A, Resnati G, Terraneo G (2016) The Halogen Bond. *Chem Rev* 116(4):2478–2601. <https://doi.org/10.1021/acs.chemrev.5b00484>
12. Gilday LC, Robinson SW, Barendt TA, Langton MJ, Mullaney BR, Beer PD (2015) Halogen Bonding in Supramolecular Chemistry. *Chem Rev* 115(15):7118–7195. <https://doi.org/10.1021/cr500674c>
13. Thornber CW (1979) Isosterism and molecular modification in drug design. *Chem Soc Rev* 8(4):563–580. <https://doi.org/10.1039/cs9790800563>
14. Patani GA, LaVoie EJ (1996) Bioisosterism: A Rational Approach in Drug Design. *Chem Rev* 96(8):3147–3176. <https://doi.org/10.1021/cr950066q>
15. Jayashree BS, Nikhil PS, Soumyajeet P (2022) Bioisosterism in Drug Discovery and Development - An Overview. *Med Chem* 18(9):915–925. <https://doi.org/10.2174/1573406418666220127124228>
16. Verma A, Waiker DK, Gupta PS, Kumar M, Shrivastava SK (2025) Bioisosterism: an approach to develop new anti-cancer agents. *Eur J Med Chem* 300:118166. <https://doi.org/10.1016/j.ejmech.2025.118166>
17. Brown N (2012) *Bioisosterism in Medicinal Chemistry*, in *Bioisosteres in Medicinal Chemistry*. pp. 1–14
18. Krautwald S, Nilewski C, Mori M, Shiomi K, Ōmura S, Carreira EM (2016) Bioisosteric Exchange of C - Chloro and Methyl Substituents: Synthesis and Initial Biological Studies of Atpenin A5 Analogues. *Angew Chem* 128(12):4117–4121. <https://doi.org/10.1002/ange.201511672>
19. Edwards MR, Jones W, Motherwell WDS, Shields GP (2001) Crystal Engineering and Chloro-Methyl Interchange—a CSD Analysis. *Mol Cryst Liq Cryst Sect A* 356(1):337–353. <https://doi.org/10.1080/10587250108023713>

20. Li C-P, Du M (2011) Role of solvents in coordination supramolecular systems. *Chem Commun* 47(21):5958–5972. <https://doi.org/10.1039/c1cc10935a>
21. Bokach NA, Kukushkin VY (2025) From covalent to noncovalent: The role of metals in activating ligand sites toward noncovalent interactions (NCIs). *Coord Chem Rev* 529:216440. <https://doi.org/10.1016/j.ccr.2025.216440>
22. Braga D, Grepioni F, Desiraju GR (1998) Crystal Engineering and Organometallic Architecture. *Chem Rev* 98(4):1375–1406. <https://doi.org/10.1021/cr960091b>
23. Tiekink ERT (2017) Supramolecular assembly based on emerging intermolecular interactions of particular interest to coordination chemists. *Coord Chem Rev* 345:209–228. <https://doi.org/10.1016/j.ccr.2017.01.009>
24. Li K, Ming Tong GS, Wan Q, Cheng G, Tong W-Y, Ang W-H, Kwong W-L, Che C-M (2016) Highly phosphorescent platinum(ii) emitters: photophysics, materials and biological applications. *Chem Sci* 7(3):1653–1673. <https://doi.org/10.1039/C5SC03766B>
25. Amouri H (2022) Luminescent Complexes of Platinum, Iridium, and Coinage Metals Containing N-Heterocyclic Carbene Ligands: Design, Structural Diversity, and Photophysical Properties. *Chem Rev.* <https://doi.org/10.1021/acs.chemrev.2c00206>
26. Yam VWW, Law ASY (2020) Luminescent d(8) metal complexes of platinum(II) and gold(III): From photophysics to photofunctional materials and probes. *Coord Chem Rev* 414:213298. <https://doi.org/10.1016/j.ccr.2020.213298>
27. Ravotto L, Ceroni P (2017) Aggregation induced phosphorescence of metal complexes: From principles to applications. *Coord Chem Rev* 346:62–76. <https://doi.org/https://doi.org/10.1016/j.ccr.2017.01.006>
28. Han Y, Gao Z, Wang C, Zhong R, Wang F (2020) Recent progress on supramolecular assembly of organoplatinum(II) complexes into long-range ordered nanostructures. *Coord Chem Rev* 414:213300. <https://doi.org/https://doi.org/10.1016/j.ccr.2020.213300>
29. Sculfort S, Braunstein P (2011) Intramolecular d10–d10 interactions in heterometallic clusters of the transition metals. *Chem Soc Rev* 40(5):2741–2760. <https://doi.org/10.1039/C0CS00102C>
30. Ito A, Iwamura M, Sakuda E (2022) Excited-state dynamics of luminescent transition metal complexes with metallophilic and donor–acceptor interactions. *Coord Chem Rev* 467:214610. <https://doi.org/https://doi.org/10.1016/j.ccr.2022.214610>
31. Katz MJ, Sakai K, Leznoff DB (2008) The use of aurophilic and other metal-metal interactions as crystal engineering design elements to increase structural dimensionality. *Chem Soc Rev* 37(9):1884–1895. <https://doi.org/10.1039/B709061G>
32. Cave GWV, Fanizzi FP, Deeth RJ, Errington W, Rourke JP (2000) C – H Activation Induced by Water. Monocyclometalated to Dicyclometalated: CANAC Tridentate Platinum Complexes. *Organometallics* 19(7):1355–1364. <https://doi.org/10.1021/om9910423>
33. Sheldrick GM (2008) A short history of SHELX. *Acta Crystallogr A* 64:112–122. <https://doi.org/10.1107/S0108767307043930>

34. Dolomanov OV, Bourhis LJ, Gildea RJ, Howard JAK, Puschmann H (2008) OLEX2: a complete structure solution, refinement and analysis program. *J Appl Crystallogr* 42(2):339–341. <https://doi.org/10.1107/S0021889808042726>
35. Agilent CAPRO (2014) Agilent Technologies Ltd: Yarnton; Oxfordshire
36. Kishi S, Kato M (2003) Thermal and Photo Control of the Linkage Isomerism of Bis(thiocyanato)(2,2'-bipyridine)platinum(II). *Inorg Chem* 42(26):8728–8734. <https://doi.org/10.1021/ic034524m>
37. Paviglianiti AJ, Minn DJ, Fultz WC, Burmeister JL (1989) The conjunctive response to steric hindrance in dithiocyanato[bis(diphenylphosphino)alkyl or aryl]palladium(II) complexes: a new look at a classic series. *Inorg Chim Acta* 159(1):65–82. [https://doi.org/10.1016/S0020-1693\(00\)80897-X](https://doi.org/10.1016/S0020-1693(00)80897-X)
38. Nakamoto K (2008) *Infrared and Raman Spectra of Inorganic and Coordination Compounds: Part A: Theory and Applications in Inorganic Chemistry, 6th Edition.* : John Wiley & Sons, Inc. 432
39. Luzyanin KV, Pombeiro AJL (2012) *Carbene complexes derived from metal-bound isocyanides*, in *Isocyanide chemistry*, V. Nenajdenko, Editor. Wiley-VCH. pp. 531–550
40. Kinzhalov MA, Boyarskii VP (2015) Structure of isocyanide palladium(II) complexes and their reactivity toward nitrogen nucleophiles. *Russ J Gen Chem* 85(10):2313–2333. <https://doi.org/10.1134/S1070363215100175>
41. Ramozzi R, Cheron N, Braidia B, Hiberty PC, Fleurat-Lessard P (2012) A valence bond view of isocyanides' electronic structure. *New J Chem* 36(5):1137–1140. <https://doi.org/10.1039/c2nj40050b>
42. Boyarskiy VP, Bokach NA, Luzyanin KV, Kukushkin VY (2015) Metal-Mediated and Metal-Catalyzed Reactions of Isocyanides. *Chem Rev* 115:2698–2779. <https://doi.org/10.1021/cr500380d>
43. Katkova SA, Luzyanin KV, Novikov AS, Kinzhalov MA (2021) Modulation of luminescence properties for [cyclometalated]-PtII(isocyanide) complexes upon co-crystallisation with halosubstituted perfluorinated arenes. *New J Chem* 45(6):2948–2952. <https://doi.org/10.1039/D0NJ05457G>
44. Mitchell PCH, Williams RJP (1960) 382. The infrared spectra and general properties of inorganic thiocyanates. *J Chem Soc* 1912–1918. <https://doi.org/10.1039/JR9600001912>
45. Nakamoto K (1970) *Infrared spectra of inorganic and coordination compounds*, 2nd edn. Wiley, New York
46. Tau KD, Meek DW (1979) Platinum(II) complexes of the chelating triphosphine bis(3-(diphenylphosphino)propyl)phenylphosphine. Phosphorus-31 NMR studies of the cis and trans influence on these model compounds. *Inorg Chem* 18(12):3574–3580. <https://doi.org/10.1021/ic50202a057>
47. Bertini I, Sabatini A (2002) Infrared Spectra of Substituted Thiocyanate Complexes. The Effect of the Substituent on Bond Type. II *Inorg Chem* 5(6):1025–1028. <https://doi.org/10.1021/ic50040a017>
48. Kashina MV, Kinzhalov MA, Tupikina EY, Kukushkin VY (2023) Linear and Bent Noncovalent M...SCN–M' Interactions: The Case of Palladium(II) and Platinum(II) Thiocyanate Species. *Cryst Growth Des* 23(6):4322–4335. <https://doi.org/10.1021/acs.cgd.3c00116>

49. Antonova EV, Kashina MV, Ivanov DM, Bokach NA, Kinzhalov MA (2025) Crystal engineering with ambidentate thiocyanate: thiocyanate nitrogen as a halogen bond acceptor in platinum(II) complexes. *CrystEngComm* 27(42):6942–6948. <https://doi.org/10.1039/D5CE00678C>
50. Antonova EV, Kinzhalov MA (2026) Synthesis, Structure, and Luminescence of N-Coordinated Thiocyanate Platinum(II) Complex Stabilized by Halogen Bonds. *J Struct Chem* 67(3):700–712. <https://doi.org/10.1134/S0022476626030224>
51. Irmiler P, Winter RF (2016) Complexes trans-Pt(BODIPY)X(PEt₃)₂: excitation energy-dependent fluorescence and phosphorescence emissions, oxygen sensing and photocatalysis. *Dalton Trans* 45(25):10420–10434. <https://doi.org/10.1039/c6dt01623e>
52. Pazireh S, Babadi Aghakhanpour R, Fuertes S, Sicilia V, Niroomand Hosseini F, Nabavizadeh SM (2019) A double rollover cycloplatinated(II) skeleton: a versatile platform for tuning emission by chelating and non-chelating ancillary ligand systems. *Dalton Trans* 48(17):5713–5724. <https://doi.org/10.1039/c9dt00807a>
53. Bombicz P (2024) What is isostructurality? Questions on the definition. *IUCrJ* 11(Pt 1):3–6. <https://doi.org/10.1107/s2052252523010436>
54. Fábián L, Kálmán A (1999) Volumetric measure of isostructurality. *Acta Crystallogr B* 55(Pt 6):1099–1108. <https://doi.org/10.1107/s0108768199009325>
55. Kalman A, Parkanyi L, Argay G (1993) Classification of the isostructurality of organic molecules in the crystalline state. *Acta Crystallogr B* 49(6):1039–1049. <https://doi.org/10.1107/S010876819300610X>
56. Anderson CM, Greenberg MW, LaFratta CN, Lum RH, Oppenheimer EI, Duplessis TS, Tulloch KM, Tanski JM (2025) Dual-Emitting Cyclometalated Platinum Compounds with Isocyanide Ligands. *ACS Omega* 10(41):49052–49060. <https://doi.org/10.1021/acsomega.5c07648>
57. Bondi A (1964) Van der Waals Volumes and Radii. *J Phys Chem* 68(3):441–451. <https://doi.org/10.1021/j100785a001>
58. Alvarez S (2013) A cartography of the van der Waals territories. *Dalton Trans* 42(24):8617–8636. <https://doi.org/10.1039/C3DT50599E>
59. Katkova SA, Mikherdov AS, Sokolova EV, Novikov AS, Starova GL, Kinzhalov MA (2022) Intermolecular (Isocyano group)⋯PtII interactions involving coordinated isocyanides in cyclometalated PtII complexes. *J Mol Struct* 1253:132230. <https://doi.org/10.1016/j.molstruc.2021.132230>
60. Katkova SA, Antonova EV, Cheranyova AM, Ivanov DM, Kinzhalov MA (2023) Solid State Phosphorescence Enhancement of PtII-Based Emitters via Combination of π-Hole(Isocyano Group)⋯dz²[PtII] and I⋯Cl Halogen-Bonding Interactions. *Inorganics* 11(10):403. <https://doi.org/10.3390/inorganics11100403>
61. Katkova SA, Mikherdov AS, Kinzhalov MA, Novikov AS, Zolotarev AA, Boyarskiy VP, Kukushkin VY (2019) (Isocyano Group pi-Hole)⋯ dz²-M-II Interactions of (Isocyanide) M-II Complexes, in which Positively Charged Metal Centers (d(8)-M = Pt, Pd) Act as Nucleophiles. *Chem.Eur. J.* 25(36):8590–8598. <https://doi.org/10.1002/chem.201901187>

62. Mikherdov AS, Kinzhalov MA, Novikov AS, Boyarskiy VP, Boyarskaya IA, Avdontceva MS, Kukushkin VY (2018) Ligation-Enhanced π -Hole $\cdots\pi$ Interactions Involving Isocyanides: Effect of π -Hole $\cdots\pi$ Noncovalent Bonding on Conformational Stabilization of Acyclic Diaminocarbene Ligands. *Inorg Chem* 57(11):6722–6733. <https://doi.org/10.1021/acs.inorgchem.8b01027>
63. Mikherdov AS, Katkova SA, Novikov AS, Efremova MM, Reutskaya EY, Kinzhalov MA (2020) (Isocyano group) $\cdots$ lone pair interactions involving coordinated isocyanides: experimental, theoretical and CSD studies. *CrystEngComm* 22(7):1154–1159. <https://doi.org/10.1039/C9CE01741K>
64. Smirnov AS, Kinzhalov MA, Gomila RM, Frontera A, Bokach NA, Kukushkin VY (2023) Isocyanide π -Hole Interactions Supported by Auophilic Forces. *Crystals* 13(8):1177. <https://doi.org/10.3390/cryst13081177>
65. Zheng Q, Borsley S, Nichol GS, Duarte F, Cockroft SL (2019) The Energetic Significance of Metallophilic Interactions. *Angew Chem Int Ed* 58(36):12617–12623. <https://doi.org/10.1002/anie.201904207>
66. Solomatina AI, Chelushkin PS, Abakumova TO, Zhemkov VA, Kim M, Bezprozvanny I, Gurzhiy VV, Melnikov AS, Anufrikov YA, Koshevoy IO, Su S-H, Chou P-T, Tunik SP (2019) Reactions of Cyclometalated Platinum(II) [Pt(N $\wedge$ C)(PR₃)Cl] Complexes with Imidazole and Imidazole-Containing Biomolecules: Fine-Tuning of Reactivity and Photophysical Properties via Ligand Design. *Inorg Chem* 58(1):204–217. <https://doi.org/10.1021/acs.inorgchem.8b02204>
67. Jamshidi M, Babaghasabha M, Shahsavari HR, Nabavizadeh SM (2017) The influence of thiolate ligands on the luminescence properties of cycloplatinated(ii) complexes. *Dalton Trans* 46(45):15919–15927. <https://doi.org/10.1039/C7DT03599C>
68. Dobrynin MV, Sokolova EV, Kinzhalov MA, Smirnov AS, Starova GL, Kukushkin VY, Islamova RM (2021) Cyclometalated Platinum(II) Complexes Simultaneously Catalyze the Cross-Linking of Polysiloxanes and Function as Luminophores. *ACS Appl Polym Mater* 3(2):857–866. <https://doi.org/10.1021/acsapm.0c01190>
69. Moreno MT, Lalinde Peña E, Martínez-Junquera M, Alfaro-Arnedo E, López I, Larráyoz I, Pichel JGG (2021) Luminescent Cyclometalated Platinum(II) Complexes with Acyclic Diaminocarbene Ligands: Structural, Photophysical and Biological Properties. *Dalton Trans* 50:4539–4554. <https://doi.org/10.1039/D1DT00480H>
70. Nguyen YH, Wu Y, Dang VQ, Jiang C, Teets TS (2024) Combined Nucleophilic and Electrophilic Functionalization to Optimize Blue Phosphorescence in Cyclometalated Platinum Complexes. *J Am Chem Soc* 146(13):9224–9229. <https://doi.org/10.1021/jacs.4c00203>

Figures

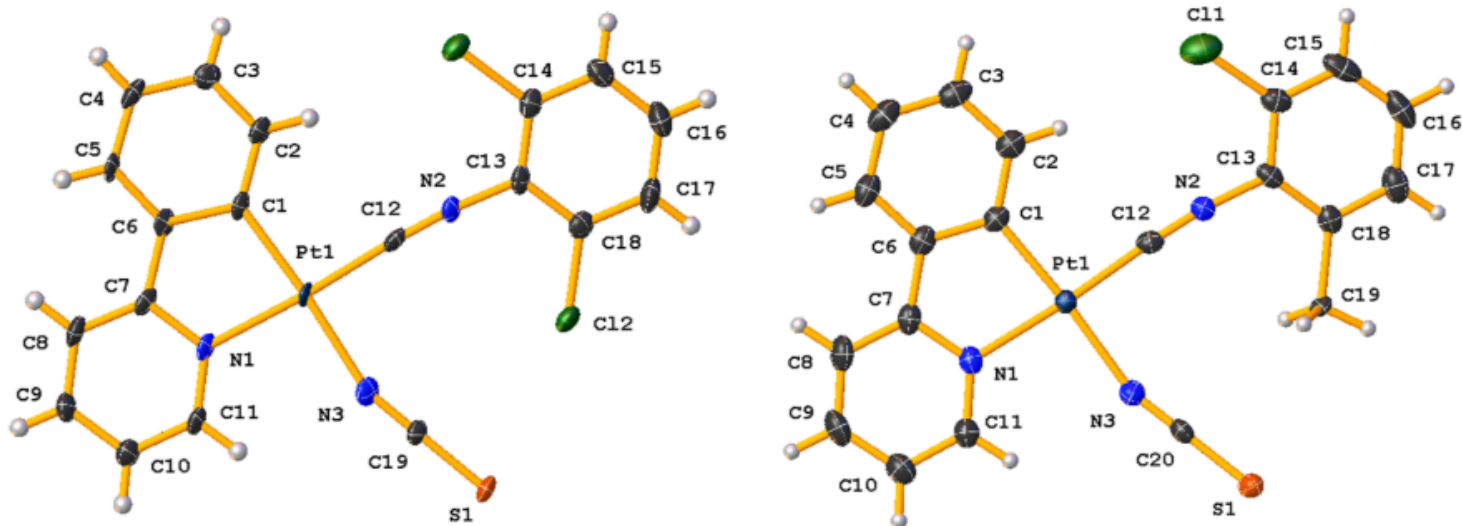


Figure 1

X-ray structures of **1^{II}** (left) and **2·CHCl₃** (right, CHCl₃ omitted for clarity). Structures of **1^I** and **2** are similar.

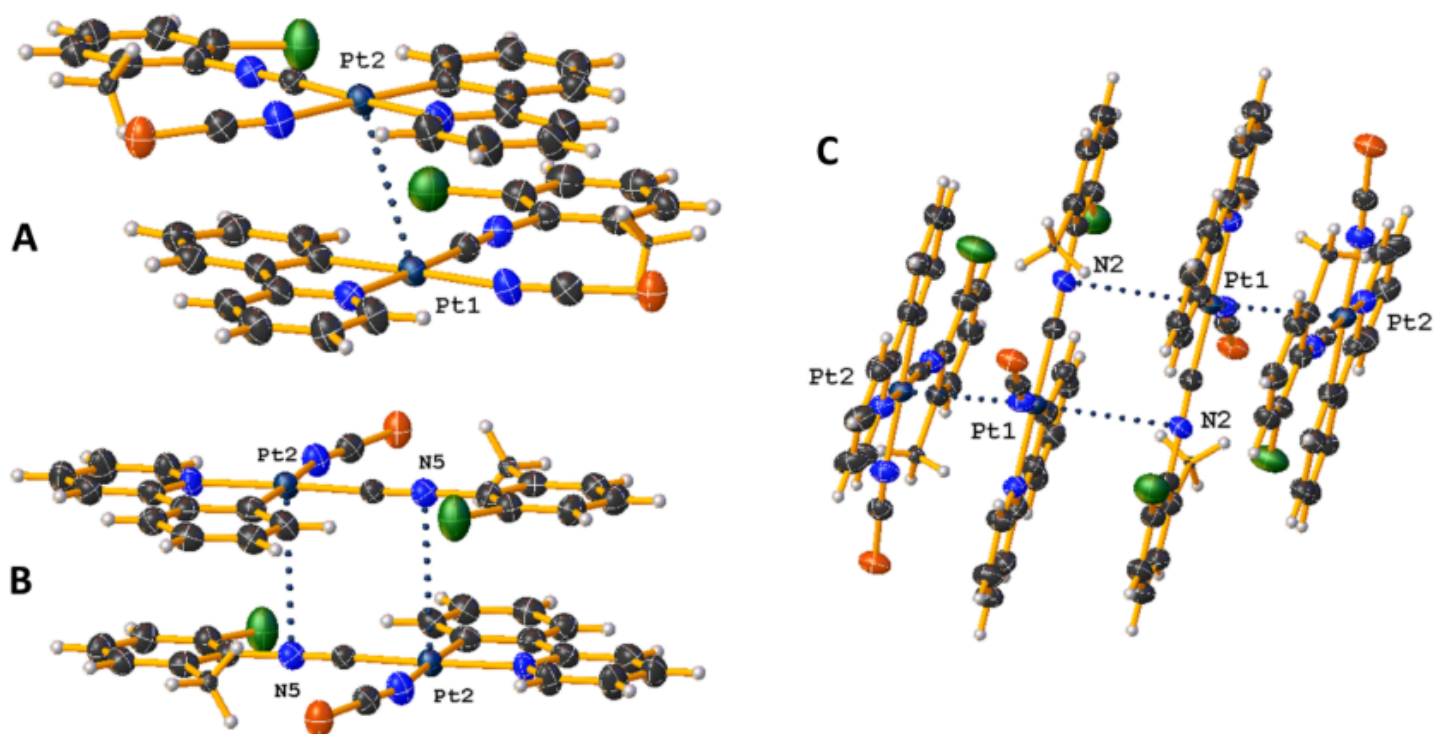


Figure 2

Supramolecular 1D architecture of **2** (**C**) occurred by the interplay of Pt···Pt metallophilic contacts (**A**) with π -hole(isocyano group)··· d_z^2 -[Pt] interactions (**B**). Supramolecular 1D architecture of **1^I** is similar.

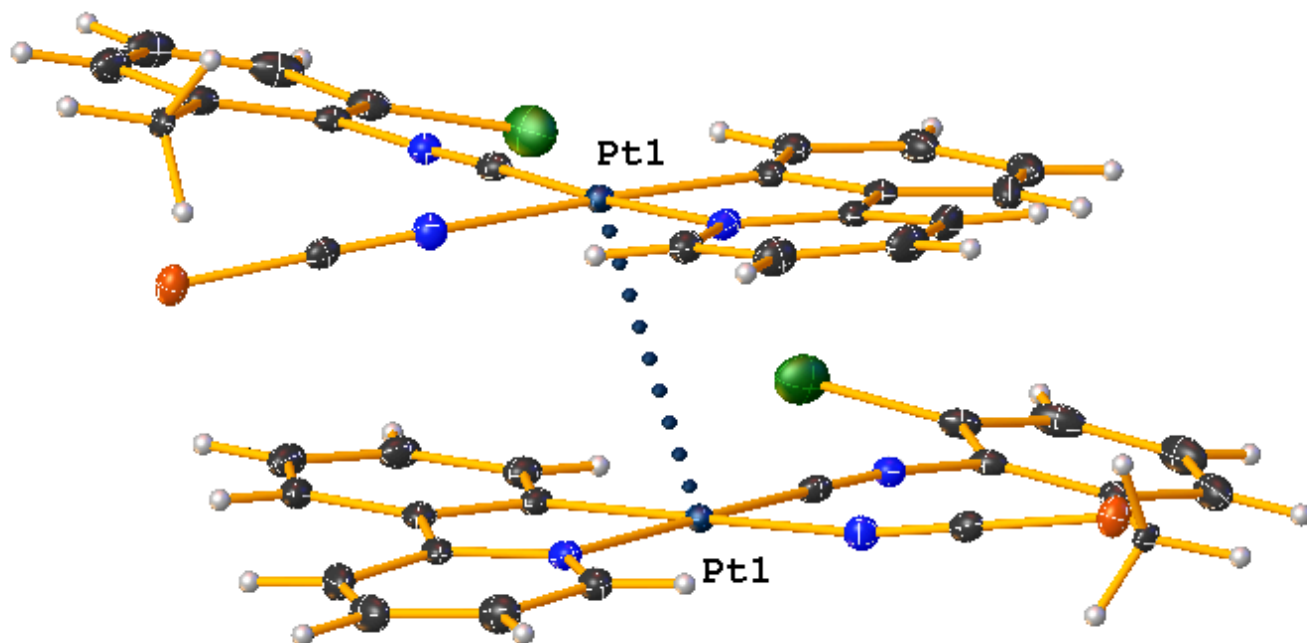


Figure 3

Supramolecular dimer of **2**·CHCl₃ formed by Pt···Pt metallophilic contacts. Supramolecular architecture of **1**^{II} is similar.

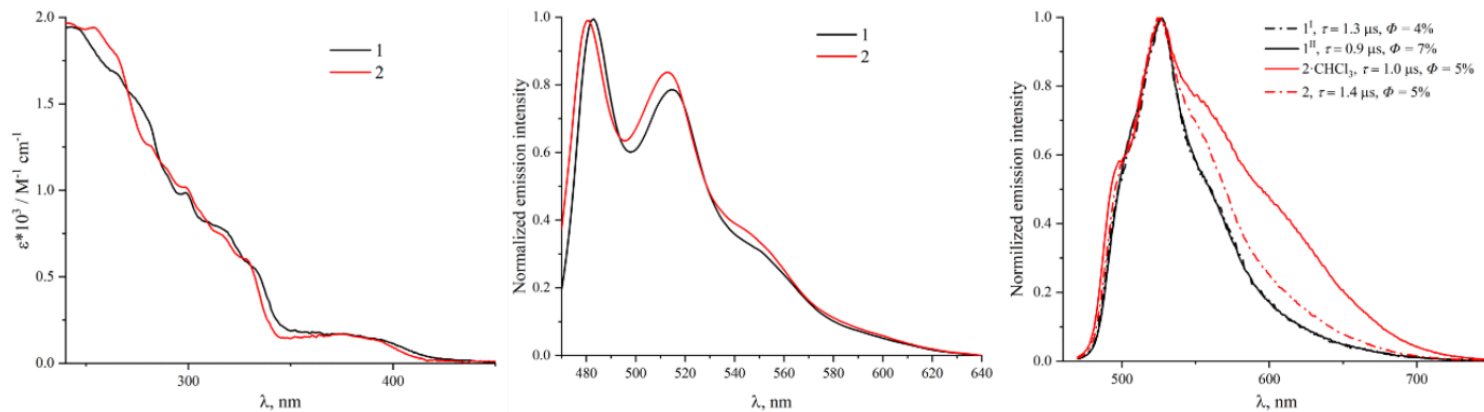


Figure 4

Absorption spectra (left) and normalized emission (middle) spectra of **1** and **2** in CH₂Cl₂ (1.0×10^{-5} M, 298 K), and normalized emission spectra in solid state (right).

Supplementary Files

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