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ARTICLE

A concerted evolution of supramolecular interactions in a {cation; metal complex; π -acid; solvent} anion- π system

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Combined Single-Crystal XRD, solution ^{13}C and ^{195}Pt NMR, solid-state ^{195}Pt NMR and UV-vis measurements, together with comprehensive (TD)DFT calculations, are used to describe the supramolecular interactions and sequential concerted structural transformation occurring in a $\{\text{PPh}_4^+; [\text{Pt}(\text{CN})_4]^{2-}; \text{TCP}; \text{CH}_2\text{Cl}_2\}$ supramolecular system (TCP – tetracyanopyrazine). In the solid-state, a mixture of needle-like co-crystals first appears, $(\text{PPh}_4)_2\{[\text{TCP}][\text{Pt}(\text{CN})_4]\}$ (**1**) and $(\text{PPh}_4)_2\{[\text{TCP}][\text{Pt}(\text{CN})_4]\cdot 2\text{CH}_2\text{Cl}_2\}$ (**2**), and subsequent recrystallization leads to block-shaped co-crystals of $(\text{PPh}_4)_2\{[\text{TCP}]_2[\text{Pt}(\text{CN})_4]\cdot 2\text{CH}_2\text{Cl}_2\}$ (**3**), wherein double $\{\text{Pt}(\text{CN})_4\}^{2-}; \text{TCP}\}$ and triple $\{[\text{Pt}(\text{CN})_4]^{2-}; \text{TCP}; \text{CH}_2\text{Cl}_2\}$ and $\{\text{PPh}_4^+; [\text{Pt}(\text{CN})_4]^{2-}; \text{TCP}\}$ synthons present either in **1** or **2** are reproduced in **3**. The structural pathway (**1/2**→**3**) is accompanied by a 1D-to-2D modular evolution of anion- π interactions between $[\text{Pt}(\text{CN})_4]^{2-}$ and π -acidic TCP that seems to be driven, as indicated by the calculations, not by maximizing their strength but rather optimizing other crystal interactions, *e.g.* between PPh_4^+ cations. Formation of the corresponding $\{[\text{Pt}(\text{CN})_4]^{2-}; \pi\text{-acid}\}$ anion- π contacts in solution is evidenced by ^{13}C NMR shifts and by new low-energy electronic absorption in the visible region (UV-vis). Finally, a combined solution/solid-state ^{195}Pt NMR approach is used for the first time to shed light on the geometry and interactions involving such aggregates; it shows that the degree of trapping of $[\text{Pt}(\text{CN})_4]^{2-}$ near a π -acidic surface can be monitored by ^{195}Pt NMR chemical shifts. The results give fresh insight into block arrangement tactics and characterization of hybrid organic-inorganic co-crystal salts, and into aggregation controlled properties.

Introduction

The general appeal and functional performance of anion- π systems, based largely on anion recognition, binding and transport, are determined by molecular shape matching, electronic structures and charge density distribution of the involved molecular entities.^{1–12} The electronic density around the anions can be arranged spherically, spread over rod-like, polygonal or polyhedral motifs, or localized at particular sites within larger molecular systems. In anion- π assemblies, negatively charged fragments interact with the positive electrostatic potential spread over the unsaturated π -conjugated systems of nearby double bonds or aromatic rings, which are most often framed by electron withdrawing groups or/and N-heteroatoms. The anion- π synthons are accompanied by the cationic counterpart (counter-cation subnetwork,

appended cationic function, proximity of coordinated cations) and often supported by auxiliary interactions (hydrogen bonds, co-stacked aromatic rings) which sometimes result in the formation of nest-like or cage-like supramolecular structures.^{13–18} The strength and extent of such interactions are governed by redox potentials, nucleophilic character, and degree of polarizability of the involved components.^{13, 19–24}

A complete description of anion recognition and binding by π -acidic components requires a characterization of their interactions in solution; most often such work involves comparative colorimetric or/and spectroscopic reactivity tests followed by the determination of the molar ratio of components in the synthon and of the corresponding association constant. This is most frequently done using spectrophotometric UV-vis, fluorescence, NMR or potentiometric titration techniques. The solution data are then supported by structural and physicochemical descriptions of the contacts in the solid state or/and by computational modelling, with the goal to provide an insight into potential models of intermolecular interactions in solution.^{6–8, 16, 17, 19, 20, 23}

We are strongly interested in obtaining the most complete information concerning the anion- π interactions involving anionic *d* metal ion complexes, which were very scarcely exploited in anion- π systems^{16, 25, 26} but are widely used in the construction of multifunctional coordination-based materials. Along this line, we reported recently on shape matching and Charge-Transfer (CT) anion- π interactions along the 1D

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columnar stacks $\{[M(CN)_x]^{n-}; HAT(CN)_6\}_\infty$ ($x = 4, 6-8$; $M = Ni, Pd, Pt, Fe, Co, W, Re$; $HAT(CN)_6$ = hexaazatriphenylene-hexacarbonitrile) in crystalline compounds and in related adducts in solution.²⁷⁻²⁹ In particular, the square-planar $[M(CN)_4]^{2-}$ based systems attracted our attention because of the possible reorientation movements (rotation, sliding *etc.*) of the flat cross-like anionic moieties with respect to a π -acidic surface of $HAT(CN)_6$.²⁸ The two main goals of this work is (i) to check for such features in other anion- π systems with $[M(CN)_4]^{2-}$ in solution and in the solid state, and (ii) to pursue their deeper understanding by exploring the use of heavy metal isotope solid-state NMR (ssNMR) spectroscopy as a tool³⁰ for characterizing the anion- π supramolecular structure. This should provide valuable insight into the underlying anion- π interactions that complements data from the more commonly applied 1H , ^{13}C , or nX NMR (X – halogen) measurements.^{19,31}

Accordingly, we focus our attention here on the characterization of structural arrangement and intermolecular interactions in assemblies involving tetracyanopyrazine (TCP).^{13,25,26,32,33} The related series of {anion; TCP} adducts (anion = Cl^- , Br^- , I^- , SCN^- , NO_2^- , NO_3^- , $(HSO_4)_2^{2-}$, $CH_3SO_3^-$, $TCPSO_3^-$, $[MnCl_4]^{2-}$, $[ZnBr_4]^{2-}$, $[CdI_4]^{2-}$, $[Cd_2Cl_6]^{2-}$) were classified according to their tendencies (i) to form coloured CT species in solution and in the solid state, and (ii) to form the corresponding crystalline phases. Among the reported compounds, only spherical anions tended to be cage-trapped in the 2D or 3D network of TCP,^{13,33} while all other anions formed consistently columnar stacks, with different degree of intra-column bending.²⁵ Besides the known ion-induced polarization and electrostatic character of anion- π interactions present in such systems, the importance of the CT contribution (due to the orbital overlap between HOMO of anion and LUMO of π -acid) was distinguished. Further consideration of systems involving the $[CuBr_2]^-$, $[PtCl_4]^{2-}$, $[Pt_2Br_6]^{2-}$ and $[PtBr_6]^{2-}$ anions highlighted the effects of orbital overlap and CT character on the formation of the specific 1D adducts.²⁶ Collectively, the reported crystal structures of TCP-based anion- π systems reveal, as with $HAT(CN)_6$, a systematically occurring 1D structural trend and serve as a good example of the general block-like organization of components that is commonly observed in co-crystal assemblies.^{31,34-38} Aakeröy suggested that the most important advantage of co-crystals composed of robust infinite chains or layers is the degree of predictable structural periodicity, thanks to the dominating non-covalent interactions; such predictability is essential for the design and synthesis of materials with tuneable physical properties.³⁹ Such viewpoint is in agreements with the energy frameworks approach^{40,41} that uses calculations of pair-wise interactions energy to describe the structural stability and physical properties of co-crystal structures with the block-like components arrangement.

Within this context we report herein a four-component hybrid organic-inorganic $\{PPh_4^+; [Pt(CN)_4]^{2-}; TCP; solvent\}_\infty$ system with a rich structural space that includes several types of anion- π CT interactions. Crystallization studies ultimately culminate in a reproduction of unique synthons, from one stage to the next, that combine to create a 2D anion- π network and allow for an unprecedented breaking of the 1D stacking regime

for TCP-based anion- π networks. We also present a comprehensive experimental-computational characterization of the observed systems, involving for the first time ^{195}Pt NMR spectroscopy, which allowed us to fully describe the trapping of $[Pt(CN)_4]^{2-}$ anions within the cavities created by PPh_4^+ cations and π -acidic polyazaphenylene-polycarbonitriles (TCP, $HAT(CN)_6$), observed simultaneously in solution and in the solid state.

Results and discussion

The $\{PPh_4^+; [Pt(CN)_4]^{2-}; TCP; CH_2Cl_2\}$ assemblies have been studied extensively in both the solid state and in solution, in order to evaluate the pertinent parameters that govern the synthons' formation and their role in the system's overall stability.

Solid-state studies

Three different phases composed of $[Pt(CN)_4]^{2-}$, TCP, PPh_4^+ with or without CH_2Cl_2 solvent molecules have been isolated as single crystals. They have been experimentally studied using X-Ray Diffraction on Single Crystals, Powder X-Ray Diffraction, along with solid-state ^{195}Pt NMR and UV-vis electronic absorption spectroscopies. Their electronic structure has been analysed based on DFT calculations.

Crystal structures and supramolecular synthons evolution

Thorough observations of reaction mixtures of $(PPh_4)_2[Pt(CN)_4]$ and TCP in CH_2Cl_2 allowed us to distinguish two different stages: (i) an early crystallization (pale yellow needles) and (ii) a subsequent recrystallization (stable pale yellow blocks), (see Fig. 1a,b and Figs. S1-S3 and the related video mp4 file, ESI); the sequence of events possibly enhanced by minimizing the surface energy at the crystal-solution interface. Among the needle-like crystals, two different crystalline phases were observed by XRD studies: $(PPh_4)_2\{[TCP][Pt(CN)_4]\}$ (**1**) and $(PPh_4)_2\{[TCP][Pt(CN)_4]\cdot 2CH_2Cl_2\}$ (**2**); the block crystals present the formula $(PPh_4)_2\{[TCP]_2[Pt(CN)_4]\cdot 2CH_2Cl_2\}$ (**3**) (see crystallographic data in Figs. 1c-e, Figs. S4-S13, Tables S1-S4). Compounds **1-3** crystallize in the *P*-1 space group. A uniformity of **1-3** was confirmed by PXRD diffractograms (Fig. S14). Compound **1**, $(PPh_4)_2\{[TCP][Pt(CN)_4]\}$, is well-characterized as 1D $\{[Pt(CN)_4]^{2-}; TCP\}_n$ stacks surrounded by corrugated layers of PPh_4^+ . Such 1D arrangements of $\{[Pt(CN)_4]^{2-}; TCP\}_n$ are analogous to the anion- π columns observed in the crystal structure of $[M(CN)_4]^{2-}$ with $HAT(CN)_6$.²⁸ The planes of $[Pt(CN)_4]^{2-}$ and TCP (green in Fig. 1c left) are oriented close to parallel (with an interplanar angle of *ca.* 15 deg) and the contact distances between $[Pt(CN)_4]^{2-}$ and TCP are in the 3.33-3.71 Å range. An almost parallel $[Pt(CN)_4]^{2-}\cdots TCP$ orientation is consistent with what we expected and what was observed from molecular modelling of $[Pt(CN)_4]^{2-}/TCP$ clusters (Fig. S22).²⁶

Compound **2**, $(PPh_4)_2\{[TCP][Pt(CN)_4]\cdot 2CH_2Cl_2\}$, also contains 1D $\{[Pt(CN)_4]^{2-}; TCP\}_n$ supramolecular chains, however, in this case, mutual orientation of the complex and π -acid is almost perfectly perpendicular. The remote N2 atoms of *trans*-

Figure 1. (a, b) Representative examples of photographs illustrating the recrystallization process for 1 and 2 (needles) towards 3 (blocks). White arrows in panel (a) indicate the example region of vanishing needle crystal. The crystals are labelled accordingly. For more photographs and animations see SI. (c) Mutual orientation between $[\text{Pt}(\text{CN})_4]^{2-}$ and TCP in the crystal structures of 1-3. (d) Bulk projections showing the combinations of the structural features of compounds 1 and 2 in compound 3. Colours and styles: $[\text{Pt}(\text{CN})_4]^{2-}$ – purple, “parallel” TCP – green, “perpendicular” TCP – yellow, CH_2Cl_2 – pale green and grey. PPh_4^+ cations were omitted to increase readability. (e) Multiple Phenyl Embraces (MPE) illustrating mutual orientation between cations species in the crystal structures of 1-3. MPE code (adapted from Ref. 42): TQPE – Translational Quadruple Phenyl Embrace, PQPE – Parallel Quadruple Phenyl Embrace, SPE – Sextuple Phenyl Embrace. Note that the Double Phenyl Embrace (DPE) and Parallel Quadruple Phenyl Embrace (PQPE) can also be found in 1.

positioned cyanides in $[\text{Pt}(\text{CN})_4]^{2-}$ point towards the centroids of C-C_{ring} bonds of TCP (yellow in Fig. 1c right) with a distance of 2.80 Å and C≡N...centroid angle of 173.7 deg. The perpendicular synthon is stabilized by CH_2Cl_2 solvent molecules forming weak hydrogen bonds with N_{cyanide} atoms of $[\text{Pt}(\text{CN})_4]^{2-}$ (C-H...N distances of 2.58 and 2.66 Å) and lone-pair...π contacts

between-Cl and π-deficient NC-C-C-CN part of TCP (contact distance ca. 3.5 Å).

In contrast to 1 and 2, the crystal structure of 3, $(\text{PPh}_4)_2[\text{TCP}]_2[\text{Pt}(\text{CN})_4] \cdot 2\text{CH}_2\text{Cl}_2$, exhibits a 2D supramolecular network of anion-π contacts. The *trans*-positioned N2 atoms of $[\text{Pt}(\text{CN})_4]^{2-}$ have contacts with two adjacent TCP molecules to

form perpendicular anion- π synthons that are analogous to what has been observed in **2** (yellow in Fig. 1c middle, contact distance *ca.* 3.00 Å and the C2-N2...centroid angle of 169.4 deg). The *trans*-positioned N1 atoms of $[\text{Pt}(\text{CN})_4]^{2-}$ point towards the centroids of C- C_{ring} bonds of the second type of TCP (green in Fig. 1c middle, contact distance *ca.* 2.93 Å and the C1-N1...centroid angle of 115.2 deg). The latter contacts are somewhat related to the ones found in **1**, but in the case of **3** TCP is significantly shifted outside the projection of the $[\text{Pt}(\text{CN})_4]^{2-}$ plane such that only the C1N1 cyanide ligand is located above the C3N3 nitrile group. Like in **2**, CH_2Cl_2 molecules in compound **3** are integrated into the perpendicularly arranged $\{[\text{Pt}(\text{CN})_4]^{2-}; \text{TCP}\}$ sub-chains, creating C-H...C_{cyanide} contacts of 2.7 Å and -Cl... $(\text{NC-C-C-CN})_{\text{TCP}}$ lone-pair... π contacts of 3.5 Å.

To summarize this part, while the anion- π contacts in **1** adopt the close-to-parallel stacking that was observed recently in $\{[\text{M}(\text{CN})_4]^{2-}; \text{HAT}(\text{CN})_6\}_{\infty}$ columns,²⁸ in **2** and **3** the N atoms of $[\text{Pt}(\text{CN})_4]^{2-}$ are projected in a perpendicular or slanted manner onto the centroid of C- C_{ring} bonds located between the N heteroatoms and nitrile groups. This particular region of TCP has been frequently observed to accept anions, due to the favourable orbital overlap effect and electrostatic attraction of anions at this site. Interestingly, in **2** and **3** the anions that bind on opposing sides of the TCP molecular plane, also bind on opposite sides of the TCP ring. This results in an inversion center of symmetry (with respect to the anion contacts) that agrees with the polarization of the electrostatic potential around TCP owing to a close contact with anionic species.³³

The structural evolution of **1,2**→**3** results in more exposure of the $[\text{Pt}(\text{CN})_4]^{2-}$ and TCP molecular surfaces to the surrounding environment, which consists mostly of nearby cations. Indeed, anion- π reconstruction is accompanied by: (i) a decrease of the $\text{pyzN}\cdots\text{P}_{\text{cation}}$ distance from 5.8 Å in **1** to 4.6 Å in **2** and **3**, and overall shortening of $\text{TCPN}\cdots\text{ring}_{\text{phenyl}}$ contacts (Figs. S11-S12), (ii) a shortening of nearest-neighbour $\text{PPh}_4^+\cdots\text{PPh}_4^+$ contacts, to adopt Multiple Phenyl Embraces (MPE) geometries, such as Sextuple Phenyl Embrace (SPE), which favour more stabilizing interactions between the phenyl groups⁴² (Fig. 1e and Table S8), and (iii) a general reduction of the number of cation-cation contacts shorter than 10 Å (Fig. S29). All of these factors are creating a unique 2D anion- π connectivity in **3** (Fig. 1d, Figs. S7, S13) that was not previously observed in the reported anion- π systems based on TCP and polyatomic anions.^{25,26}

The time-dependent crystallization sequence itself can reasonably be understood as the consequence of a competition between the formation of kinetic (crystals **1** and **2**) and thermodynamic (crystals **3**) products. Kinetic products are formed first, and exist in equilibrium with adducts in solution. A delayed formation of more stable compound **3** is accompanied by dissolution of crystals **1** and **2** resulting in breaking of their synthons. **3** demonstrate some of the structural features observed in **1** and **2**, including primarily almost perfectly reproduced supramolecular $\{[\text{Pt}(\text{CN})_4]^{2-}; \text{TCP}\}_{\infty}$ chains with the perpendicular orientation of the anion- π components, assisted closely by PPh_4^+ cations and CH_2Cl_2 solvent molecules.

¹⁹⁵Pt NMR spectroscopy

Figure 2. ¹⁹⁵Pt solid-state NMR spectra for **1**, **3**, $(\text{PPh}_4)_2[\text{Pt}(\text{CN})_4]\cdot\text{H}_2\text{O}$ (**Pt**), and **Pt-HAT(CN)₆**. For interpretation see text and compare Figure 5 and Figure 6.

Table 1. Parameters of the ¹⁹⁵Pt solid-state NMR spectra for **1**, **3**, $(\text{PPh}_4)_2[\text{Pt}(\text{CN})_4]\cdot\text{H}_2\text{O}$ (**Pt**) and **Pt-HAT(CN)₆**, resulting from the fitting procedure.^a

	1	Pt-HAT(CN)₆	3	Pt
$\delta(\text{iso})$	-4703.3	-4615.9	-4836.3	-4830.9
$\delta(\text{CSA})$	1618	1533	1779	1759
$\eta(\text{CSA})$	0.0	0.105	0.0	0.0
$\delta(11)$	-3085	-3082	-3057	-3072
$\delta(22)$	-5512	-5382	-5726	-5710
$\delta(33)$	-5512	-5382	-5726	-5710

^a $\delta(\text{iso})$ – representation of the "isotropic chemical shift", the gravity centre of the band due to averaging of CSA (chemical shift anisotropy). In ppm.

$\delta(\text{CSA})$ – representation of the anisotropy of the electronic cloud surrounding the nucleus. In ppm.

$\eta(\text{CSA})$ – representation of the CSA asymmetry; 0.0 – minimum asymmetry (axial symmetry), 1.0 – maximum asymmetry.

$\delta(11)$, $\delta(22)$, $\delta(33)$ – chemical shift tensor elements. In ppm.

Considering the quite different chemical environments around the $[\text{Pt}(\text{CN})_4]^{2-}$ moieties in **1** and in **2/3**, ¹⁹⁵Pt ssNMR studies of **1** and **3** in their polycrystalline form were undertaken to study an impact of these different environments on the ¹⁹⁵Pt chemical shift. The spectra were compared with each other and with two reference systems: 1) a related anion- π compound that contains $\text{HAT}(\text{CN})_6$ as the π -acid instead of TCP, (**Pt-HAT(CN)₆**),²⁸ and 2) the parent salt structure without a π -acidic component, $(\text{PPh}_4)_2[\text{Pt}(\text{CN})_4]\cdot\text{H}_2\text{O}$ (**Pt**) (see Figs. S5 and S6). The spectra of **Pt**, **1**, **3** and **Pt-HAT(CN)₆** consistently display the axial character of multiline sets located in the (-2700;-6500 ppm) range (Fig. 2, Table 1, Fig. S16), which agrees with the overall similar geometries of the $[\text{Pt}(\text{CN})_4]^{2-}$ complexes (planar in **Pt**, **1** and **3**, or almost planar in **Pt-HAT(CN)₆**).²⁸ The isotropic chemical shift for **1**, -4703 ppm, and for **Pt-HAT(CN)₆**, -4615 ppm, are notably downfield shifted compared to the shifts observed for **Pt** (-4831 ppm), and **3** (-4836 ppm). The large downfield shift that is typically observed as the result of an additive oxidation of square-planar Pt(II) to octahedral Pt(IV) complex,^{43,44} can be traced back to the presence of strong interactions between the Pt centre and its out-of-plane ligands.^{45,46} Although in the case presented here one must of course consider the

contribution of interactions from the complex with the whole surroundings (including the cations and solvent molecules), the Pt nucleus deshielding observed for **1** and **Pt-HAT(CN)₆** can be intuitively correlated with the presence of a close-to-parallel anion- π interaction involving a direct interaction between the lone-pair d -orbital system of Pt centres and π -acidic surface (Fig. 1c, Fig. S17, see also computational characterization below). The larger effect in the case of **Pt-HAT(CN)₆** also correlates well, in this respect, with the higher degree of “planar overlap” (and interaction energy) between HAT(CN)₆ and [Pt(CN)₄]²⁻, owing to the larger size of this π -acid compared to TCP. A direct Pt... π -acid contact is not present in neither **3** nor **Pt**, which appears to be consistent with their similar chemical shifts. The observed downfield shift in the **1** and **Pt-HAT(CN)₆** crystals therefore seems to characterize well the “trapping” of the metal complex near π -deficient TCP or HAT(CN)₆ platforms, and inspired to use NMR studies to help characterize such interactions in solution (see the dedicated part below).

UV-vis electronic spectroscopy

UV-vis electronic spectra (in diffuse reflectance mode) were carried out for samples of crystals **1** and **3** and for their precursors, crystals of parent salt (PPh₄)₂[Pt(CN)₄] $\cdot$ H₂O (**Pt**) and of TCP (Fig. 3). Both **1** and **3** demonstrate a significant increase in absorption, compared to their precursors, in the spectral region 350–450 nm, which can confidently be associated with CT-type anion- π interactions between [Pt(CN)₄]²⁻ and TCP moieties. This was corroborated by the analysis of the computed densities of states for **1**, **2**, and **3** structures (Fig. S25), which shows that the lowest-energy unoccupied / highest-energy occupied states arise mostly from the TCP / complex anion molecules. Notable differences in the electronic absorption of **1** and **3** clearly reflect thus different intermolecular anion- π interactions between [Pt(CN)₄]²⁻ and TCP (‘parallel’ in **1** and ‘perpendicular’ or ‘parallel/offset’ in **3**, as described above). Alongside the ssNMR studies, these results clearly establish the distinct electronic signatures of the different anion- π motifs. We will use the solid-state data to interpret studies of adducts in CH₂Cl₂ solution (see below).

Electronic structure characterization via DFT calculations

Density Functional Theory (DFT) calculations were used to examine the key differences between the intermolecular interactions in **1**, **2**, and **3**; see ESI for further computational details and complementary results. Fig. 4a presents a Non-Covalent Interaction (NCI)⁴⁷ analysis of the interactions around TCP in **1** and **2**; the NCI approach uses the Reduced Density Gradient (RDG) to help identify and characterize non-covalent interactions. Attractive regions which correspond to anion- π interactions are clearly visible above TCP and, as expected, evidently differ in each structure because of the differences in the local chemical environments. In **1**, a multisite anion- π contact (on each face) is observed with a direct interaction between the metal centre and the TCP π -system, whereas in **2**, there is one site of such direct contact, but it is accompanied by a lone-pair... π interaction between CH₂Cl₂ and TCP. In both **1** and **2**, interactions between TCP and other crystal components (mostly PPh₄⁺) are visible elsewhere, which confirms the

Figure 3. Solid-state electronic absorption spectra (as Kubelka-Munk, K-M, functions) of **1** and **3** together with the spectra of their precursors.

importance of such interactions in stabilizing the structures. The nature of the interactions between TCP and the adjacent [Pt(CN)₄]²⁻ in **1–3** was then further studied using the ETS-NOCV⁴⁸ method, and they revealed that the anion- π contacts have an overall weak CT character and, also, that in **1**, there is a clear redistribution of electronic charge density from the lone-pair metal d orbitals towards TCP (see Fig. 4b and S21).

As presented in Fig. 4c, the anion- π structural motifs in **1** and **2** are directly linked with the neighbouring stacks of PPh₄⁺ cations; the red bars indicate the periodicity of these columnar synthons and show how the different stacking of [Pt(CN)₄]²⁻/TCP is accompanied by differences in the contacts between the cations. The nearest-neighbours intermolecular interactions of [Pt(CN)₄]²⁻/TCP and PPh₄⁺/PPh₄⁺ in **1**, **2**, and **3** were therefore examined, and the strongest interactions of each type are shown in Fig. 4d. As can be seen, the anion- π contact that characterizes **2** and **3** is weakened in comparison with the one of **1**, but this is compensated by the interactions of TCP and [Pt(CN)₄]²⁻ with CH₂Cl₂. Furthermore, as expected, the pair-wise interactions between cations are more stable (*via* dispersion forces interactions, see Table S8) in **2** and **3**. The raw strength of the anion- π interactions appears thus to favour the formation of **1**, but the capacity to incorporate solvent molecules and optimize other supramolecular interactions (like those between cations) favours the formation of **2** and **3**. A comparison of the strengths of pair-wise molecular interactions in **1**, **2**, and **3** with those present in the related [PtCl₄]²⁻/TCP/NPr₄⁺ crystal structure (labelled as ‘PtCl₄’ in Fig. 4d)²⁶ reveals a distinctly different signature. First, the absolute strength of the anion- π interaction in the PtCl₄ structure is considerably stronger (this relates, as we show in Figs. S20–S21 and Table S7, to an increase in the CT character of the anion- π bonding). Second, the NPr₄⁺ charge is less screened and consequently, this increases the interaction energies between the anions and cations. The contrast of the ‘PtCl₄’ pair-wise binding energies with those of **1**, **2**, and **3** implies that the important driving forces for the modular structural evolution (**1,2**→**3**) reported here are the weak CT component of anion- π interactions and the screened charge of the cation; collectively they help dampen attractions and repulsions between nearby molecules and allow the system to have the required flexibility for a global saturation of anion- π contacts without having each complex anion form two anion- π synthons with each nearby TCP molecule (as in **1** and in the [PtCl₄]²⁻-based structure).

Solution-state studies

cyanide carbon atoms C_{CN-Pt} become broadened, less intense,

Figure 4. (a) Results of an NCI analysis around TCP in **1** and **2**. The position of atoms which are in contact with the TCP π-system are coloured in red. (b) Dominant (orbital energy values, in kcal/mol, given in parentheses) ETS-NOCV contributions to deformation density in [Pt(CN)₄]²⁻/TCP clusters extracted from the optimized structures of **1** and **2**. The regions in which there is an increase / a decrease in electronic charge density, relative to the isolated components, are coloured red / blue. (c) Representation of the interplay between the anion-π contacts and the stacking of PPh₄⁺ in **1** and **2**. (d) Computed binding energies (in kcal/mol) of the strongest pair-wise interactions between molecule A and molecule B in an A/B pair, $\Delta E_{\text{bind}} = E(A/B) - E(A) - E(B)$, in **1-3**. Also shown, for comparison, as [PtCl₄]²⁻ is the analogous set of results for the reported crystal structure of TCP with [PtCl₄]²⁻ and NPr₄⁺.²⁶

Solution ¹³C and ¹⁹⁵Pt NMR along with UV-vis electronic absorption spectroscopic studies were performed for the {PPh₄⁺;[Pt(CN)₄]²⁻;TCP;CH₂Cl₂} (**Pt-TCP**) assembly. For a comparison, the corresponding NMR results measured for {PPh₄⁺;[Pt(CN)₄]²⁻;HAT(CN)₆;MeCN} (**Pt-HAT(CN)₆**) system have also been provided.

¹³C NMR spectroscopy

The ¹³C NMR spectra of the mixtures **Pt-TCP** in CD₂Cl₂ and **Pt-HAT(CN)₆** in CD₃CN (relative to the spectra of their precursors in the appropriate solvents) exhibit a notable downfield shift of peaks assigned to the C_{nitrile} atoms of the π-acceptor, by *ca.* +(0.1-0.26), while signals from [Pt(CN)₄]²⁻

and upfield shifted (Table 2, Figs. S18-S19, Tables S5-S6). A visible downfield shift is also observed for C_{int} atoms of the internal ring in HAT(CN)₆. C_{ext} (C4° pyrazine) atoms appear either deshielded (TCP) or shielded (HAT(CN)₆). Note that in the case of the **Pt-TCP** solution, the spectra evolve in time scale of hours (Table 2 and Fig. S18). The magnitude of the observed changes is comparable to the literature data,¹⁹ and can be associated with the presence of anion-π interactions within the {[Pt(CN)₄]²⁻;π-acid} aggregates (pairs or clusters), as implied by the DFT calculations for [Pt(CN)₄]²⁻/TCP and [Pt(CN)₄]²⁻/HAT(CN)₆ binary clusters.

There is generally a good agreement between the computed and experimental data (see Tables S10-S15, Figs. S22, S26, S27). The calculated results obtained for the pristine fragments ([Pt(CN)₄]²⁻, TCP and HAT(CN)₆) are almost uniformly shifted when compared to the experiment, affording a correct reproduction of the general relative positions of particular peaks. Moreover, as in the experiment, overall small changes in calculated chemical shifts for the adduct vs. its isolated components were observed, the sign of which (not always agreeing with the experimental observation) appeared strongly dependent on the relative orientation of [Pt(CN)₄]²⁻ and π-acceptor. Collectively, these results imply a notable degree of intermolecular clustering and flexibility of the [Pt(CN)₄]²⁻/π-acid structure in solution for both systems, as was suggested recently for {[M(CN)₄]²⁻;HAT(CN)₆} based on UV-vis studies. The exact intermolecular orientation can be located within the parallel-to-perpendicular “spectrum”, following different orientations observed in **1-3**, and in the recent literature reports.^{25,26,28}

Table 2. Observed ¹³C solution-state NMR chemical shifts of CN⁻ ligands in [Pt(CN)₄]²⁻ (C_{CN-Pt}), and of -CN substituents (C_{nitrile}) and C4° pyrazine (C_{ext}) and benzene (C_{int}) rings in π-acid. For further details, see Figs. S18-S19, and Tables S5-S6.

	C _{CN-Pt}	C _{nitrile}	C _{ext}	C _{int}
TCP in CD ₂ Cl ₂				
Pt-TCP (fresh)	122.31	111.00 br	134.64 br	-
Pt-TCP (after 24 h)	122.12 br	110.98	134.64	-
TCP	-	110.72	134.54	-
(PPh ₄) ₂ [Pt(CN) ₄]	122.28	-	-	-
HAT(CN) ₆ in CD ₃ CN				
Pt-HAT(CN) ₆	121.96 br	114.02	136.24	143.33
HAT(CN) ₆	-	113.90	136.38	143.10
(PPh ₄) ₂ [Pt(CN) ₄]	122.48	-	-	-

br = broadening and loss of amplitude intensity.

Figure 5. ^{195}Pt solution-state NMR spectra of the mixtures $(\text{PPh}_4)_2[\text{Pt}(\text{CN})_4] + \text{TCP}$ in CD_2Cl_2 (a) and $(\text{PPh}_4)_2[\text{Pt}(\text{CN})_4] + \text{HAT}(\text{CN})_6$ in CD_3CN (b) together with the respective reference spectra of $(\text{PPh}_4)_2[\text{Pt}(\text{CN})_4]$ salt in the corresponding solvents.

^{195}Pt NMR spectroscopy

For the recorded spectra in different solutions, the ^{195}Pt NMR peaks exhibit notable downfield shift, +8 ppm for Pt-TCP in CD_2Cl_2 and +53 ppm for Pt-HAT(CN) $_6$ in CD_3CN , compared to their corresponding $(\text{PPh}_4)_2[\text{Pt}(\text{CN})_4]$ reference solutions (Fig. 5). The magnitude of these shifts (e.g. +53 ppm with Pt-HAT(CN) $_6$) is similar to what has been observed in previous studies of external chemical effects on ^{195}Pt NMR (e.g. a -32 ppm upfield shift was observed upon confining $[\text{Pt}(\text{CN})_6]^{2-}$ anions in a Pd_2L_4 cavity (L = ribbon-shaped [6]polynorbornane) *via* four hydrogen bonds $\text{Pt}-\text{CN}\cdots\text{HN}-(\text{C}=\text{O})\text{R}_2$ ³⁰). The downfield tendency of both the Pt-HAT(CN) $_6$ and Pt-TCP shifts is in line with the ^{195}Pt ssNMR results (Fig. 6a). Following the discussion on the ^{195}Pt ssNMR results presented above, the deshielding observed in solution can be thus related to the direct anion- π interaction of $[\text{Pt}(\text{CN})_4]^{2-}$ with the strongly electron-deficient regions of the π -acidic ring(s) of TCP and HAT(CN) $_6$. The smaller shift for Pt-TCP vs. Pt-HAT(CN) $_6$ can be attributed to weaker anion- π interactions, due to the higher mobility of $[\text{Pt}(\text{CN})_4]^{2-}$ moieties within the corresponding supramolecular $\{\pi\text{-acid}; \text{cation}; \text{solvent}\}$ assemblies and due to smaller effective “planar overlap” between the complex and π -acid. Both

Figure 6. (a) Downfield shifts in ^{195}Pt NMR spectra of $\{[\text{Pt}(\text{CN})_4]^{2-}; \pi\text{-acid}\}$ adducts in solution (CD_2Cl_2 for Pt-TCP, CD_3CN for Pt-HAT(CN) $_6$) and in solid state (**1** and Pt-HAT(CN) $_6$) relative to the reference systems (for details see text and ESI). (b) Schematic representation of caging of $\text{Pt}(\text{CN})_4]^{2-}$ between the flat π -acidic aza- and poliazacarbonitrile molecules (TCP / HAT(CN) $_6$ depicted as small / large red-laced blue disc in (a)).

parameters, mobility of $[\text{Pt}(\text{CN})_4]^{2-}$ and “planar overlap”, can be intuitively correlated with the size of π -acid ring systems; the more extended one in HAT(CN) $_6$ contributes stronger to the anion trapping (Fig. 7b), which could be directly reflected by the larger downfield shift of the related NMR peak. In the case of the Pt-TCP solution, the time-dependent spectra show a slight “backward” upfield shift and broadening of the signal in the time scale of hours (Fig. 5a; see discussion below).

UV-vis electronic spectroscopy

UV-vis spectrum measured for the mixed components of the $[\text{Pt}(\text{CN})_4]^{2-}/\text{TCP}$ system in CH_2Cl_2 solution demonstrates additional UV-vis intensity in the 350–500 nm range, compared to the sum of their individual spectra (Fig. 7a). This is in line with the electronic spectra measured for **1** and **3** crystals and (Fig. 3), and is indicative of the presence of CT-type anion- π adducts between $[\text{Pt}(\text{CN})_4]^{2-}$ and TCP moieties also in solution. TDDFT calculations performed for the selected cluster models of different $[\text{Pt}(\text{CN})_4]^{2-}/\text{TCP}$ contacts possible in solution (and observed in the crystal structure of early phases **1** and **2**) indeed nicely reproduce the appearance of the additional absorption intensity at the low-energy tail of the TCP spectrum upon the introduction of the $[\text{Pt}(\text{CN})_4]^{2-}$ complex interacting with TCP (Fig. 7b, Figs. S22–S24, Table S9). Importantly, the underlying excitations reveal predominant $[\text{Pt}(\text{CN})_4]^{2-} \rightarrow \text{TCP}$ CT character and their energy clearly depends on the structure of the $[\text{Pt}(\text{CN})_4]^{2-}/\text{TCP}$ complex, wherein perpendicular ($\perp$) motif results in higher-energy (shorter-wavelength) excitations than the parallel ($\parallel$) one, as shown in Figure 7b.

Notably, the low-energy UV-vis feature evolves over a time scale of hours, showing the increase in intensity and some onset of the band structuring only within the range 360–430 nm. This time dependency is in accordance with the time dependence that was observed in the ^{13}C and ^{195}Pt NMR spectra. The modifications of the new CT absorptions that are observed over time occur strictly within the “original” 360–430 nm range, and, furthermore, we noted only modest changes in the ^{13}C NMR

Figure 7. (a) Experimental UV-vis electronic spectra for $\{PPh_4^+;[Pt(CN)_4]^{2-};TCP;CH_2Cl_2\}$ assemblies in CH_2Cl_2 solution referenced to the sum of the spectra of the related pristine components ($(PPh_4)_2[Pt(CN)_4]$ and TCP); measured at $c = 0.0045 \text{ mol/dm}^3$. (b) The corresponding TDDFT-simulated spectra for the selected parallel (||) and perpendicular ($\perp$) $[Pt(CN)_4]^{2-}/TCP$ clusters (shown in the lower panel) together with their assumed 50:50 mixture. For details see text and ESI (Fig. S22–S23).

spectra; this allows us to exclude the possibility of reduction or decomposition of TCP.³²

Our proposed interpretation of the observations in CH_2Cl_2 solution are therefore as follows. Immediately after mixing of components, a set of CT anion- π $[Pt(CN)_4]^{2-}/TCP$ adducts, involving also PPh_4^+ and CH_2Cl_2 , appears, and these adducts are in equilibrium with their separated components. The parallel (||) and perpendicular ($\perp$) orientations between $[Pt(CN)_4]^{2-}$ and TCP, observed in the crystal structures of **1** and **2**, respectively, are likely decent representations of anion- π motifs on opposite extremes of the adduct continuum in solution. From this, we speculate that the measured spectrum in solution can be considered as some superposition of spectral fingerprints from the ‘continuum’ of adduct geometries; as an illustration, the average of the two computed TDDFT UV-vis spectra is shown in Figure 7b. A significant presence of motifs with the close-to-parallel orientation between $[Pt(CN)_4]^{2-}$ and TCP can be inferred from the ^{195}Pt NMR data.

Having ruled out the occurrence of reduction or decomposition of TCP (see above), the UV-vis spectral modifications over time are tentatively interpreted in terms of possible successive intermolecular rearrangement involving various aggregates of building blocks. Some lability of the primary set aggregates could be due to the comparable sizes of the flat $[Pt(CN)_4]^{2-}$ and TCP components (and consequently their higher relative mobility), the variety and complexity of interactions involving PPh_4^+ cations, the significant polarizability of the positive potential around TCP π -acid due to the proximity of anionic species,³³ and the meddling action of CH_2Cl_2 solvent molecules.⁴⁹ The significant influence of the CH_2Cl_2 solvent is

supported by the time-dependent crystallization processes that occur in more concentrated solutions compared to those used in solution studies, and in a comparable time scale of hours. The signatures of an evolution of supramolecular assemblies are also apparent in the spectral changes from solution NMR studies, although the character of these changes does not allow for a detailed and straightforward description of the process. More insight into the dynamic behavior of the $\{PPh_4^+;[Pt(CN)_4]^{2-};TCP;CH_2Cl_2\}$ assemblies in CH_2Cl_2 solution could likely be obtained from molecular dynamics simulations, but this is beyond the scope of this work and will be studied further at a later time. As mentioned above, the lack of time-dependence in the UV-vis and NMR spectra of $HAT(CN)_6$ anion- π adducts in solution is likely related with a ‘trapping’ effect of the metal complex by the larger π -acidic surface area of $HAT(CN)_6$, and this further supports a reduced degree of trapping and higher mobility of the TCP-based components in solution.

Conclusions

In this work a complete solid- and solution-state study of a four-component $\{PPh_4^+;[Pt(CN)_4]^{2-};TCP;solvant\}$ supramolecular assembly is presented. Structural characterization in the solid state revealed a solvent-assisted a partial or an almost complete reproduction of multicomponent synthons when the initial needle-like co-crystals (**1**, **2**) are recrystallized into a final block-shaped co-crystal **3**; this process is accompanied by a 1D-to-2D evolution of anion- π interactions between $[Pt(CN)_4]^{2-}$ and π -acidic TCP. As supported by the calculations, the anion- π transformation seems to be driven not by maximizing the anion- π contact strength but rather by optimizing other crystal interactions, *e.g.* between PPh_4^+ cations within multiple phenyl embraces geometries. The observed “non-rigidity” of the 1D columnar {complex anion; π -acid} organization probably relies on the minimization of the size difference between π -acidic TCP and $[Pt(CN)_4]^{2-}$, which underlines the importance of the size of the components used in the formation of such anion- π assemblies. We also applied, for the first time, ^{195}Pt solid-state NMR technique to study Pt-based supramolecular systems involving {anionic metal complex; π -acid} block substructures. This allowed us to reveal distinct effects of structurally different anion- π synthons on the observed ^{195}Pt NMR chemical shifts. The highlighted property-structure correlations in the solid state was then used to demonstrate the trapping of $[Pt(CN)_4]^{2-}$ anions within the cavities created by PPh_4^+ cations and π -acidic polyazaphenylenepolycarbonitriles in solution. The approach is planned to be further verified by characterizing other related supramolecular assemblies.

Experimental studies on complementary assemblies are currently underway, with an increasing number of components, and they are expected to contribute further to the understanding of behaviour of mixed complex multicomponent supramolecular systems. For example, experiments towards the controlled aggregation^{50–52} and functions may be proposed, involving multicomponent luminescent systems with columnar

aggregation of different flat molecules, *e.g.* active complexes and luminescence halogenobenzene modifiers.

Experimental

Materials and methods

Materials

$K_2[Pt(CN)_4] \cdot 2H_2O$ and PPh_4Br were purchased from a commercial source (Aldrich) and used as obtained. Monohydrate $[PPh_4]^+$ salts of $[Pt(CN)_4]^{2-}$ were obtained by metathesis between $K_2[Pt(CN)_4]$ and PPh_4Br in aqueous solution, with the yields of ~ 90 – 95% . TCP ,⁵³ $HAT(CN)_6$ ²⁸ and $(PPh_4)_2\{[HAT(CN)_6][Pt(CN)_4]\} \cdot 3MeCN$ ²⁸ were obtained using the literature protocols. CH_2Cl_2 and $MeCN$ solvents of the analytical grade was purchased from a commercial sources. The fresh portions were used for the synthesis, as obtained or in the dried form (activated molecular sieves), without any particular differences to be observed.

Techniques

Infrared spectra (IR) were measured with tiny crystalline objects or powder samples in the 3500 – 675 cm^{-1} range using a Nicolet iN10 MX FTIR microscope, in transmission mode. The crystals were immersed in the Apiezon grease to prevent loss of crystallization solvent. Elemental analyses were performed on an Elementar Vario Micro Cube CHNS analyzer. UV-vis-NIR measurements were carried out with a PerkinElmer Lambda 35 spectrophotometer. Measurements on solutions were performed with the use of tandem cuvettes. ^{13}C NMR spectra were recorded at room temperature with a Bruker (300, 400, 500 or 600 MHz) NMR spectrometer. ^{13}C chemical shifts were determined using residual signals of the deuterated solvents (CD_2Cl_2 , CD_3CN) and are reported in parts per million (ppm) relative to Me_4Si .

All $^{195}Pt\{^1H\}$ solution NMR experiments were performed at $23^\circ C$ on a BRUKER Avance III HD 500 MHz spectrometer, equipped with a 5 mm broad band He cryoprobe. NMR spectra were acquired at 107.0370952 MHz , with $4\text{ }\mu s$ pulses, 400 scans, 3 s for acquisition time and 2 s for recovery delays. The spectral width was fixed to 53472 Hz . Spectral reference was realized by measuring ^{195}Pt NMR chemical shift of K_2PtCl_4 in D_2O solution (1 M), giving a single peak at -1617 ppm . $^{195}Pt\{^1H\}$ solid-state NMR experiments were performed at room temperature on two different wide-bore spectrometers (BrukerTM). Samples of **3**, $(PPh_4)_2[Pt(CN)_4] \cdot H_2O$ **Pt**, and **Pt-HAT(CN)₆** were acquired on an AVANCE 300MHz operating at a frequency of 65.569 MHz for ^{195}Pt , while the a sample **1** was obtained on an AVANCE 750MHz (161.283 MHz for ^{195}Pt). The three first were spun at 12 kHz in a double resonance MAS (Magic Angle Spinning) probe designed for 4 mm o. d. zirconia rotors closed with vespel caps. **1** was packed inside a 2.5 mm o.d. zirconia rotor (vespel caps) and spun at 30 kHz in another double resonance MAS probe (BrukerTM). The temperature was controlled in both cases through BCUTM systems from the same vendor. It must be noted that platinum 195 is part of these heavy nuclei exhibiting very wide chemical shift ranges (over 15000 ppm) and conversely

huge Chemical Shift Anisotropies (CSA) making often difficult nor impossible to properly acquire such spectra in the solid state. Therefore, for spectral coverage purposes, all the spectra were acquired using a single short pulse (20° pulse flip angle in both cases) followed by digitization of the free induction decay undergoing proton decoupling. These single pulses were set to $2\text{ }\mu s$ (**3**, **Pt**, **Pt-HAT(CN)₆**) and $1\text{ }\mu s$ (**1**) to ensure correct coverage for the needed spectral windows (0.5 MHz and 1.6 MHz respectively). Filtering out probes background signal was obtained by setting prescan delays to start acquisition on top of the first or second rotational echo (83.333 and $66.667\text{ }\mu s$ for 12 and 30 kHz MAS rates). Proton decoupling during acquisition was done by using SPINAL-64⁵⁴ at 100 kHz (4 mm spinners) and 180 kHz (2.5 mm spinner) RF fields and recycling delays were set to 30 seconds . Chemical shift are given respective to solid $K_2[PtCl_6]$ in the same experimental conditions (single peak set at 0 ppm , substitution method). A 200 Hz Lorentzian filter was applied prior to Fourier transform and CSA fitting was done with TOPSPINTM v3.5 software from Bruker.

X-Ray Diffraction

Single crystal X-ray diffraction data for all crystals were collected using Bruker D8 Quest Eco diffractometer equipped with Photon50 CMOS detector, $Mo\text{ K}\alpha$ ($\lambda = 0.71073\text{ \AA}$) radiation source with a graphite monochromator and Bruker Cryoflex II cooling system. Crystals for measurement were taken from mother solution and mounted on MiteGen Microloops using NVH immersion oil. Measurements were performed at 220 K (**1**), 120 K (**2,3**) and 100 K ($(PPh_4)_2[Pt(CN)_4] \cdot H_2O$, **Pt**). Data reduction and cell parameter refinement were performed using Apex software with included SAINT and SADABS programs. Intensities of reflections for the sample absorption were corrected using multiscan method. Structures were solved by intrinsic phasing method and refined anisotropically with weighted full-matrix least squares on F^2 using SHELXT⁵⁵ and SHELXL⁵⁶ programs with Olex 2 graphic interface.⁵⁷ Hydrogen atoms within structures were placed in idealized positions and refined using riding coordinate model with isotropic displacement parameter set at 1.2 times U_{eq} of appropriate carrier atoms. Crystal data and structure refinement were summarized below, (Table S1). The structural figures were prepared using latest Mercury software⁵⁸ CCDC reference numbers for the crystal structures are 1949024 (**1**), 1949025 (**2**), 1949026 (**3**), and 1949027 ($(PPh_4)_2[Pt(CN)_4] \cdot H_2O$, **Pt**). PXRD patterns were recorded on a PANalytical X'Pert PRO MPD diffractometer with a capillary spinning add-on using a $Cu\text{-K}\alpha$ radiation source. The measurement was carried out immediately after sample preparation.

Computational details

All calculations were performed using Density Functional Theory (DFT) methods within either the Vienna Ab-Initio Simulation Package (VASP),⁵⁹ for models of periodic networks, or the Gaussian 09 (G09)⁶⁰ and the Amsterdam Density Functional 2016 (ADF2016)⁶¹ programs, for models of molecular clusters. The computational analysis protocol that was adopted follows in general that which was

established for related systems.²⁷⁻²⁹ The modelling of molecular clusters, to generate the data for Figure 3d, used a dichloromethane-based continuum solvent model PCM, as implemented in the G09 package. Further details about the computations, including *e.g.* exchange-correlation functionals, basis sets, treatment of relativistic and solvent effects, *etc.*, and references are given in the ESI.

Crystallisation conditions

Compound 1-3

(PPh₄)₂[[TCP][Pt(CN)₄]] (1) (*The thin needle crystals*)

(PPh₄)₂[[TCP][Pt(CN)₄]]·2CH₂Cl₂ (2) (*The needle crystals*)

(PPh₄)₂[[TCP]₂[Pt(CN)₄]]·2CH₂Cl₂ (3) (*The block crystals*)

Single crystals of **1**, **2** and **3** systems were obtained by mixing (PPh₄)₂[Pt(CN)₄] and TCP solutions in CH₂Cl₂. Freshly prepared (PPh₄)₂[Pt(CN)₄]·H₂O (55.4 mg, 0.056 mmol, 5 cm³ CH₂Cl₂) and TCP (10 mg, 0.056 mmol, 4 cm³ CH₂Cl₂) solutions were carefully mixed and tightly closed. After mixing, the solution turned yellow.

The mixture of pale-yellow needles of **1** and **2** appear during the first stage of crystallization, typically over a dozen of minutes. During the following time, the order of several hours, the needles slowly vanished to be replaced by the block crystals of **3**. In some cases, all types of crystals were present even in the first stage of crystallization. It was also possible to isolate the pure product of **1**, just by a quick separation from the mother liquid, however, the yield from the single batch was very low. The single objects of **1**, **2** and **3** could be systematically retrieved from the reaction mixture to be characterized by SC XRD. The needle crystals of **1** and block crystals of **3** could be reproducibly retrieved after washing with cold CH₂Cl₂ as a pure product to be fully characterized by elemental analyses, single crystal X-ray diffraction, powder X-ray diffraction, IR spectroscopy, UV-vis spectroscopy and solid state ¹⁹⁵Pt NMR measurements.

Compound 1: Yield: 10 %. Elemental analysis: Calcd (%) for C₆₀H₄₀N₁₀P₂Pt (**1**): C, 62.23; H, 3.48; N, 12.09. Found: C, 61.61; H, 3.42; N, 11.79. IR: 2260vw ν(C≡N)_b, 2102s ν(C≡N)_a, 2096s ν(C≡N)_a. The peaks for the ν(C≡N) vibrations in **1** are of very low intensity, which is due to its relatively amount in the crystals (Fig. S15). This effect was also observed previously for the related peaks for HAT(CN)₆ congener in its co-crystal adducts with polycyanidometalates.²⁷⁻²⁹

Compound 3: Yield: ~60%. Elemental analysis: Calcd (%) for C₇₀H₄₄Cl₄N₁₆P₂Pt (**3**): C, 55.75; H, 2.941; N, 14.86. Found: C, 55.65; H, 2.881; N, 14.70. IR: ("a" index: [Pt(CN)₄]²⁻; "b" index: TCP) (cm⁻¹): 2249m ν(C≡N)_b, 2245(sh) ν(C≡N)_b, 2129(sh) ν(C≡N)_a, 2118s ν(C≡N)_a, 2096w ν(C≡N)_a, 2080m ν(C≡N)_a.

The confirmation of the phase purity of **1** and **3** was performed by PXRD measurements (Fig. S14), and was verified before the each solid state measurement. The chemical composition of **1** and **3** found from the elemental analysis is in a good agreement with the SC XRD analysis. The chemical compositions of **2** was determined based on the results of crystal structure solution and refinement.

Conflicts of interest

There are no conflicts to declare.

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