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The Isocyanide Complexes $cis-[MCl_2(CNC_6H_4-4-X)_2]$ ($M = Pd, Pt$; $X = Cl, Br$) as Tectons in Crystal Engineering Involving Halogen Bonds

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Abstract: The isocyanide complexes $cis-[MCl_2(CNC_6H_4-4-X)_2]$ ($M = Pd$; $X = Cl, Br$; $M = Pt$; $X = Br$) form isomorphous crystal structures exhibiting the Cl/Br and Pd/Pt exchanges featuring 1D chains upon crystallisation. Crystal packing is supported by the C–X $\cdots$ X–C halogen bonds (HaBs), C–H $\cdots$ X–C hydrogen bonds (HB), X $\cdots$ M semicoordination, and C $\cdots$ C contacts between the C atoms of aryl isocyanide ligands. The results of DFT calculations and topological analysis indicate that all the above contact types belong to attractive noncovalent interactions. A projection of the electron localization function (ELF) and an inspection of the electron density (ED) and the electrostatic potential (ESP) reveal the amphiphilic nature of X atoms playing the role of HaB donors, HaB and HB acceptors, and a nucleophilic partner in X $\cdots$ M semicoordination.

Keywords: isocyanides; crystal engineering; halogen bonding; palladium(II); platinum(II)

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1. Introduction

Strategies of crystal engineering towards the design of solids with controllable structure and tunable physicochemical properties are amongst the well-recognized tools for material chemistry [1–5]. The emergence of halogen bonding (HaB; for reviews on HaB see references [6–10]) during the construction of supramolecular aggregates opens up a route for the optimisation of their valuable properties, such as catalytic activity [11–15], solubility [16,17], melting point [18], thermal expansion [19–22], colour [23–27], luminescence [28–41], sensing [42,43], biological [44], and magnetic [45] properties. Various tectons [46], including organic species or metal complexes featuring organic ligands, are widely used in crystal engineering involving HaBs [5,6,47–49].

In the course of our previous studies, we have developed a new class of organometallic tectons involving HaBs, i.e., palladium(II) and platinum(II) complexes with halogen-substituted aryl isocyanides $trans-[MX'_2(CNC_6H_4-4-X)_2]$ ($M = Pd, Pt$; $X' = Br, I$; $X = Cl, Br, I$) [16,50,51]. Throughout experimental and theoretical studies [16,50,51], we have shown that halogen atoms in isocyanide ligands (X) have areas with a positive ESP corresponding to a σ -hole position, which makes these halogens potential HaB donors. At the same time, halides (X') bonded to a metal centre carry a negative ESP on the whole of their surface and can act solely as HaB acceptors. These metal complexes simultaneously bear two σ hD (X) and two σ hA (X') that are oriented perpendicularly. We discovered that the crystallization of $trans-[PdI_2(CNC_6H_4-4-X)_2]$ ($X = Br, I$) led to isostructural 1D chains linked by two-centre C–X $\cdots$ I–Pd HaBs [16]. Furthermore, we showed that the isocyanide complexes $trans-[MBr_2(CNC_6H_4-4-X)_2]$ ($M = Pd, Pt$; $X = Br, I$) exhibit similar structural motifs in the solid state, defined by four-centre nodes supported by the cyclic HaB [51] and, in the presence of $CH_2X^S_2$ ($X^S = Cl, Br, I$), form hexagon-like structures including two-centre HaBs with dihalomethanes as the structure-directing interactions [50].

Pursuing our interest in crystal engineering involving halogen bonding and their effect on properties and reactivity (for our recent works on HaBs see references [16,50–55])

and references therein), in the current study we undertook a joint synthetic and theoretical study concerning *cis*-bis(isocyanide) complexes *cis*-[PdCl₂(CNC₆H₄-4-X)₂] (X = Cl **1**, Br **2**) and *cis*-[PtCl₂(CNC₆H₄-4-Br)₂] (**3**), in which we explored the potential of these organometallics as useful 2σhD/2σhA systems for HaB-involving crystal engineering.

2. Materials and Methods

2.1. Materials and Instrumentation

Solvents, PdCl₂, K₂PtCl₄, formic acid, and anilines were obtained from commercial sources and used as received. Complexes [PdCl₂(MeCN)₂], *cis*/*trans*-[PtCl₂(EtCN)₂] and isocyanides [16] were prepared using the literature methods. Complexes *cis*-[PdCl₂(CNC₆H₄-4-X)₂] (X = Cl **1**, Br **2**) and *cis*-[PtCl₂(CNC₆H₄-4-Br)₂] (**3**) were synthesised as reported earlier [16]. The authenticity of known species **1–3** was established upon comparison of their ¹H NMR spectra with those previously reported [16].

2.2. X-ray Structure Determination

Single crystals for the X-ray diffraction experiments were grown by slow evaporation of C₂H₄Cl₂ solutions. Suitable single crystals were selected and mounted on a MiTe-Gen tip via crystallographic oil. Data were collected using Xcalibur, Eos diffractometer (monochromated MoKα radiation, λ = 0.71073 Å) at 100(2) K. In each case, the structure was solved with a ShelXT [56] structure solution program using Intrinsic Phasing and refined with a ShelXL [56] refinement package incorporated in the OLEX2 program package [57] using Least Squares minimization. Empirical absorption correction was applied in the CrysAlisPro [58] program complex using spherical harmonics, implemented in SCALE3 ABSPACK scaling algorithm. For crystallographic data and refinement parameters, see Supplementary Material (Tables S1–S4, Figures S1 and S2). CCDC 2,089,926–2,089,928 contain the supplementary crystallographic data for this paper. These data are provided free of charge by The Cambridge Crystallographic Data Centre.

2.3. Computational Details

The DFT calculations of dimeric clusters based on experimentally obtained coordinates were performed using Gaussian-09 [59]. The Douglas–Kroll–Hess 2nd-order scalar relativistic calculations requesting relativistic core Hamiltonian were carried out using the DZP-DKH basis sets for all atoms [60–63]. The topological analysis [64], ELF [65] projections, and ED and ESP profiles [66] along bond paths were performed by applying Multiwfn 3.8 [67]. Views of dimeric clusters were created using Chemcraft [68].

3. Results and Discussion

3.1. General Description of the X-ray Structures

We found that the crystallisation of *cis*-[MCl₂(CNC₆H₄-4-X)₂] (M = Pd, X = Cl (**1**); Br (**2**); M = Pt, X = Br (**3**)) from C₂H₄Cl₂ solutions at RT leads to unsolvated structures **1–3** (Figure 1). In each case, only one type of crystal was obtained, despite significant variation of the crystallisation conditions (e.g., temperature, rate of evaporation). Compounds **1–3** crystallise in the same *P*2₁/*c* space group and are isomorphous; each crystallographically independent part contains one molecule of complex. In all the structures, the metal centre adopts a slightly distorted square-planar geometry. The isocyanide ligands are in the *cis*-position and this observation agrees with the availability of two ν(C≡N) bands in the FTIR spectra. The metal–carbon distances (1.905(6)–1.941(4) Å) are comparable to those reported for the related palladium and platinum isocyanide complexes [50,69–73]. The M–C≡N–C fragments in all structures are almost linear (Table S2). In the isocyanide ligand, the CN triple bond length (1.138(4)–1.150(7) Å) has a normal value for the typical triple CN bond (1.136–1.144 Å) and is close to those observed in the related isocyanide complexes [50,69–73].

Figure 1. View of complexes 1–3 with the atomic numbering scheme. Thermal ellipsoids are drawn with the 50% probability. Hydrogen labels are omitted for simplicity.

The inspection of the XRD data (Figure 2, Figures S1 and S2) combined with the Hirshfeld surface analysis [74] (Figures S5–S7) revealed intrinsic intermolecular contacts. In the structures of 1–3, several types of noncovalent contacts define their crystal packing (Figure 2, Figures S1 and S2), i.e., C–X···X'–C interactions (supporting by C–H···X–C hydrogen bonds), a pair of X···M, and C···C contacts between the C atoms from an isocyanato group and from a benzene ring. The detailed discussion of the parameters and nature of these interactions is given in Sections 3.2–3.5. These cooperative interactions connect molecules of the metal complex, providing their association to give 1D chains (Figure S3). These 1D chains are bound by the intermolecular C–H···Cl–M contacts discussed in Section S2, complementing a 3D crystal packing (Figure S4).

Figure 2. Noncovalent interactions in 1. Dotted line indicates the C–Cl···Cl'–C HaBs (a), C–H···Cl–C hydrogen bonds (b), Cl···Pd semicoordination (c), and C···C contacts (d). All other crystal structures look similar, and they are reported in Figures S2 and S3 (Supporting Information).

3.2. C–X···X′–C Halogen Bonding

In the structures of **1–3**, the C–X···X′–C short contacts between the halogen substitutes in the benzene rings comprise 99–103% of the sum of the Bondi vdW radii [75]; the corresponding angles around the X centre are close to 180° (C–X···X′ = 155.78(11)–162.69(9)°; Table 1) and those around X′ are close to 90° (X···X′–C = 96.87(6)–101.05(11)°; Table 1).

Table 1. Characteristic parameters of C–X···X′–C HaBs in **1–3**.

Structure	$d(\text{X}\cdots\text{X}')$, Å	$\angle(\text{C}-\text{X}\cdots\text{X}')$, °	$\angle(\text{X}\cdots\text{X}'-\text{C})$, °	R
1	3.5933(13)	155.78(11)	101.05(11)	1.03 ¹ /1.01 ²
2	3.6923(5)	162.69(9)	97.01(9)	0.99 ¹
3	3.6759(9)	161.87(17)	96.87(16)	0.99 ¹

¹ R is the ratio of the X···X′ distance to the sum of Bondi vdW radii [75]. ² R is the ratio of the X···X′ distance to the sum of Rowland vdW radii [76].

These data indicate that these short contacts are of HaB nature, according to the IUPAC criteria for Type II halogen interactions [77], and the halogen atom from X acts as an σ h donor, which interacts with a nucleophilic lump of an X′ atom. In these structures, the target organometallic molecule serves as both an HaB donor and an HaB acceptor. The HaB combination of C–X···X′–C between different isocyanide ligands linking neighbouring complexes provides their association to give 1D supramolecular chains (Figure S3).

The nature of the C–X···X′–C interactions and the supporting C–H···X–C hydrogen bonds were further evaluated for the analogous complex–complex dimeric clusters of type I (Figure 3).

Figure 3. View of dimeric cluster of type I for **1**.

The topological analysis of electron density [78] allows the (3, −1) bond critical points (BCPs) for halogen bonding in the clusters to be found. Negative [79] and small values of $\text{sign}(\lambda_2)\rho$ at the BCPs confirm the attractive and noncovalent nature of the interactions (Table 2). The Lagrangian kinetic energy $G(r)$ and potential energy density $V(r)$ at the BCPs are in the ratio $-G(r)/V(r) > 1$, and these interactions can be considered as purely noncovalent [80]. The same observations can be performed for all the other analysed noncovalent interactions (see below).

The positions of lone pairs can be illustrated using the electron localization function (ELF) [65,81–83] projections (Figure 4). The X···X′ bond paths go through the lone pair blue areas of X′ with high ELF values and less blue areas with low ELF values around X corresponding to σ h.

Table 2. Values of the density of all electrons with λ_2 sign— $\text{sign}(\lambda_2)\rho$, potential energy density— $V(r)$, Lagrangian kinetic energy— $G(r)$ (a.u.) at the BCPs, corresponding to different noncovalent interactions in dimeric clusters of all types.

Cluster	Interaction	$\text{Sign}(\lambda_2)\rho$	$V(r)$	$G(r)$
(1) ₂	Cl...Cl'	−0.006	−0.003	0.004
(2) ₂	Br...Br'	−0.007	−0.004	0.004
(3) ₂	Br...Br'	−0.007	−0.004	0.004
(1) ₂	H...Cl	−0.004	−0.002	0.003
(2) ₂	H...Br	−0.006	−0.003	0.004
(3) ₂	H...Br	−0.006	−0.003	0.004
(1) ₂	Pd...Cl	−0.007	−0.004	0.004
(2) ₂	Pd...Br	−0.009	−0.005	0.005
(3) ₂	Pd...Br	−0.008	−0.004	0.004
(1) ₂	C...C'	−0.005	−0.002	0.003
(2) ₂	C...C'	−0.005	−0.002	0.003
(3) ₂	C...C'	−0.005	−0.002	0.003

Figure 4. ELF projections and bond paths (white lines), BCPs (blue dots), nuclear critical points (brown dots), and ring critical points (orange dots) for the C-X...X'-C and C-H...X-C interactions in the (1)₂ (left), (2)₂ (middle), and (3)₂ (right) dimeric clusters of type I.

The partner philicities in the C-X...X'-C interactions can also be confirmed by the analysis of electron density (ED) and electrostatic potential (ESP) 1D profiles along the corresponding bond paths [66,81,83,84]. In noncovalent interactions, the ED minimum along the bond path is closer to the electrophilic partner nuclear critical point, whereas the ESP minimum is located nearer to the nucleophilic partner nuclear critical point. For the C-X...X'-C HaBs (Figure 5), the positions of ED and ESP minima confirm the roles of interacting atoms.

Figure 5. The ED and ESP 1D profiles along the X...X' bond paths for the (1)₂ (left), (2)₂ (middle), and (3)₂ (right) dimeric clusters of type I.

It should be noted that the interatomic C–X···X'–C distances are roughly equivalent to the sum of the Bondi vdW radii, and the critical point parameters are small, therefore, these C–X···X'–C interactions can be classified as weak HaBs.

3.3. C–H···X–C Hydrogen Bonding

The C–H···X–C interactions in structures 1–3 correspond to the IUPAC criteria for hydrogen bonding [85]: the C–H···X distances between the hydrogen atoms in the benzene rings and the halogen substituents comprise 103–104% of the sum of the Bondi vdW radii [75]; the corresponding angles around the H centre are close to 180° (C–H···X = 149.6(4)–159.13(18)°; Table 3).

Table 3. Characteristic parameters of C–H···X–C hydrogen bonds in 1–3.

Structure	$d(\text{H}\cdots\text{X}), \text{\AA}$	$d(\text{C}(\text{H})\cdots\text{X}), \text{\AA}$	$\angle(\text{C}-\text{H}\cdots\text{X}), ^\circ$	R^1	R^2
1	3.0615(9)	3.891(3)	146.87(17)	1.04	1.07
2	3.0447(3)	3.906(3)	159.13(18)	1.03	1.06
3	3.04776(11)	3.896(7)	149.6(4)	1.03	1.07

¹ R is the ratio of the H···X distance to the sum of Bondi vdW radii [75]. ² R is the ratio of the H···X distance to the sum of Rowland vdW radii [76].

The nature of the supporting C–H···X–C hydrogen bonds were also explored for the clusters of type I (Figure 3). The H···X bond paths, similar to the HaBs, lie on the X lone pair areas, according to the ELF projections (Figure 4). Hence, the X atoms possess an amphiphilic nature being HaB donors toward X' and HB acceptors toward H. The position of ED and ESP minima for the C–H···X–C HBs confirms the roles of the interacting atoms (Figure 6). The interatomic H···X distances are larger than the sum of the Bondi vdW radii and the electron density at the BCP for these HB contacts is lower than the threshold value, 0.005 a.u.; therefore, these contacts can be classified as very weak.

Figure 6. The ED and ESP 1D profiles along the H···X bond paths for the (1)₂ (left), (2)₂ (middle), and (3)₂ (right) dimeric clusters of type I.

3.4. M···X Semicoordination

The M···X semicoordination can be treated as a 2-center/2-electron (from one atom) noncovalent linkage, where X is an appropriate nucleophilic atom. In case of semicoordination bonding, the M···X distance is less than the sum of their vdW radii but significantly larger than an average value of the corresponding M–X coordination bond [86]. The angles around M···X contact relative to other ligands tend to 90°, due to the tetragonal position of X in an otherwise square-planar complex [86]. The forces involved in the formation of the semicoordination are primarily electrostatic, but the polarisation, charge transfer, and dispersion contributions all play an important role [86].

In the crystal structures of 1–3, the halogen atoms X are located opposite to a metal centre of another complex (the angles between M···X and M coordination planes are 79.12(3)–80.959(19)°), and the distances M···X (3.6450(4)–3.7445(6) Å) are larger than the sum of the Bondi vdW radii [75], but less than the sum of the Alvarez radii [87] (Table 4)

and, as conventionally required in such cases, the existence of semicoordination required further evaluation by theoretical calculations.

Table 4. Characteristic parameters of $M\cdots X$ semicoordination in 1–3.

Structure	$d(X\cdots M)$, Å	$\angle(M\cdots X \text{ and } M \text{ Coordination Plane})$, °	$\angle(C-X\cdots M)$, °	R^1	R^2
1	3.6687(9)	79.12(2)	77.93(11)	1.09	0.92
2	3.6450(4)	80.950(19)	78.35(10)	1.05	0.91
3	3.7445(6)	79.76(4)	76.68(16)	1.07	0.90

¹ R is the ratio of the $X\cdots M$ distance to the sum of Bondi vdW radii [75]. ² R is the ratio of the $X\cdots M$ distance to the sum of Alvarez vdW radii [87].

The existence and noncovalent nature of the $M\cdots X$ semicoordination was indeed confirmed using the topological analysis (Table 2) of type II dimeric clusters (Figure 7).

Figure 7. View of dimeric cluster of type II for 1.

The ELF projections for the $M\cdots X$ semicoordination show the corresponding bond paths lying in the increased ELF areas, i.e., lone pair areas of halogen atoms (Figure 8). This observation confirms the nucleophilicity of halogens toward the metal centre.

Figure 8. ELF projections and bond paths (white lines), BCPs (blue dots), nuclear critical points (brown dots), ring critical points (orange dots), and cell critical points (green dots) for the $M\cdots X$ and $C\cdots C$ interactions in the (1)₂ (left), (2)₂ (middle), and (3)₂ (right) dimeric clusters of type II.

Similar conclusions can be withdrawn from the inspection of 1D profiles of electron density and electrostatic potential along the bond paths (Figure 9), where ED minima are closer to metal nuclei.

Figure 9. The ED and ESP 1D profiles along the M...X bond paths for the (1)₂ (left), (2)₂ (middle), and (3)₂ (right) dimeric clusters of type II.

3.5. C...C' Contacts Involving CNR Species

In compounds 1–3 the isocyano group is located strictly over a phenyl ring from another complex and this observation favours C...C' interactions in head-to-tail oriented species. The distances between the C atoms of the isocyano moiety and C atoms of the benzene rings comprise 97–100% of the Rowland vdW radii [76] (Table 5).

Table 5. Characteristic parameters of C...C' contacts involving CNR species in 1–3.

Structure	$d(\text{C}\cdots\text{C}')$, Å	R
1	3.430(6)	0.97
2	3.497(5)	0.99
3	3.454(11)	0.98

R is the ratio of the C...C' distance to the sum of Rowland vdW radii [76].

The existence of π -stacking interactions was also confirmed by the theoretical calculations for the dimeric clusters of type II (Figure 7). The parameters of electron density in the BCPs confirmed the attractive and noncovalent nature of the interactions. ELF projections (Figure 8) for the interactions cannot give any information about the philicities of partners.

However, the nonpolar nature of the stacking C...C' interactions can be confirmed by very close or even the same positions of ED and ESP minima along the corresponding bond paths (Figure 10).

Figure 10. The ED and ESP 1D profiles along the C...C' bond paths for the (1)₂ (left), (2)₂ (middle), and (3)₂ (right) dimeric clusters of type II.

4. Conclusions

In the course of this study, we have prepared a series of isomorphous crystalline complexes exhibiting the double Cl/Br and Pd/Pt exchanges. The isocyanide complexes *cis*-[MCl₂(CNC₆H₄-4-X)₂] feature both HaB donor and acceptor sites and their interplay produces HaB-supported 1D chains. The results of DFT calculations, topological analysis,

ELF projections, and the inspection of the 1D profiles of ED and ESP indicate that all three types of contacts are attractive noncovalent interactions. These findings open a direction for the application of the isocyanide complexes *cis*-[MCl₂(CNC₆H₄-4-X)₂] (M = Pd, Pt; X = Cl, Br) as tectons for HaB-involving crystal engineering.

Supplementary Materials: The following are available online at <https://www.mdpi.com/article/10.3390/cryst11070799/s1>. Table S1. Crystal data and structure refinement for 1–3. Table S2. Selected bond lengths (Å) and angles (°) in 1–3. Table S3. Characteristic parameters of C–H···Cl–M hydrogen bonds in 1–3. Table S4. Results of the Hirshfeld surface analysis. Figure S1. Noncovalent interactions in 2. Dotted line indicates the C–Br···Br′–C HaBs (a), C–H···Br–C hydrogen bonds (b), Cl···Pd semicoordination (c), and C···C contacts (d). Figure S2. Noncovalent interactions in 3. Dotted line indicates the C–Br···Br′–C HaBs (a), C–H···Br–C hydrogen bonds (b), Br···Pt semicoordination (c), and C···C contacts (d). Figure S3. 1D chains of HaB-bonded hexagon-like structures of 1–3. Figure S4. 1D chains of 1–3 complex molecules bound by C–H···Cl–M hydrogen bonds. Figure S5. Hirshfeld surfaces for 1–3. Figure S6. Contributions of various intermolecular contacts to the molecular Hirshfeld surfaces of 1–3 complex molecules. Figure S7. HOMO and LUMO orbital diagrams of 1–3 obtained by XX.

Author Contributions: M.V.K. performed synthetic work, crystallization, and analysed the data. D.M.I. performed the X-ray experiment, structure determinations, and theoretical calculations. M.A.K. performed synthetic work and supervised the research. All authors made equal contributions in the manuscript's preparation. All authors have read and agreed to the published version of the manuscript.

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