

# M–X···X'–C Halogen-Bonded Network Formation in MX<sub>2</sub>(4-halopyridine)<sub>2</sub> Complexes (M = Pd, Pt; X = Cl, I; X' = Cl, Br, I)

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**ABSTRACT:** The syntheses and crystal structures of five compounds, *trans*-[MCl<sub>2</sub>(4-Xpy)<sub>2</sub>] (M = Pd, Pt; 4-Xpy = 4-halopyridine; X = Cl, Br) and *trans*-[PdI<sub>2</sub>(4-Ipy)<sub>2</sub>], are reported. All except *trans*-[PdCl<sub>2</sub>(4-Clpy)<sub>2</sub>] adopt crystal structures comprising 1D or 2D networks propagated via intermolecular M–X···X'–C halogen bonds. Halogen bond geometries exhibit near linear angles (157–173°) at the organic halogen (C–X') and much smaller angles (85–112°) at the inorganic halogen (M–X), consistent with the behavior of these halogen environments as electrophile and nucleophile, respectively. Powder diffraction studies suggest that these compounds are polymorphic.

## Introduction

The design and synthesis of crystals using crystal engineering<sup>1</sup> is often divided into two approaches, one based upon directional intermolecular interactions<sup>2</sup> and the other based upon use of coordination bonds<sup>3</sup> to propagate networks in the solid state. In the former category, the interactions of choice are most often hydrogen bonds, which are directional and reasonably strong and offer the choice of linking molecules via a large number of functional groups that possess hydrogen-bond donor and/or acceptor functions.

In the past few years, there has been a growing recognition that a class of interactions known as halogen bonds offers many of the same opportunities as hydrogen bonds for forming reliable connections between molecules and ions. Although such interactions have been known for many years,<sup>4</sup> a better understanding of their nature has only begun to emerge more recently. The recognition of their potential strength and directionality has also begun to lead to a number of potential applications such as anion receptors,<sup>5</sup> control of molecular positioning for topochemical reactions,<sup>6</sup> conducting materials,<sup>7</sup> liquid crystals,<sup>8</sup> fluorinated coatings,<sup>9</sup> and other applications, as has recently been reviewed by Metrangola, Resnati, and co-workers.<sup>10</sup>

Halogen bonds are Lewis acid–Lewis base interactions between an organic halide group, C–X, or dihalogen, X–X (X = halogen), serving as the Lewis acid, and a Lewis base, e.g., C–X···B. The interaction is typically linear at the (organic) halogen, consistent with maximizing the two main directional attractive contributions to the interaction energy, electrostatics and charge transfer, and minimizing the exchange repulsion, which is also directional.<sup>11,12</sup>

Recently, we have developed a new class of highly directional halogen bonds M–X···X'–C.<sup>12–16</sup> These interactions employ the properties of terminal metal halides (M–X) as directional Lewis bases, in a manner previously identified<sup>17</sup> and developed<sup>18–21</sup> in hydrogen-bonding applications. In a series of systematic experimental and theoretical studies, we have shown that the attractive nature of these interactions is principally governed by electrostatics and that M–X···X'–C interactions can be reliably formed between ionic or neutral molecular species.<sup>12</sup> In one such study, we examined the networks formed

and the relative strengths of M–X···X'–C interactions in the series of compounds *trans*-[MCl<sub>2</sub>(3-Xpy)<sub>2</sub>] (M = Pd, Pt; 3-Xpy = 3-halopyridine; X = I, Br, Cl, F).<sup>12a</sup> Here we report an extension of this study using structural isomers *trans*-[MCl<sub>2</sub>(4-Xpy)<sub>2</sub>] (M = Pd, Pt; X = Cl, Br) along with the related compound *trans*-[PdI<sub>2</sub>(4-Ipy)<sub>2</sub>].

## Experimental Section

**General.** All reagents (purchased from Aldrich or Lancaster) and solvents were used as received. Single crystals of all compounds were prepared by solvent diffusion methods A or B. An alternative method (C) was employed to prepare samples as powders. The elemental analyses and the yields refer to the powder samples. Elemental analyses were conducted by the Elemental Analysis Service, Department of Chemistry, University of Sheffield. Powder diffraction data were obtained using Cu K $\alpha$  radiation on a Bruker D8 diffractometer in reflection mode and are presented along with patterns calculated from the single-crystal data in the Supporting Information (Figure S2).

**Method A.** Crystals were obtained by diffusion between immiscible layers at room temperature (20 °C). In small vials, an acidified aqueous phase containing the metal salt was layered upon a CH<sub>2</sub>Cl<sub>2</sub> phase containing the halopyridine. All the vials were sealed with a plastic lid during crystal growth.

**Method B.** Crystals were obtained at room temperature (20 °C) by a method based on slow diffusion in U-shaped tubes (internal diameter 5 mm). Methanolic solutions containing the metal salt and the halopyridine, respectively, were prepared, and the latter was acidified using HCl. The two solutions were layered in separate arms of the U-tube above a basal layer of CH<sub>2</sub>Cl<sub>2</sub>. Both arms of the U-tube were then sealed with Parafilm.

**Method C.** Powders were typically obtained by mixing 100 mg of Na<sub>2</sub>PdCl<sub>4</sub> or K<sub>2</sub>PtCl<sub>4</sub> with the stoichiometric quantity of 4-halopyridinium chloride ([4-XpyH]Cl; X = Cl, Br) previously dissolved in H<sub>2</sub>O (pH ~ 9). The powders were repeatedly rinsed with H<sub>2</sub>O, dried overnight at 35–40 °C, and lightly ground with a pestle and mortar before powder X-ray diffraction.

**Synthesis of *trans*-[PtCl<sub>2</sub>(4-Clpy)<sub>2</sub>] (1).** 4-Chloropyridinium chloride, [4-ClpyH]Cl (20 mg, 0.133 mmol), was dissolved in 2 mL of H<sub>2</sub>O (pH ~ 8 with addition of KOH) and extracted in CH<sub>2</sub>Cl<sub>2</sub> (2 mL). K<sub>2</sub>PtCl<sub>4</sub> (30 mg, 0.072 mmol) in 2 mL of water acidified (pH ~ 1) using hydrochloric acid was layered on the CH<sub>2</sub>Cl<sub>2</sub> solution (method A). Yellow prismatic crystals of **1** resulted after 3 weeks. A powder sample of **1** was obtained in 25.5% yield within a few hours by mixing solutions I and II, prepared as follows (method C). Solution I: 100 mg of K<sub>2</sub>PtCl<sub>4</sub> was dissolved in 2 mL of H<sub>2</sub>O. Solution II: 72 mg of 4-chloropyridinium chloride was dissolved in 5 mL of H<sub>2</sub>O (pH adjusted to ca. 10 by addition of KOH). Anal. Calcd: C, 24.44; H, 1.64; N, 5.70. Found: C, 24.19; H, 1.46; N, 5.57. The powder diffraction pattern (bulk sample) is not consistent with the pattern calculated from single-

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Table 1. Data Collection and Structure Refinement Information

	PtCl <sub>2</sub> (4-Clpy) <sub>2</sub> (1)	PtCl <sub>2</sub> (4-Brpy) <sub>2</sub> (2)	PdCl <sub>2</sub> (4-Clpy) <sub>2</sub> (3)	PdCl <sub>2</sub> (4-Brpy) <sub>2</sub> (4)	PdI <sub>2</sub> (4-Ipy) <sub>2</sub> (5)
crystal color	yellow	yellow	yellow	yellow	red
crystal size (mm)	0.50 × 0.30 × 0.24	0.40 × 0.37 × 0.21	0.18 × 0.12 × 0.08	0.30 × 0.25 × 0.20	0.12 × 0.10 × 0.09
crystal system	triclinic	monoclinic	triclinic	triclinic	monoclinic
space group, Z	P1, 1	P2 <sub>1</sub> /c, 2	P1, 1	P1, 1	P2 <sub>1</sub> /c, 2
a (Å)	5.3827(1)	6.199(1)	3.9039(8)	5.465(1)	7.905(3)
b (Å)	6.9293(2)	14.139(3)	7.655(2)	6.960(1)	12.629(5)
c (Å)	9.4909(2)	7.770(1)	11.740(3)	9.593(2)	8.764(3)
α (deg)	75.219(2)	90	106.368(4)	75.117(3)	90
β (deg)	83.950(2)	96.826(3)	90.135(4)	84.477(3)	98.975(7)
γ (deg)	83.355(2)	90	98.920(4)	84.631(3)	90
V (Å <sup>3</sup> )	338.92(1)	676.2(2)	332.2(1)	350.1(1)	864.2(6)
density (mg/m <sup>3</sup> )	2.416	2.859	2.022	2.340	2.960
temperature (K)	150(5)	150(5)	150(5)	150(5)	150(5)
μ(Mo Kα) (mm <sup>-1</sup> )	11.115	16.657	2.177	7.391	8.201
θ range (deg)	3.05–27.44	2.64–23.33	2.82–28.70	3.04–27.52	3.06–28.33
reflns collected	6195	5400	4129	3378	6302
ind reflns, n (R <sub>int</sub> )	1436 (0.049)	978 (0.088)	1781 (0.036)	1448 (0.020)	2048 (0.043)
reflns used in refinement	1436	978	1781	1448	2048
L.S. parameters (p)	79	79	79	79	79
R1(F), <sup>a</sup> I > 2.0σ(I)	0.0240	0.0359	0.0465	0.0334	0.0330
wR2(F <sup>2</sup> ), <sup>a</sup> all data	0.0659	0.0964	0.1133	0.1306	0.0656
S(F <sup>2</sup> ), <sup>a</sup> all data	1.083	1.171	1.039	1.241	0.949

$$^a R1(F) = \sum(|F_o| - |F_c|)/\sum|F_o|; wR2(F^2) = [\sum w(F_o^2 - F_c^2)^2/\sum wF_o^4]^{1/2}; S(F^2) = [\sum w(F_o^2 - F_c^2)^2/(n - p)]^{1/2}.$$

crystal data, but the good match of the composition with the experimental elemental analysis suggests a polymorphic phase.

**Synthesis of *trans*-[PtCl<sub>2</sub>(4-Brpy)<sub>2</sub>] (2).** 4-Bromopyridinium chloride, [4-BrpyH]Cl (27 mg, 0.130 mmol), was dissolved in 2 mL of H<sub>2</sub>O (pH adjusted to ca. 8 by addition of KOH) and extracted into CH<sub>2</sub>Cl<sub>2</sub> (2 mL). K<sub>2</sub>PtCl<sub>4</sub> (30 mg, 0.072 mmol) in 2 mL of water acidified (pH ~ 1) using hydrochloric acid was layered on the CH<sub>2</sub>Cl<sub>2</sub> solution (method A). Yellow prismatic crystals of **2** resulted after 3 weeks. A powder sample of **2** was obtained in 20.8% yield within a few hours by mixing solutions I and II, prepared as follows (method C). Solution I: 100 mg of K<sub>2</sub>PtCl<sub>4</sub> was dissolved in 2 mL of H<sub>2</sub>O. Solution II: 95 mg of 4-bromopyridinium chloride was dissolved in 5 mL of H<sub>2</sub>O (pH adjusted to ca. 10 by addition of KOH). Anal. Calcd: C, 20.73; H, 1.39; N, 4.84. Found: C, 19.73; H, 1.29; N, 4.52. The powder diffraction pattern (bulk sample) was not consistent with the pattern calculated from single crystal data, but the reasonable match of the composition with the experimental elemental analysis suggests a polymorphic phase (the minor discrepancy is probably due to impurities).

**Synthesis of *trans*-[PdCl<sub>2</sub>(4-Clpy)<sub>2</sub>] (3).** 4-Chloropyridinium chloride, [4-ClpyH]Cl (50 mg, 0.333 mmol), was dissolved in 2 mL of H<sub>2</sub>O (pH adjusted to ca. 8 by addition of KOH) and extracted into CH<sub>2</sub>Cl<sub>2</sub> (2 mL). 2 mL of a solution prepared by dissolving K<sub>2</sub>PdCl<sub>6</sub> (10 mg, 0.025 mmol) in 15 mL of aqueous HCl (3.7%) was then layered on the CH<sub>2</sub>Cl<sub>2</sub> solution (method A). Thick needle shaped yellow crystals of **3** resulted after 2 weeks. A powder sample of **3** was obtained in 48.1% yield within a few seconds by mixing solutions I and II, prepared as follows (method C). Solution I: 100 mg of Na<sub>2</sub>PdCl<sub>4</sub> was dissolved in 2 mL of H<sub>2</sub>O. Solution II: 100 mg of 4-chloropyridinium chloride was dissolved in 12 mL of H<sub>2</sub>O (pH adjusted to ca. 8 with addition of KOH). Anal. Calcd: C, 29.86; H, 2.01; N, 6.97. Found: C, 29.28; H, 1.90; N, 6.48. The powder diffraction pattern (bulk sample) was reasonably consistent with the pattern calculated from single-crystal data.

**Synthesis of *trans*-[PdCl<sub>2</sub>(4-Brpy)<sub>2</sub>] (4).** 4-Bromopyridinium chloride, [4-BrpyH]Cl (33 mg, 0.170 mmol), was dissolved in the minimum amount of aqueous HCl (37%), and then that solution was added to 2 mL of MeOH. Na<sub>2</sub>PdCl<sub>4</sub> (25 mg, 0.085 mmol) was dissolved in 2 mL of MeOH. 1 mL of each solution, respectively, was layered in separate arms of a U-tube above CH<sub>2</sub>Cl<sub>2</sub> (2 mL). Yellow prismatic crystals of **4** resulted after 5 weeks (method B). A powder sample of **4** was obtained in 36.2% yield within a few seconds by mixing solutions I and II, prepared as follows (method C). Solution I: 165 mg of Na<sub>2</sub>-PdCl<sub>4</sub> was dissolved in 2 mL of H<sub>2</sub>O. Solution II: 180 mg of 4-bromopyridinium chloride was dissolved in 12 mL of H<sub>2</sub>O (pH adjusted to ca. 8 by addition of KOH). Anal. Calcd: C, 24.35; H, 1.63; N, 5.68. Found: C, 24.31; H, 1.42; N, 5.24. The powder diffraction pattern (bulk sample) was not consistent with the pattern calculated

from single-crystal data, but the good match of the composition with the experimental elemental analysis suggests a polymorphic phase.

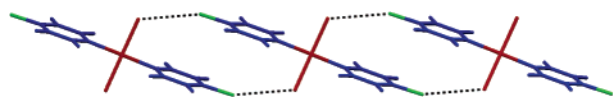
**Synthesis of *trans*-[PdI<sub>2</sub>(4-Ipy)<sub>2</sub>] (5).** 4-Iodopyridine, 4-Ipy (70 mg, 0.341 mmol), was dissolved in 2 mL of 1:1 MeOH/CH<sub>2</sub>Cl<sub>2</sub>, and the resulting dark colored precipitate was separated from the pale green solution [sol. A]. K<sub>2</sub>PdCl<sub>6</sub> (10 mg, 0.025 mmol) was dissolved in 15 mL of HCl (3.7%) [sol. B]. 2 mL of solution B was layered on solution A (method A). A black precipitate formed very rapidly but was not removed. Red prismatic crystals were obtained in very low yield after 2 weeks. Insufficient crystalline product prevented any bulk analyses from being performed.

**Crystallography.** X-ray data were collected on a Bruker SMART 1000 diffractometer using Mo Kα radiation. Crystal structures were solved and refined against all F<sup>2</sup> values using the SHELXTL suite of programs.<sup>22</sup> A summary of the data collection and structure refinement information is provided in Table 1. Data were corrected for absorption using empirical methods (SADABS) based upon symmetry-equivalent reflections combined with measurements at different azimuthal angles.<sup>23</sup> Non-hydrogen atoms were refined anisotropically. All reported hydrogen-bond geometries are based upon H-atom positions that have been adjusted along their bond vector to positions consistent with their expected nuclear positions (C–H = 1.083 Å and N–H = 1.01 Å).<sup>24</sup> In the analysis of intermolecular interactions, reference is made to sums of van der Waals radii for the pairs of interacting atoms based upon the survey by Bondi (viz.: Cl⋯Cl = 3.50 Å; Br⋯Cl = 3.60 Å; I⋯Cl = 3.73 Å; Br⋯Br = 3.70 Å; Br⋯I = 3.83 Å; I⋯I = 3.98 Å; Cl⋯H = 2.95 Å; Br⋯H = 3.05 Å; I⋯H = 3.16 Å).<sup>25</sup>

## Results

Reaction of K<sub>2</sub>PtCl<sub>4</sub>, Na<sub>2</sub>PdCl<sub>4</sub>, or K<sub>2</sub>PdCl<sub>6</sub> with the appropriate 4-halopyridinium chloride [4-XpyH]Cl (X = Cl, Br) or 4-iodopyridine (under acidic conditions) permitted the preparation of the compounds *trans*-[MCl<sub>2</sub>(4-Xpy)<sub>2</sub>] (M = Pt, Pd; X = Cl, Br). A byproduct *trans*-[PdI<sub>2</sub>(4-Ipy)<sub>2</sub>] was also obtained. Initial trials using direct mixing of miscible solutions of the two reactants yielded microcrystalline powders. Thus, slow mixing of solutions of the two reactants via immiscible phases (method A) was necessary to prepare crystals of the compounds **1–3** and **5** that were of suitable size for single-crystal X-ray diffraction studies. Method B, using the U-tubes, permitted the slowest mixing and proved necessary to prepare crystals of the compound **4**.

Compounds **1–5** were characterized by low-temperature X-ray crystallography. All compounds crystallize such that the *trans*-[MX<sub>2</sub>(4-X'py)<sub>2</sub>] molecules adopt a crystallographically

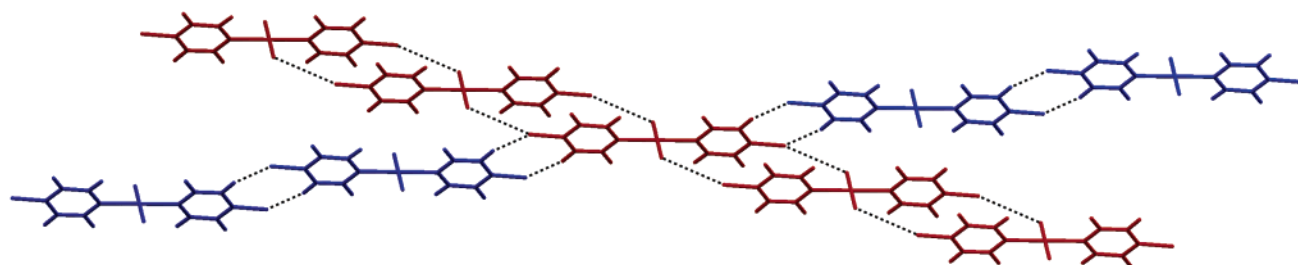


**Figure 1.** M-Cl...X-C halogen-bonded tapes in **1** (and **4**). Metal atoms and halide ligands are shown in red, organic halogens in green, and remaining atoms in blue.

imposed centrosymmetric conformation. Compounds **1–4** gave satisfactory elemental analyses, but powder diffraction studies confirmed for **1**, **2**, and **4** that rapid crystallization has led to a different (polymorphic) phase from that identified from the single-crystal structure determination.

In the structures of all compounds except **3**, a network of molecules is linked via M-X...X'-C halogen bonds. Molecules are further linked via C-H...Cl hydrogen bonds and  $\pi$ -stacking interactions. Two halogen-bonded network types were found, namely, 1D tapes in which each molecule is linked to two neighbors via pairs of M-X...X'-C interactions, and 2D layers in which each molecule is linked to four neighbors in a (4,4) grid via individual M-X...X'-C interactions. Compound **3** exhibits no M-X...X'-C halogen bonds but instead forms tapes in which each molecule is linked to two neighbors via pairs of C-H...Cl-Pd hydrogen bonds.

**Halogen-Bonded Tape Structures of PtCl<sub>2</sub>(4-Clpy)<sub>2</sub> (**1**) and PdCl<sub>2</sub>(4-Brpy)<sub>2</sub> (**4**).** The forms of compounds **1** and **4** characterized by single-crystal diffraction are isostructural, as confirmed by unit cell parameters, and comprise tape motifs based on M-X...X'-C halogen bonds that propagate in the (1, 0, -1) direction (Figure 1). The molecules are centrosymmetric but not planar with the Cl-M-Cl vector twisted out of the plane of the pyridine rings, yielding torsion angles C-N-Pt-Cl of 56.3(4) and 55.1(4)° for **1** and C-N-Pd-Cl of 58.2(5) and 55.4(5)° for **4**. Halogen bond geometries exhibit characteristic directional behavior<sup>12–16</sup> with markedly bent interactions at the inorganic halogen and closer to linear approaches at the organic halogen [(Pt)Cl...Cl(C) = 3.511(2) Å, Pt-Cl...Cl = 111.6(1)°, and C-Cl...Cl = 157.4(2)° for **1**; (Pd)Cl...Br(C) = 3.516(2) Å, Pd-Cl...Br = 112.0(1)°, and C-Br...Cl = 159.1(2)° for **4**]. These tapes are cross-linked via C-H...Cl-M hydrogen bonds [shortest (C)H...Cl(Pt) = 2.686 Å, C-H...Cl = 133.7°, and Pt-Cl...H = 124.9° for **1**; (C)H...Cl(Pd) = 2.708 Å, C-H...Cl = 131.9°, and Pd-Cl...H = 125.2° for **4**] and R<sub>2</sub><sup>2</sup>(8) C-H...X-C weak hydrogen-bonded rings [blue tape in Figure 2; (C)H...Cl(C) = 2.937 Å, C-H...Cl = 168.5°, and C-Cl...H = 125.0° for **1**; (C)H...Br(C) = 3.013 Å, C-H...Br = 165.0°, and C-Br...H = 127.6° for **4**], with the latter being supported by further C-H...Cl-M hydrogen bonds [H...Cl = 2.802 Å (**1**) and 2.849 Å (**4**)]. The  $\pi$ -stacking interaction between centrosymmetrically related rings of neighboring molecules also contributes a cohesive force along the tapes.



**Figure 2.** Relationship between the M-Cl...X-C halogen-bonded tapes (molecules shown in red) and cross-linking via tapes propagated through R<sub>2</sub><sup>2</sup>(8) C-H...X-C hydrogen-bonded rings (molecules shown in blue) for compound **1** (and **4**).

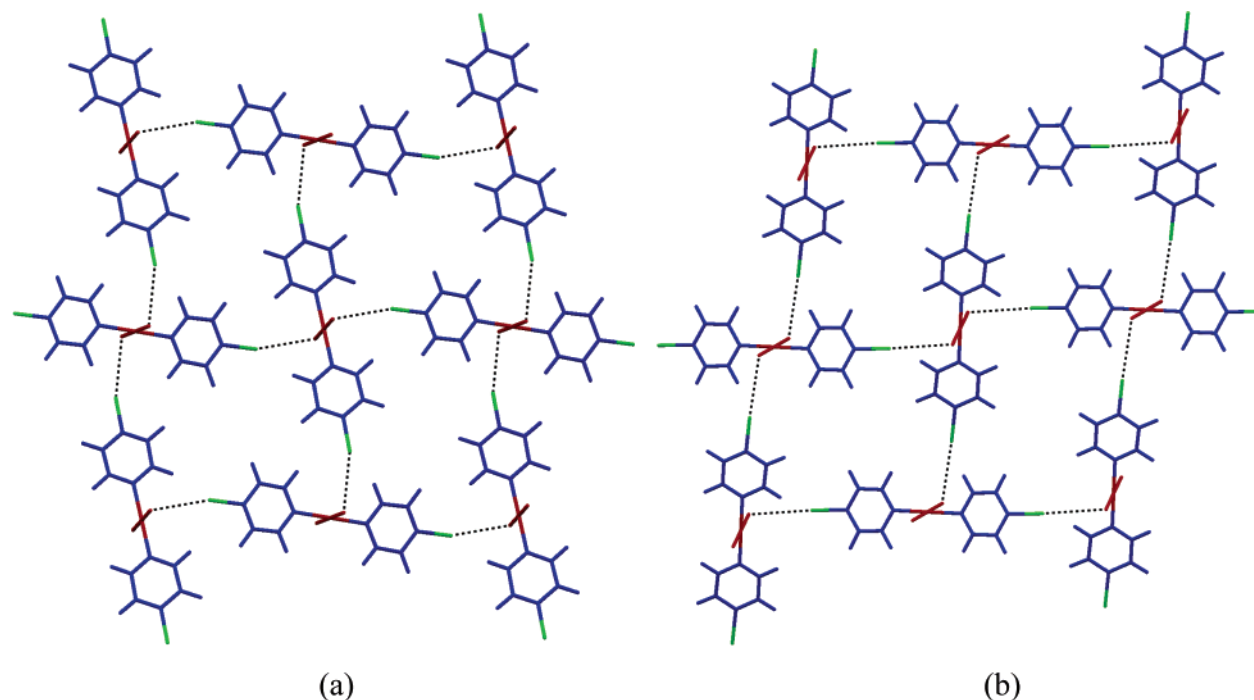
**Two-Dimensional (4,4) Nets Based on M-X...X'-C Halogen-Bonded Links in PtCl<sub>2</sub>(4-Brpy)<sub>2</sub> (**2**) and PdI<sub>2</sub>(4-Ipy)<sub>2</sub> (**5**).** The forms of compounds **2** and **5** characterized by single-crystal diffraction contain molecules linked via M-X...X'-C halogen bonds into two-dimensional networks of (4,4) topology that propagate approximately parallel to the *ab* plane. The two structures are similar but not isostructural, as seen in Figure 3. The Cl-M-Cl vector is almost orthogonal to the pyridine ring planes [torsion angles C-N-Pd-Cl = 83.0(6)° and 83.4(7)° for **2** and 82.6(4)° and 80.5(5)° for **5**].

The halogen bonds show short halogen-halogen separations accompanied by angular orientation at the inorganic halogen and approximately linear interactions at the organic halogen [(Pt)Cl...Br(C) = 3.325(3) Å, Pt-Cl...Br = 85.4(1)°, and C-Br...Cl = 163.6(3)° for **2**; (Pd)I...I(C) = 3.670(1) Å, Pd-I...I = 87.7(2)°, and C-I...I = 172.1(2)° for **5**]. The halogen bonds are supported by weak C-H...X-C hydrogen bonds across the corners of the quadrilaterals formed by the (4,4) nets [See Supporting Information, Figure S1; (C)H...Br(C) = 2.984 Å, C-H...Br = 140.8°, and C-Br...H = 121.1° for **2**; C-H...I-C = 3.006 Å, C-H...I = 142.0°, and C-I...H = 106.5° for **5**].

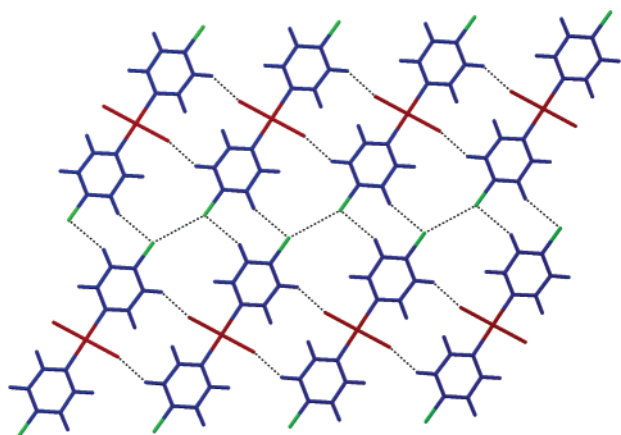
Stacking of the nets along the *c*-axis does not give rise to close  $\pi$ -stacking of aromatic rings; all inter-ring separations exceed 4 Å. However, the orientation of M-X bonds along the stacking axis leads to relatively short symmetric M-X...X-M contacts between molecules situated in every other layer [(Pt)Cl...Cl(Pt) = 3.457(5) Å and Pt-Cl...Cl = 150.5(1)° in **2**; (Pd)I...I(Pd) = 3.773(2) Å and Pd-I...I = 155.0(2)° in **5**]. The geometry of these interactions suggests that this is an approach of least repulsion rather than attraction. These close contacts are, however, mediated by C-H...X-M hydrogen bonds [(C)H...Cl(Pt) = 2.709 Å, Pt-Cl...H = 113.8°, C-H...Cl = 128.9°, (C)H...Cl(Pt) = 2.818 Å, Pt-Cl...H = 113.8°, and C-H...Cl = 158.45° for **2**; (C)H...I(Pd) = 2.928 Å, Pd-I...H = 88.5°, and C-H...I = 175.4° for **5**] and are examined in more detail in the Discussion section (see also Figure 5).

**Absence of Halogen Bonds in the Structure of PdCl<sub>2</sub>(4-Clpy)<sub>2</sub> (**3**).** Compound **3** adopts a layer structure (Figure 4) that is probably best described in terms of 1D tape motifs that propagate parallel to the *b*-axis direction, in which molecules are linked via C-H...Cl-Pd hydrogen bonds that adopt a R<sub>2</sub><sup>2</sup>(12) ring arrangement [(C)H...Cl(Pd) = 2.599 Å, C-H...Cl = 145.4°, and Pd-Cl...H = 112.5°]. The tapes are then linked via R<sub>2</sub><sup>2</sup>(8) C-H...Cl-C hydrogen-bonded rings [(C)H...Cl(C) = 3.112 Å, C-H...Cl = 150.5°, and C-Cl...H = 93.4°] and also give rise to relatively short C-Cl...Cl-C contacts [(C)-Cl...Cl(C) = 3.385(3) Å and C-Cl...Cl = 148.4(2)°]. The molecular conformation is similar to that observed for compounds **1** and **4** [C-N-Pd-Cl = 57.1(3) and 53.4(3)°] and permits offset  $\pi$ -stacking interactions between layers accompanied by further C-H...Cl-Pd hydrogen bonds.





**Figure 3.** Networks of (4,4) topology adopted by (a) compound **2** and (b) compound **5**. Colors as in Figure 1.



**Figure 4.** Structure of **3** showing tapes propagated by  $\text{C-H}\cdots\text{Cl}$ -Pd hydrogen bonds running horizontally (along the  $b$ -axis) and intertape  $R_2^2(8)$   $\text{C-H}\cdots\text{Cl}$ -C hydrogen-bonded rings and  $\text{C-Cl}\cdots\text{Cl}$ -C contacts. Colors as in Figure 1.

## Discussion

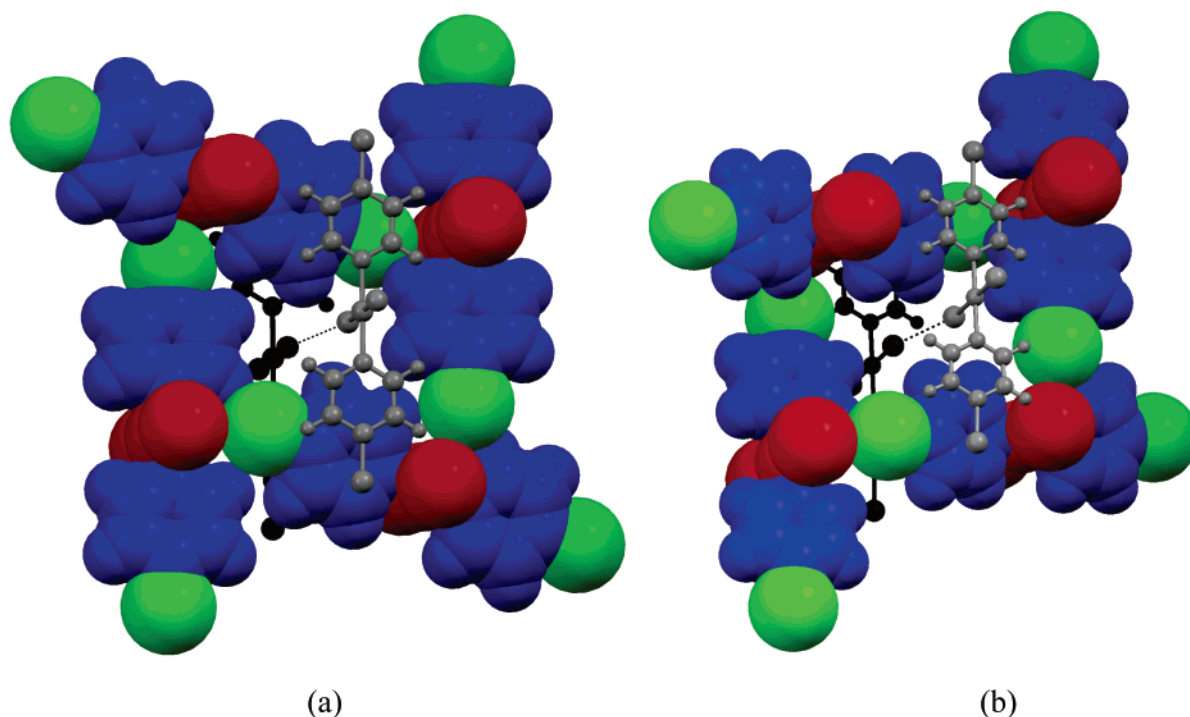
**Supramolecular Synthons and Networks.** In the previous study of the systems  $\text{trans-MCl}_2(3\text{-Xpy})_2$  ( $\text{X} = \text{halogen}$ ;  $\text{M} = \text{Pt}, \text{Pd}$ ), our focus was on identifying the supramolecular motifs that led to the assembly of these molecules into noncovalent networks and particularly on the reliability of the  $\text{M-X}\cdots\text{X}'\text{-C}$  interaction as a supramolecular synthon.<sup>12a</sup> The present study of the structural isomers of those compounds,  $\text{trans-MCl}_2(4\text{-Xpy})_2$  ( $\text{M} = \text{Pt}, \text{Pd}$ ;  $\text{X} = \text{Cl}, \text{Br}$ ), and of  $\text{trans-PdI}_2(4\text{-Ipy})_2$  provides additional insight into the effectiveness of the  $\text{M-X}\cdots\text{X}'\text{-C}$  synthon, which will be discussed in the context of other supporting and competing interactions.

In the previous study, two types of networks predominated, namely tapes in which each molecule was connected via pairs of  $\text{M-X}\cdots\text{X}'\text{-C}$  halogen bonds to two neighbors and layer structures comprising (4,4) nets in which each molecule was linked to four others in the same layer via  $\text{M-X}\cdots\text{X}'\text{-C}$  halogen

bonds. In the present study, similar networks are found in the structures of compounds **1**, **2**, **4**, and **5**.

The ribbonlike motifs found in the structures of **1** and **4** resemble those found for  $\text{PtCl}_2(3\text{-Xpy})_2$  ( $\text{X} = \text{Cl}, \text{Br}$ ) and  $\text{PdCl}_2(3\text{-IPy})_2$  in the earlier study<sup>12a</sup> despite the change in the position of the organic halogen. These halogen-bonded ribbons are then linked into the overall 3D structure via  $\text{C-H}\cdots\text{Cl-M}$  hydrogen bonds and offset  $\pi$ -stacking interactions between centrosymmetrically related molecules.

Compounds **2** and **5** adopt (4,4) net structures propagated via  $\text{M-X}\cdots\text{X}'\text{-C}$  halogen bonds, as observed for the structures of  $\text{PtCl}_2(3\text{-Xpy})_2$  ( $\text{X} = \text{Br}, \text{I}$ ) and  $\text{PdCl}_2(3\text{-Xpy})_2$  ( $\text{X} = \text{Cl}, \text{Br}$ ). The orthogonal orientation of inorganic and organic halogens in compounds **2** and **5** leads to an approximately orthogonal orientation of molecules linked via halogen bonds (ca.  $60^\circ$  for **2** and  $90^\circ$  for **5**) and gives rise to holes into which the halide ligands from molecules in layers above and below are inserted (Figure 5). Importantly, the size of the hole is greater for **5**, where iodide ligands need to be accommodated, than in **2**, where chloride ligands are employed. This change in size of the hole is achieved by some deviation from linearity for the weaker  $\text{Pt-Cl}\cdots\text{Br-C}$  halogen bonds found in **2** [ $\text{C-Br}\cdots\text{Cl} = 163.6(3)^\circ$ ]. The location of each halide ligand within these holes is supported by a pair of  $\text{C-H}\cdots\text{X-M}$  ( $\text{X} = \text{Cl}, \text{I}$ ) hydrogen bonds and facilitated by the orthogonal arrangement of the halide and pyridine ligands within each molecule [ $\text{C-N-M-X}$  torsion angle  $80\text{--}84^\circ$ , in contrast to ca.  $55^\circ$  for compounds **1**, **3**, and **4** and  $\text{MCl}_2(3\text{-Xpy})_2$  compounds]. The electropositive cavity provided by the pyridine  $\text{C-H}$  groups is presumably what also allows the halide ligands from the two molecules (colored black and gray in Figure 5) to approach each other and overcome the repulsive  $\text{M-X}\cdots\text{X-M}$  interaction. In contrast, the (4,4) nets adopted by the 3-halopyridine compounds contain molecules whose principal axis lies at an angle of ca.  $30^\circ$  to that of neighboring molecules, leading to a more compact network into which halide ligands from the neighboring layer cannot be inserted.



**Figure 5.** View of four molecules for networks of (a) compound **2** and (b) compound **5** (colors as in Figure 1) showing the hole in which the halide ligand from molecules of the next layers (black, below; gray, above) sits.  $M-X\cdots X-M$  contact is highlighted.

**Table 2.** Geometries of  $M-X\cdots X'-C$  Halogen Bonds

halogen bond	$X\cdots X'$ (Å)	$M-X\cdots X'$ (deg)	$C-X'\cdots X$ (deg)	$r_X + r_{X'}$ (Å)	$R_{XX'}$
<b>1</b> Pt-Cl $\cdots$ Cl-C	3.511(2)	111.6(1)	157.4(2)	3.50	1.003
<b>2</b> Pt-Cl $\cdots$ Br-C	3.325(3)	85.4(1)	163.6(3)	3.60	0.923
<b>4</b> Pd-Cl $\cdots$ Br-C	3.516(2)	112.0(1)	159.1(2)	3.60	0.976
<b>5</b> Pd-I $\cdots$ I-C	3.670(1)	87.7(2)	172.1(2)	3.96	0.926

**Table 3.** Geometries of  $M-X\cdots X-M$  and  $C-X\cdots X-C$  Contacts

interaction	$X\cdots X$ (Å)	$(M,C)-X\cdots X$ (deg)	$2r_X$ (Å)	$R_{XX}$
<b>1</b> C-Cl $\cdots$ Cl-C	3.479(3)	136.5(2)	3.50	0.994
<b>2</b> Pt-Cl $\cdots$ Cl-Pt	3.457(5)	150.5(1)	3.50	0.987
<b>3</b> C-Cl $\cdots$ Cl-C	3.385(3)	148.4(2)	3.50	0.967
<b>4</b> C-Br $\cdots$ Br-C	3.575(2)	134.9(2)	3.70	0.966
<b>5</b> Pd-I $\cdots$ I-Pd	3.773(2)	155.0(2)	3.96	0.952

In contrast to the structures adopted by compounds **1**, **2**, **4**, and **5** and the previously reported  $MCl_2(3-Xpy)_2$  compounds ( $X \neq F$ ), in the structure of compound **3**, halogen bonds, here  $Pd-Cl\cdots Cl-C$ , are not formed. Instead, ribbons are propagated by  $C-H\cdots Cl-Pd$  hydrogen bonds employing the C-H in the 3-position of the pyridine rings in a manner analogous to the use of the 3-halo substituents ( $X'$ ) used in formation of  $M-X\cdots X'-C$  halogen-bonded tapes in  $PtCl_2(3-Xpy)_2$  ( $X = Cl, Br$ ) and  $PdCl_2(3-IPy)_2$ .<sup>12a</sup> Neighboring tapes give rise to a symmetric  $C-Cl\cdots Cl-C$ , which like the short  $M-X\cdots X-M$  contacts in compounds **2** and **5** is inevitably repulsive, as the geometry confirms (vide infra), but is supported by weak attractive  $R_2^2(8)$   $C-H\cdots Cl-C$  hydrogen-bonded ring interactions. Similar  $C-X\cdots X-C$  contacts are found in the structures of **1** and **4**.

**Halogen Bonds and Halogen-Halogen Contacts.** The geometries of the  $M-X\cdots X'-C$  halogen bonds and short  $M-X\cdots X-M$  or  $C-X\cdots X-C$  contacts are summarized in Tables 2 and 3, respectively. Halogen bond geometries are consistent with previous observations in that large  $C-X'\cdots X$  angles are observed (approaching linearity), whereas markedly bent  $M-X\cdots X'$  geometries are found, consistent with the established behavior<sup>12-16</sup> of the organic halogen as Lewis acid and the

inorganic halogen as Lewis base. There is a general decrease in the normalized halogen bond length  $R_{XX'}$  concomitant with  $C-X'\cdots X$  angles closer to linearity upon increasing Lewis acidity of the organic halogen (i.e. from Cl to Br to I), consistent with established trends.<sup>12</sup> The halogen bonds found in compounds **2** and **5** are rather short for such interactions between neutral molecules<sup>12a</sup> and indeed show halogen-halogen separations approaching those between ions.<sup>12b</sup> A possible reason for this is that the adjacent  $C-H\cdots X-C$  hydrogen bonds (vide supra, Figure S1) may play a supporting role and thereby strengthen the halogen bonds.

It is important to contrast the attractive, highly directional, and asymmetric  $M-X\cdots X'-C$  halogen bonds with the symmetric  $M-X\cdots X-M$  or  $C-X\cdots X-C$  contacts observed in all five structures herein. There has been much debate regarding the nature of  $C-X\cdots X-C$  interactions<sup>4,11b</sup> but no such discussion that we are aware of corresponding to  $M-X\cdots X-M$  interactions. Symmetric interactions of this type necessarily will be electrostatically repulsive, i.e.,  $M-X^{\delta-}\cdots X^{\delta-}-M$  for all  $M-X\cdots X$  angles and  $C-X^{\delta+}\cdots X^{\delta+}-C$  for large  $C-X\cdots X$  angles (ca.  $C-X\cdots X \geq 130^\circ$ ) and  $C-X^{\delta-}\cdots X^{\delta-}-C$  for smaller  $C-X\cdots X$  angles (ca.  $C-X\cdots X \leq 130^\circ$ ), based upon electrostatic potential calculations.<sup>26</sup> Charge transfer contributions to these interactions are also likely to be minimal since an asymmetric arrangement with one large (near linear) and one small (near  $90^\circ$ )  $M-X\cdots X$  or  $C-X\cdots X$  angle would be needed. Thus, given that dispersion and polarization contributions are likely to give only a small attractive contribution,<sup>11a,b</sup> the inevitable conclusion is that these symmetric  $M-X\cdots X-M$  and  $C-X\cdots X-C$  are repulsive in nature. This is consistent with the fact that in each case these close contacts are supported by attractive  $C-H\cdots X-M$  or  $C-H\cdots X-C$  hydrogen bonds.

**Polymorphism.** For compounds **1-4**, powder samples were prepared by much more rapid crystallization than the method used for preparation of single crystals. In all cases but compound **3**, the measured powder pattern showed that the powder sample did not correspond to the same crystal structure as obtained from

the single crystal despite the correspondence in composition established by elemental analyses. This strongly indicates the formation of polymorphic forms of compounds **1**, **2**, and **4** under the different crystallization conditions, although efforts to match powder patterns from within this set of compounds with the single-crystal structures of the others did not give any clear indications of the structures of the powder samples (e.g. see Figure S3). Powder diffraction data were of insufficient quality to undertake ab initio structure determination. However, the polymorphism implicit for the compounds herein was anticipated following a similar conclusion from the study of the related MCl<sub>2</sub>(3-Xpy)<sub>2</sub> systems.

### Conclusions

The reliability of M–X···X'–C halogen bonds as supramolecular synthons between neutral molecules has been confirmed in this study of MX<sub>2</sub>(4-X'py)<sub>2</sub> compounds. Four of the five crystal structures reported contain networks propagated via such interactions, in all cases exhibiting consistent geometry with large (157–173°) angles at the organic halogen (C–X') and much smaller angles (85–112°) at the inorganic halogen (M–X). However, some limitations are realized in that Pd–Cl···Cl–C halogen bonds are not formed in the crystal structure of *trans*-[PdCl<sub>2</sub>(4-Cl-py)<sub>2</sub>] (**3**). Powder diffraction studies strongly suggest that these compounds are polymorphic, as might be anticipated from earlier studies of the related MCl<sub>2</sub>(3-Xpy)<sub>2</sub> compounds. Significant further investigation will be needed to establish the extent of the polymorphism.

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**Supporting Information Available:** X-ray crystallographic files in CIF format for compounds **1**–**5**. Experimental and calculated powder patterns for compounds **1**–**4**. Figure showing all intermolecular interactions at nodes in (4,4) nets in structures of compounds **2** and **5**. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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