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1. Introduction

The phenomenon of halogen bonding (XB) comprises one of the basic concepts of physical chemistry related to intermolecular forces. All aspects of chemistry and physics of XB have been receiving rapidly growing interest during the past decade. Various applications of XB have been recently reviewed and they include XB-involving crystal engineering,^{1–3} catalysis,^{4–9} synthetic coordination chemistry,¹⁰ polymer chemistry,¹¹ and non-covalent aspects of medicinal chemistry;^{12–15} notably, XB is also important in human functions.¹⁶ As far as XB acceptors are concerned, these centers include electronegative hetero-atoms bearing lone pair(s) such as halogens (F, Cl, Br, and I), O, S, N, P *etc.* atoms, electron-donating carbon (*e.g.* $-C \equiv C^-$ or π -systems in alkenes,

Metal-involving halogen bond $Ar-I\cdots[d_{z^2}Pt^{II}]$ in a platinum acetylacetonate complex[†]

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A combined XRD and theoretical study for two adducts, [Pt(acac)_2]·2(1,3,5-FIB) and [Pd(acac)_2]·1,3,5-FIB (Hacac = acetylacetone; 1,3,5-FIB = 1,3,5-triiiodotrifluorobenzene), reveals that differences in the type formed halogen bond (XB) depend on the identity of the metal center. Only [Pt(acac)_2] forms rare two-center metal-involving XB Ar–I···[d_z₂Pt^{II}] (where the positively charged Pt^{II} center acts as a nucleophile toward an iodine σ -hole), while three-center bifurcated XB I··· η^2 (O,O) was detected in both adducts. The observed linkage Ar–I···[d_z₂Pt^{II}] provides an experimental argument favoring the previously established (by a kinetic study) XB-formation step upon oxidative addition of I₂ to [Pt(acac)₂]. The variable temperature XRD study of [Pt(acac)₂]·2(1,3,5-FIB) (100–300 K; five XRD experiments) demonstrates that the I···Pt and I···O contacts weaken simultaneously on heating that allows the consideration of the Pt1–O2 bond as an integrated XB acceptor. Appropriate DFT calculations (M06/DZP-DKH level of theory) performed by single-point "quasi-solid state" calculations with topological analysis of the electron density distribution within the framework of the Bader theory (QTAIM method), confirmed the existence of the two-center metal-involving XB I····Pt in the structure of [Pt(acac)₂]·2(1,3,5-FIB) and three-center I···· η^2 (O,O) bifurcated XBs for both adducts. All these interactions exhibit a non-covalent nature with estimated energies in the range of 2.1–4.3 kcal mol⁻¹.

alkynes, and arenes), and even d_{z^2} -orbital donating positively charged metal centers (for our recent studies see ref. 17–19).

Currently, metal-involving XB has been identified for Ni^{II}, Rh^I, Pd^{II}, Pt^{II}, Au⁰, and Au^I (ref. 17–19) centers. In particular, a strong σ -hole (σ h) donor such as I₂ forms XBs with Rh^{1,20}, Pd^{II},²¹ and Pt^{II}.²² Iodine centers of R^{EWG}I organic species could also behave as σ h donors, *e.g.* in 2-iodopyrazine derivatives of Ni^{II}, Pd^{II}, and Pt^{II}, ^{23,24} adducts of tetraiodoethylene with Au^I species,²⁵ and adducts of *trans*- $[MX_2(NCNMe_2)_2]$ (M = Pt, Pd; X = Cl, Br) with iodoform.^{17,19} A XB is also formed upon interactions between iodoperfluorobenzenes and gold nanoparticles in water solutions²⁶ and, in addition, a non-covalent C-I…Au⁰ XB was detected for a gold nanogap.^{27,28} Other halogens such as Cl and Br behave as XB donors toward metal centers significantly more rarely and only ClCH₂-Cl···Au^I (ref. 29) and $Br_2XC-Br\cdots M^{II}$ (X = H or Br; M = Pd, Pt)^{17,18} short contacts were previously identified.

Besides their role in crystal engineering, XBs involving d⁸metal centers (d⁸M = Rh^I, Pd^{II}, Pt^{II}) are of interest for understanding the mechanisms of oxidative addition reactions. XB may be able to stabilize intermediates and/or transition states of the oxidative addition steps of metalcatalyzed cross-coupling reactions (for instance, Suzuki, Heck, Sonogashira, *etc.*). Theoretical calculations suggested

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that an Ar–I···Pd XB is formed in the intermediate of the oxidative addition of aryl iodides.^{30,31} Our previous work¹⁷ fully supported these assumptions by the experimental recognition of C–X···d⁸M^{II} (M = Pd, Pt) contacts in *trans*- $[MX_2(NCNMe_2)_2]$ ·2CHX₃ (X = Br, I; M = Pd, Pt) adducts.

It is noteworthy that in some instances the usage of complexes bearing (halide)[M] moieties for the design of adducts with σh -(X)····d⁸M^{II} linkages led to bifurcated σh - $(X) \cdots \eta^2 ([d^8 M^{II}], Cl)$ halogen bonds, specifically for the adducts of trans-[PtCl₂(NCNR₂)₂] with CBr₄ (ref. 18) or CHI₃.¹⁹ Planning to study how formal replacement of Cl for other non-halide anionic ligands affects weak interactions with d⁸M^{II} centers (including regular two-center XB or three-center bifurcated XB), we obtained the adducts $[Pt(acac)_2] \cdot 2(1,3,5)$ FIB) and $[Pd(acac)_2] \cdot 1, 3, 5$ -FIB (Hacac = acetylacetone) with 1,3,5-triiodotrifluorobenzene (1,3,5-FIB). In the platinum acetylacetonate adduct, we detected and confirmed theoretically the existence of a metal-involving $Ar-I\cdots[d_{z^2}Pt^{II}]$ XB. The observed linkage provides an experimental argument favoring the previously established (by a kinetic study³²) XBformation step upon oxidative addition of I_2 to $[Pt(acac)_2]$.

2. Results and discussion

2.1. Triiodotrifluorobenzene adducts and general description of their XRD structures

The complexes $[M(acac)_2]$ (M = Pd, Pt) and 1,3,5-FIB were cocrystallized in CHCl₃–MeOH solutions at RT to form the adducts $[Pt(acac)_2]\cdot2(1,3,5-FIB)$ and $[Pd(acac)_2]\cdot1,3,5-FIB$, whose structures were studied by XRD. These two adducts exhibit different $[M(acac)_2]$: FIB molar ratios and also different crystal lattice parameters. In both adducts, the M–O (M = Pd, Pt), C2–O1, and C2–C3 bond distances and the O–M–O angles are equal, within 3σ , to those in the unassociated congeners $[M(acac)_2]^{33,34}$ and in the relevant adducts $[M(acac)_2]\cdot1,4$ -FIB (M = Pd, Pt; 1,4-FIB = 1,4-diiodotetrafluorobenzene)³⁵ that we studied earlier.

2.1.1. Non-covalent interactions in $[Pt(acac)_2] \cdot 2(1,3,5-FIB)$ at 100 K. The structure of $[Pt(acac)_2] \cdot 2(1,3,5-FIB)$ is composed of one type of $[Pt(acac)_2]$ and one type of 1,3,5-FIB molecule. By contrast to the adducts $[Pt(acac)_2] \cdot (1,4-FIB)^{35}$ and $[Pd(acac)_2] \cdot (1,3,5-FIB)$ (this work), the complex $[Pt(acac)_2]$ does not form stacks. However, each $[Pt(acac)_2]$ is surrounded by eight 1,3,5-FIBs and form different types of short contacts. Thus, three-center bifurcated XB $I \cdots \eta^2$ (O,O) between one iodine atom of 1,3,5-FIB and two O atoms from an



Fig. 1 Short contacts in the structure of [Pt(acac)₂]·2(1,3,5-FIB).

acetylacetonate ligand was detected (Fig. 1). This contact demonstrates a significant difference in two I \cdots O distances (Table 1). The I2S atom of 1,3,5-FIB also forms a contact with the Pt1 and O2 atoms of [Pt(acac)₂] (Fig. 1).

Interestingly, in $[Pt(acac)_2] \cdot 2(1,3,5-FIB)$, the Ar^F-I···Pt contact (3.4077(3) Å) is shorter than the previously reported¹⁹ I₂CH–I···Pt XBs (3.4276(5)–3.4389(5) Å), measured at 100 K for trans-[PtCl₂(NCNMe₂)₂]·2CHI₃ and trans-[PtCl₂(NCNMe₂)₂] $\cdot 0.5$ CHCl₃ $\cdot 1.5$ CHI₃. It is only slightly longer (within 3σ) than in trans-[PtBr₂(NCNR₂)₂]·2CHI₃ (3.4023(5) Å at 100 K). These data can be rationalized by different nucleophilicities of the platinum(II) centers in all these PtII species, which are comparable to bromide and acetylacetonate complexes and they are slightly lower than that for the chloride complex. CHI3 and 1,3,5-FIB demonstrate comparable XB donor abilities; for the C-I···X⁻ XBs, the average I···X distances are 3.194 vs. 3.161 Å for X = Cl, 3.268 vs. 3.334 Å for X = Br, and 3.556 vs. 3.525 Å for X = I, correspondingly, according to the CCDC statistics. 1,3,5-FIB molecules form C-H…I HBs with the CH and Me groups from one acetylacetonate ligand. Notably, interactions with iodine atoms are geometrically the strongest according to the d_{norm} plot over the Hirshfeld surface^{36,37} (Fig. 2).

The most intriguing feature of the structure of $[Pt(acac)_2] \cdot 2(1,3,5-FIB)$ is the availability of metal-involving $I \cdots [d_{z^2}Pt^{II}]$ XBs. The same I atom forms an $I \cdots O$ contact, and at the

Table 1 Short contacts in the structure of [Pt(acac) ₂]·2(1,3,5-FIB)						
Contact	D…A distance, Å	I^a	Angles around D…A, °	Comments		
I2S…Pt1	3.4077(3)	0.91	C4S-I2S…Pt1 168.83(9)	XB		
I2S…O2	3.370(2)	0.96	C4S-I2S…O2 153.72(10)	Presumably XB		
I1S…O1	3.094(2)	0.88	C2S-I1S…O1 165.93(9)	Bifurcated XB		
I1S…O2	3.374(2)	0.96	C2S-I1S…O1 144.12(9)	Bifurcated XB		
I3S…I3S	3.5943(7)	0.91	C6S-I3SI3S 146.76(3)	Type I contact		

^{*a*} I = the ratio between the D···A distance and ΣvdW radii for D and A.



Fig. 2 The Hirshfeld surface of the $[Pt(acac)_2]$ moiety in the $[Pt(acac)_2]$ ·2(1,3,5-FIB) crystal colored by d_{norm} values. Black dashed lines denote the most shortened contacts.

same time, the I···Pt interaction provides a greater contribution as compared to I···O, based on interatomic distance and angle analysis (Table 1). In order to study the nature and strengths of these contacts, variable temperature XRD and theoretical studies for $[Pt(acac)_2]\cdot 2(1,3,5-FIB)$ were performed (sections 2.1.2 and 2.1.3).

2.1.2. Variable temperature XRD study of $[Pt(acac)_2]$ -2(1,3,5-FIB). The variable temperature XRD studies of $[Pt(acac)_2]$ -2(1,3,5-FIB) were performed to compare the response of different intermolecular interactions on the change of external conditions (100–300 K, 5 XRD experiments at 50 K per step). The detailed discussion of the corresponding trends is given in the ESI[†] (see also Tables S1– S5 and Fig. S1), while the main features of geometric contact behaviors are summarized below.

It is of particular importance that all XBs were found to be pronouncedly less flexible with respect to the temperature change than any other shortened intermolecular contact. The heating from 100 to 300 K leads to significant weakening of the H2A…I2S HB and stacking interaction (the H2A…I2S and interplanar distance between the acetylacetonate ligands increased by 0.114 Å and 0.147 Å, respectively, from 3.1570(2) and 3.349(6) to 3.2706(3) and 3.496(8) Å), whereas the largest change of interatomic distances corresponding to XBs is only 0.081 Å (for O1…I1S from 3.094(2) to 3.175(3) Å). These geometrical trends (Table S3[†]) were confirmed by the analysis of contributions to Hirshfeld surfaces at different temperatures (Table S4[†]) and the inspection of changes of Hirshfeld volumes of the Pt(acac)₂ and 1,3,5-FIB moieties (Tables S5[†]), and were also in line with the anisotropy of crystal thermal expansion (Tables S1, S2 and Fig. S1[†]).

While the insignificant lengthening (0.064 Å) of the I3S \cdots I3S distance upon heating is expected because of the rather substantial strength of the corresponding XB. It is noteworthy that this strength can be estimated by comparison of I3S \cdots I3S distances with other type I I \cdots I separations obtained from CSD.³⁸ The behavior of bifurcated XBs formed by the I1S and I2S atoms is more intriguing as these interactions exhibit dramatically different temperature induced changes. The bifurcated XBs formed by the I1S atom combines a very conservative I1S \cdots O2 contact (lengthening of 0.012 Å, from 3.374(2) to 3.386(3) Å) with a rather flexible

Table 2 Values of the density of all electrons – $\rho(\mathbf{r})$, Laplacian of electron density – $\nabla^2 \rho(\mathbf{r})$, energy density – $H_{\rm b}$, potential energy density – $V(\mathbf{r})$, and Lagrangian kinetic energy – $G(\mathbf{r})$ (a.u.) at the bond critical points (3, –1), corresponding to different non-covalent interactions in ([Pt(acac)_2])-(1,3,5-FIB)_4, bond lengths – l (Å), as well as energies for these contacts $E_{\rm int}$ (kcal mol⁻¹), defined by two correlations proposed exclusively for non-covalent interactions involving iodine atoms^{*a*41}

Contact	$\rho(\mathbf{r})$	$\nabla^2 \rho(\mathbf{r})$	$H_{\rm b}$	$V(\mathbf{r})$	$G(\mathbf{r})$	$E_{\rm int}^{\ \ b}$	$E_{\rm int}^{\ \ c}$	l
100 K								
I2S…Pt1	0.017	0.041	0.000	-0.010	0.010	4.3	4.2	3.408
I1S…O1	0.013	0.050	0.001	-0.010	0.011	4.3	4.6	3.094
I1S…O2	0.008	0.032	0.001	-0.005	0.007	2.1	2.9	3.374
150 K								
I2S…Pt1	0.016	0.040	0.000	-0.009	0.010	3.8	4.2	3.421
I1S…O1	0.013	0.048	0.002	-0.009	0.011	3.8	4.6	3.114
I1S…O2	0.008	0.032	0.001	-0.005	0.007	2.1	2.9	3.371
200 K								
I2S…Pt1	0.016	0.039	0.000	-0.009	0.009	3.8	3.8	3.434
I1S…O1	0.012	0.047	0.002	-0.009	0.010	3.8	4.2	3.135
I1S…O2	0.008	0.032	0.001	-0.005	0.007	2.1	2.9	3.375
250 K								
I2S…Pt1	0.015	0.038	0.000	-0.009	0.009	3.8	3.8	3.450
I1S…O1	0.012	0.045	0.002	-0.008	0.010	3.4	4.2	3.156
I1S…O2	0.008	0.031	0.001	-0.005	0.006	2.1	2.5	3.379
300 K								
I2S…Pt1	0.015	0.037	0.001	-0.008	0.009	3.4	3.8	3.466
I1S…O1	0.011	0.043	0.002	-0.008	0.009	3.4	3.8	3.175
I1S…O2	0.008	0.031	0.001	-0.005	0.006	2.1	2.5	3.386

^{*a*} The presence of a linear relationship between the energy of non-covalent interactions and electronic properties at the BCP was verified on the set of complexes featuring typical XBs: NH₃···X–R, H₂S···X–R, H₂O···X–R, HCN···X–R, C₂H₄···X–R, and CO···X–R, where X = Cl, Br, I (for details see ref. 41). ^{*b*} $E_{int} = 0.68(-V(\mathbf{r}))$. ^{*c*} $E_{int} = E_{int} = 0.67G(\mathbf{r})$.



Fig. 3 Contour line diagrams of the Laplacian distribution $\nabla^2 \rho(\mathbf{r})$, bond paths and selected zero-flux surfaces referring to non-covalent interactions I2S…Pt1 (top) and I1S…O1,O2) (bottom) in model supramolecular clusters based on the 100 K (left) and 300 K (right) data. Bond critical points (3, -1) are shown in blue, nuclear critical points (3, -3) in pale brown, and ring critical points (3, +1) in orange. Length units – Å.

I1S…O1 counterpart (lengthening of 0.081 Å, from 3.094(2) to 3.175(3) Å). It is noteworthy that the I1S…O2 interaction is significantly longer and less directional (at 100 K, the I1S…O2 distance is 3.374(2) Å; \angle (C2S-I1S…O2) 144.1(3)°) than the I1S…O1 contact (3.094(2) Å and 165.9(3)°). Thus, the interplay between two interactions was observed: while the weakening of the strong I1S…O1 interaction destabilizes crystal packing, compensation is achieved by the rigidity of the weak I1S…O2 interaction. This is not the case, however, for the second bifurcated XB involving the metal center. The

I2S…O2 contact, exhibiting similar geometric characteristics to the I1S…O2 contact at 100 K but more directional (3.370(2) Å; ∠(C4–I2S…O2) 153.7(3)°), weakens to a significantly larger extent upon heating (of 0.078 Å, from 3.370(2) to 3.448(4) Å). In contrast to the I1S bifurcate XB, the counterpart I2S…Pt1 contact lengthens significantly (of 0.058 Å, from 3.4077(3) to 3.4662(4) Å), though it corresponds to the most directed intermolecular interaction in [Pt(acac)₂] ·2(1,3,5-FIB) (∠(C4S–I2S…Pt1) 168.8(3)°). In other words, both contacts in the I2S bifurcated XB weaken simultaneously,

Table 3 Short contacts in the structure of [Pd(acac) ₂]·1,3,5-FIB						
Contact D…A	D…A distance, Å	I^{a}	Angles around D…A,°	Comments		
C5…Pd2	3.323(4)	1.00		Metallocycle stacking		
C2…Pd1	3.464(5)	1.04		Metallocycle stacking		
I2S····C5	3.266(4)	0.89	C3S-I2S····C5 174.50(13)	XB		
I1S…O2	3.260(3)	0.93	C1S-I1S…O2 150.46(14)	Bifurcated XB		
I1S…O1	3.160(3)	0.90	C1S-I1S…O1 160.30(14)	Bifurcated XB		
I3S…F1S	3.136(2)	0.91	C5S-I3S…F1S 172.15(13)	XB		
C4A…F3S	3.099(6)	0.98	C4-C4A…F3S 169.1(3)	Tetrel bonding		

^{*a*} I = the ratio between the D···A distance and Σ vdW radii for D and A.



Fig. 4 Short contacts (dotted lines) in the structure of $[Pd(acac)_2]$ -1,3,5-FIB; environment of the first (upper) and the second (lower) molecule of $[Pd(acac)_2]$.

which allows the consideration of the Pt1–O2 bond as the whole XB acceptor. A similar temperature induced behavior of the metal-involving bifurcated XB was found previously in the adduct of a Pt chloride complex with CHI₃.¹⁹ Notably, the recognition of bifurcated XBs, which is based on distance analysis and variable temperature XRD studies, is not supported by theoretical calculations and only the I…Pt contact was confirmed theoretically (see section 2.1.3). Indeed, it is known that the presence or absence of BCPs is not always indicative of non-covalent interaction.³⁹

2.1.3. Theoretical study on non-covalent interactions in $[Pt(acac)_2]\cdot 2(1,3,5-FIB)$. In order to shed light on the nature and energy of non-covalent interactions involving iodine atoms in $[Pt(acac)_2]\cdot 2(1,3,5-FIB)$, we carried out DFT



Fig. 5 The Hirshfeld surface of the first (left) and the second (right) $[Pd(acac)_2]$ moieties in the $[Pd(acac)_2] \cdot 1,3,5$ -FIB crystal colored by d_{norm} values. Black dashed lines denote the most shortened contacts.

calculations and performed topological analysis of the electron density distribution within the framework of Bader's theory (QTAIM method)⁴⁰ for model supramolecular clusters ([Pt(acac)₂])·(1,3,5-FIB)₄ (Fig. 1) based on the XRD data obtained at 100, 150, 200, 250, and 300 K, respectively (ESI,† Table S7). Results are summarized in Table 2, and the contour line diagrams of the Laplacian distribution $\nabla^2 \rho(\mathbf{r})$, bond paths, and selected zero-flux surfaces for selected non-covalent interactions in model supramolecular clusters based on the 100 K and 300 K data are shown in Fig. 3.

The QTAIM analysis performed for ([Pt(acac)₂])·(1,3,5-FIB)₄ demonstrates the presence of appropriate bond critical points (3, -1) (BCPs) for all contacts listed in Table 2. The low magnitude of the electron density (0.008-0.017 a.u.), positive values of the Laplacian (0.031-0.050 a.u.), and zero or very close to zero energy density (0.000-0.002 a.u.) in these BCPs are typical for non-covalent interactions involving halogen atoms (see, e.g., ref. 17, 24, 35, 42 and 43). We have defined energies for these weak contacts according to correlations proposed by Tsirelson et al. for non-covalent interactions involving iodine atoms,⁴¹ and one can state that their estimated strengths vary in the ranges of 3.4-4.3 (I2S…Pt1), 3.4-4.6 (I1S…O1), and 2.1-2.9 (I1S…O2) kcal mol⁻¹, respectively. The balance between the Lagrangian kinetic energy $G(\mathbf{r})$ and potential energy density $V(\mathbf{r})$ at the BCPs (3, -1) reveals the nature of these interactions, if the ratio $-G(\mathbf{r})/V(\mathbf{r}) > 1$ is satisfied, then the nature of appropriate interaction is purely non-covalent, and in case the of $-G(\mathbf{r})/$ $V(\mathbf{r}) < 1$, some covalent component takes place.⁴⁴ Based on this criterion one can state that a covalent contribution is absent in all supramolecular contacts given in Table 2.

2.1.4. Non-covalent interactions in [Pd(acac)₂]·1,3,5-FIB at 100 K. The structure of [Pd(acac)₂]·1,3,5-FIB is composed of two independent molecules of $[Pd(acac)_2]$ and one type of 1,3,5-FIB molecule. Both types of $[Pd(acac)_2]$ complexes form stacks with the shortest Pd…C distances between each metal center and the central C atom of the acetylacetonate ligand from the neighboring molecule (Table 3), similar to those found in [Pd(acac)₂]·1,4-FIB.³⁵ In addition, weak interaction between the iodine atom of 1,3,5-FIB and the central C atom of the acac ligand from [Pd(acac)₂] molecules of the second type was detected. The first type of the $[Pd(acac)_2]$ molecules is involved in the $I \cdots \eta^2(O,O)$ bifurcated XB between the iodine atom of 1,3,5-FIB and the O atoms of the acac ligand (Fig. 4), which is more symmetrical than a similar bifurcated XB in [Pt(acac)₂]·2(1,3,5-FIB) (see above). This contact also resembles the corresponding contacts $I \cdots \eta^2(O,O)$ in the [Pd(acac)₂]·1,4-FIB^{35,45} adduct. 1,3,5-FIB molecules also form C-H…I HBs with Me groups from an acetylacetonate ligand, C-C…F tetrel bonds 46 (Fig. S2†) with the same Me group, and C-I…F XBs (Fig. S2[†]) between each other.

As far as the $[Pt(acac)_2]\cdot 2(1,3,5\text{-FIB})$ crystal is concerned, the contacts formed by the iodine atoms are the shortest according to the d_{norm} value distribution over the Hirshfeld surface of the $[Pd(acac)_2]$ moiety (Fig. 5). It is noteworthy that this criterion collaterally indicates that the I···C XB is

Table 4 Values of the density of all electrons $-\rho(\mathbf{r})$, Laplacian of electron density $-\nabla^2\rho(\mathbf{r})$, energy density $-H_{\rm b}$, potential energy density $-V(\mathbf{r})$, and Lagrangian kinetic energy $-G(\mathbf{r})$ (a.u.) at the bond critical points (3, -1), corresponding to different unusual non-covalent interactions in ([Pd(acac)_2])_3 (1,3,5-FIB)_2 and ([Pd(acac)_2])_3 (1,3,5-FIB)_4, bond lengths -l (Å), as well as energies for some of these contacts $E_{\rm int}$ (kcal mol⁻¹), defined by two correlations proposed exclusively for non-covalent interactions involving iodine atoms^{*a*41}

Contact	a (m)	$\nabla^2 c(\mathbf{r})$	7.7	$V(\mathbf{r})$	$G(\mathbf{r})$	$E_{\rm int}^{\ \ b}$	$E_{\rm int}^{c}$	l
Contact	$\rho(\mathbf{r})$	$\mathbf{v} \ \rho(\mathbf{r})$	Hb					
$([Pd(acac)_2])_3 \cdot (1,3)$	3,5-FIB) ₂							
C2…Pd1	0.009	0.020	0.000	-0.005	0.005	2.1^d	2.1^d	3.464
I1S…O1	0.012	0.045	0.001	-0.008	0.010	3.4	4.2	3.159
I1S…O2	0.010	0.039	0.002	-0.007	0.008	3.0	3.4	3.259
$([Pd(acac)_2])_3 \cdot (1,3)$	3,5-FIB) ₄							
C5…Pd2	0.012	0.025	0.000	-0.007	0.006	3.0^{d}	2.5^{d}	3.323
$I2S \cdots C5$	0.012	0.038	0.001	-0.007	0.008	3.0	3.4	3.266
I3S…F1S	0.009	0.042	0.002	-0.007	0.009	3.0	3.8	3.136
C4A…F3S	0.005	0.026	0.002	-0.003	0.005	1.3^{d}	2.1^d	3.099

^{*a*} The presence of a linear relationship between the energy of non-covalent interactions and electronic properties at the BCP was verified on the set of complexes featuring typical XBs: NH₃···X-R, H₂S···X-R, H₂O···X-R, HCN···X-R, C₂H₄···X-R, and CO···X-R, where X = Cl, Br, I (for details see ref. 41). ^{*b*} $E_{int} = 0.68(-V(\mathbf{r}))$. ^{*c*} $E_{int} = 0.67G(\mathbf{r})$. ^{*d*} Note that in these cases, energy estimates should be taken into consideration with caution since the correlations with which they were obtained were originally developed exclusively for non-covalent interactions involving iodine atoms. Unfortunately, generally accepted empirical correlations between the properties of electron density at the BCPs and the strength of such non-covalent interactions are currently unavailable. However, the corresponding energy values can be easily normalized if some specific empirical correlations for determination of the strength for such non-covalent interactions will be proposed in the future.

stronger than the I··· η^2 (O,O) bifurcated XB. However, the results of DFT calculations and consequent QTAIM analysis do not confirm this assumption: estimated strengths for the I···C XB: 3.0–3.4 kcal mol⁻¹ (solid state geometry) and 2.6–2.9 kcal mol⁻¹ (optimized equilibrium gas phase geometry) *vs.* estimated strengths for the I··· η^2 (O,O) bifurcated XB: 6.4–7.6 kcal mol⁻¹ (solid state geometry) and 6.4–7.2 kcal mol⁻¹ (optimized equilibrium gas phase geometry) (see section 2.1.3 and Tables S8 and S9† for more details).

2.1.5. Theoretical study of unconventional non-covalent interactions in $[Pd(acac)_2]$ ·1,3,5-FIB. In order to shed light on the nature and energy of different unconventional non-covalent interactions in $[Pd(acac)_2]$ ·1,3,5-FIB (*viz.* the C…Pd metal-involving interaction, the I…O, I…C, and I…F XBs, and the C…F tetrel bonding), we carried out

DFT calculations and performed topological analysis of the electron density distribution within the framework of Bader's theory (QTAIM method)⁴⁰ for two model supramolecular clusters $([Pd(acac)_2])_3 \cdot (1,3,5-FIB)_2$ and $([Pd(acac)_2])_3 \cdot (1,3,5-FIB)_4$ featuring various types of short contacts based on the XRD data obtained at 100 K (ESI,† Table S7). The results are summarized in Table 4, and the contour line diagrams of the Laplacian distribution $\nabla^2 \rho(\mathbf{r})$, bond paths, and selected zero-flux surfaces for selected non-covalent interactions in model supramolecular clusters $([Pd(acac)_2])_3 \cdot (1,3,5-FIB)_2$ and $([Pd(acac)_2])_3 \cdot (1,3,5-FIB)_4$ are shown in Fig. 6 and 7.

The QTAIM analysis performed for the model supramolecular clusters $([Pd(acac)_2])_3 \cdot (1,3,5-FIB)_2$ and $([Pd(acac)_2])_3 \cdot (1,3,5-FIB)_4$ demonstrates the presence of



Fig. 6 Contour line diagrams of the Laplacian distribution $\nabla^2 \rho(\mathbf{r})$, bond paths and selected zero-flux surfaces referring to non-covalent interactions C2…Pd1 (left) and I1S…O1,O2) (right) in the model supramolecular cluster ([Pd(acac)_2])_3·(1,3,5-FIB)_2. Bond critical points (3, -1) are shown in blue, nuclear critical points (3, -3) in pale brown, and ring critical points (3, +1) in orange. Length units – Å.



Fig. 7 Contour line diagrams of the Laplacian distribution $\nabla^2 \rho(\mathbf{r})$, bond paths and selected zero-flux surfaces referring to non-covalent interactions C5...Pd2 (top, left), I25...C5 (bottom, left), I35...F1S (top, right) and C4A...F3S (bottom, right) in the model supramolecular cluster ([Pd(acac)_2])_3 (1,3,5-FIB)_4. Bond critical points (3, -1) are shown in blue, nuclear critical points (3, -3) in pale brown, and ring critical points (3, +1) in orange. Length units – Å.

appropriate BCPs (3, -1) for all the contacts listed in Table 4. The low magnitude of the electron density (0.005–0.012 a.u.), positive values of the Laplacian (0.020–0.045 a.u.), and zero or very close to zero energy density (0.000–0.002 a.u.) in these BCPs are typical for non-covalent interactions. We have defined energies for non-covalent interactions involving iodine atoms,⁴¹ and one can state that their estimated strengths vary in the ranges of 3.0–4.2 kcal mol⁻¹. The balance between the Lagrangian kinetic energy $G(\mathbf{r})$ and potential energy

density $V(\mathbf{r})$ at the BCPs⁴⁴ reveals that covalent contribution is absent in all the supramolecular contacts given in Table 4, except for C5…Pd2 in ([Pd(acac)₂])₃ \cdot (1,3,5-FIB)₄.

3. Concluding remarks

Upon examination of the XRD structures of $[Pt(acac)_2] \cdot 2(1,3,5-FIB)$ and $[Pd(acac)_2] \cdot 1,3,5-FIB$, we found that the differences of XB patterns depend on the identity of a metal center. The



Fig. 8 Patterns of XBs in the adducts of [M(acac)₂] (M = Pd, Pd)³⁵ with 1,4-FIB (a) and 1,3,5-FIB (b and c; this work).

two-center metal-involving XB was recognized only for the platinum adduct probably because the metal center exhibits better d_{z^2} -nucleophilicity than that in [Pd(acac)₂]. Our previous studies on [d8MI]-involving XBs were focused on adducts of halide complexes, *i.e.* $[MX_2L_2]$ (M = Pt^{II}, Pd^{II}; X = Cl, Br; L = an organic ligand)¹⁷⁻¹⁹ with XB donors, and in some instances, we identified bifurcated contacts R- $X' \cdots \eta^2$ (Pt,Cl) (R-X' = CBr₄, CHI₃).^{18,19} In contrast to the halide ligands with their unpronounced directionality (that is reflected in a rather flexible XB orientation),⁴⁷ the O centers of the acetylacetonate ligands in [M^{II}(acac)₂] cannot form I…n²(M,O) contacts because of the steric reasons (unfavorable for bifurcated contact directionality of the lone pair lobe at the O atom) and only the I…Pt contacts were detected. However, the I···O contact is a part of the I··· η^2 (O, O) bifurcated XB in both adducts.

The comparison of the structural features of the two types of adducts, namely $[M(acac)_2] \cdot n(1,3,5-FIB)$ (M/n = Pd/1; Pt/2;this work) and the previously published $[M(acac)_2] \cdot (1,4-FIB)$ (M = Pd, Pt),³⁵ indicates that the geometrical parameters of the perfluoroiodobenzenes can affect the types of formed non-covalent contacts. For the adducts with 1,4-FIB, where the angle between two XB donor centers in the molecule is 180°, formation of extended supramolecular structures with the same type of short contact $(M \cdots M \text{ stacking and } I \cdots \eta^2(O, O);$ Fig. 8a) was observed. For the 1,3,5-FIB adducts, where three XB donor centers are situated at $\angle 120^\circ$, extended regular structures were not formed, but another geometry of the XB donating molecule leads to other contacts (such as $I \cdots Pt$ and $I \cdots C_{acac}$) and to the appearance of certain differences between the two metal centers (Fig. 8b and c).

Our identification of the Ar-I…Pt^{II} XB (Fig. 9a) contributes to the understanding of the fine mechanism of the oxidative additions of aryl halides to d^8 -metal(II) (platinum (ref. 48) and palladium (ref. 49 and 50)) and d^{10} -metal(0)^{30,31,51} centers. We assume that the formation of the Ar-I···M^{II} XB precedes the formation of the $\eta^2(C\cdots I)\cdots M^{II}$ intermediate that is conventionally considered^{48–50} as the key step of the oxidative addition. Notably, based upon a kinetic study, the generation of the intermediate I-I···Pt^{II} (Fig. 9b) has been proposed as the first step of the oxidative addition of I_2 to the platinum(II) center in $[Pt(acac)_2]$, even before the concept of XB became generally recognized.32,52 Previous studies on fine mechanisms of oxidative additions to low-valent (in particular, d⁸-M^{II}) metal centers should be thoroughly revisited and the possibility of one more step that includes



Fig. 9 The $I \cdots Pt^{II} XB$ in the $[Pt(acac)_2] \cdot 2(1,3,5-FIB)$ adduct (a) and in the proposed intermediate of the oxidative addition of I_2 to $[Pt(acac)_2]$ (b).

an attack by ArI of metal centers to give XBs should be taken into account upon further studies.

4. Experimental

4.1. Starting materials and crystal growth

The complexes $[M(acac)_2]$ (M = Pd,⁵³ Pt⁵⁴) were prepared using published methods. Solvents were obtained from commercial sources and used as received. 1,3,5-Triiodotrifluorobenzene (1,3,5-FIB; 98%) was purchased from ABCR. Single crystals were prepared by slow evaporation of a chloroform-methanol solution (1:1, v/v) of a mixture of the corresponding $[M(acac)_2]$ and 1,3,5-FIB taken in 1:1 (M = Pd) and 1:2 (M = Pt) molar ratios at 20–25 °C.

4.2. X-ray determination

A suitable single crystal of $[Pd(acac)_2] \cdot (1,3,5-FIB)$ was studied on a SuperNova, Dual, Cu at zero, Atlas diffractometer (MoK α ($\lambda = 0.71073$)). The crystal was kept at 100(2) K during data collection. Using Olex2,⁵⁵ the structure was solved with the SHELXT structure solution program⁵⁶ using an intrinsic phasing method and refined with the SHELXL refinement package⁵⁷ using least squares minimization.

Variable-temperature single crystal X-ray diffraction studies of the [Pt(acac)₂]·2(1,3,5-FIB) adduct were performed using a Bruker APEX II DUO diffractometer equipped with an Oxford Cryosystems Cobra low-temperature device and CCD detector. Diffraction datasets were collected (MoK α -radiation, graphite monochromator, ω -scans) at five temperatures (100, 150, 200, 250, and 300 K) for the same crystal sample once mounted on a glass needle using two-part adhesive. The structure was solved by the direct method and further refined by the fullmatrix least-squares method in the isotropic-anisotropic approximation against F^2_{hkl} . Hydrogen atoms were located using Fourier synthesis of residual electron density and refined within the isotropic approximation using a riding model.

The main crystallography data and refinement details are listed in Tables S1 and S6 of the ESI.† CCDC numbers 1950660–1950665 contain all the supplementary structural and refinement data.

4.3. Computational details

The single point calculations based on the obtained experimental X-ray geometries of all the systems under study have been carried out at the DFT level of theory using the M06 functional⁵⁸ with the help of the Gaussian-09⁵⁹ (program package. The Douglas–Kroll–Hess 2nd order scalar relativistic calculations that requested a relativistic core Hamiltonian were carried out using the DZP-DKH basis sets^{60–63} for all atoms. The topological analysis of the electron density distribution with the help of the quantum theory of atoms in molecules (QTAIM) method developed by Bader⁴⁰ has been performed by using the Multiwfn program.⁶⁴ The Cartesian atomic coordinates of model supramolecular associates are shown in ESI,† Table S7.

Conflicts of interest

There are no conflicts to declare.

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