Dramatically Enhanced Solubility of Halide-Containing Organometallic Species in Diiodomethane: The Role of Solvent center dot center dot center dot Complex Halogen Bonding

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**Abstract:** In the current study, we evaluated a solubility of a number of organometallics and showed that it is noticeably improved in diiodomethane when compared to other haloalkane solvents. Better solvation properties of CH2I2 were associated with a dramatic growth of the *σ*-hole donating ability of this solvent, and that results in the formation of the uniquely strong solvent-(metal complex) halogen bonding. The strength of halogen bonding is attenuated by the introduction of additional halogens to the organometallic species due to the competitive formation of more favourable intermolecular complex-complex halogen bonding. Exceptional solvation properties of diiodomethane and its inertness towards organometallics make this solvent a good candidate for NMR solvent-of-choice, in particular, for the acquisition of insensitive spins.

Insufficient solubility is one of the major problems limiting structural characterization of compounds in solution, e.g. by NMR spectroscopy and also their application in synthesis. In particular, frequently higher reactivity and intrinsic instability of organometallic species preclude the use of many common solvents for their dissolution. Application of more inert, but often less solubilizing solvents, limits the concentration of compound resulting in significantly longer accumulation time upon NMR acquisition of insensitive nuclei (13C, 15N, *etc*). Solvation, as a process leading to a dissolution of compounds, encompasses several different types of intermolecular interactions between a solute and a solvent. These include van der Waals forces, ion-dipole interactions, hydrogen bonding (HB), as well as halogen bonding (XB) for halogen-containing species.[[1](#_ENREF_1)] Although the contribution of different interactions in solvation is recognized, their interplay is rather complex and an empirical matching of the solvent polarity to that of the solute continues to be the main approach to improving solubility.[[2](#_ENREF_2)] Among weak interactions, contribution of HB is frequently taken into account, while impact of XB is rarely considered and clearly needs an in-depth study.

In this study, we examined the solvation properties of a number of different haloalkane solvents using palladium- and platinum-isocyanide species as solvation probes. Haloalkanes are one of the most inert solvents used to solubilize organometallics; they, and their deuterated versions, are widely applied as media for solution NMR studies. Metal-isocyanides are commonly used precursors to the metal-(acyclic diaminocarbenes) that are of broad significance in catalysis.[[3](#_ENREF_3)]

A series of new and known palladium- and platinum-isocyanide complexes (**1**–**16**, Table 1) were prepared andcharacterized by CHN elemental analyses, high-resolution mass spectrometry (ESI+/‒-HRMS), FT-IR, and 1H and 13C{1H} NMR spectroscopy (see Supplementary Information (SI) for more details). The structures of complexes **10**·2CH2I2, **11**, **11**·2CH2I2, and **12** were established by single-crystal X-ray diffraction. The geometry of all the complexes in solid state and in solution were assigned on the basis of far-IR spectroscopy and X-ray diffraction (see SI). All palladium complexes **1**–**12** are isomerically pure in the solid state (*cis* for chloro, and *trans* for bromo and iodo derivatives). In solution, chloro-complexes **1**–**4** were found to be a mixture of the *cis* and *trans* isomers (60–65% of *cis* isomer at RT), whereas both the bromo and iodo species **5**–**12** contain more than 95% of the *trans* isomer. Platinum complexes (**13**–**16**) are not subject to isomerization and are pure *cis* in both solution and solid state.

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| **Table 1.** The numbering scheme of prepared metal-isocyanide complexes used as probes for solvation properties of haloalkanes. | | | | | | | | | | | | |
| X | Complex | | | | | | | | | | | |
|  | | | | |  | | | |  | | |
| H | M = Pd **1**, Pt **13** | | | | | **5** | | | | **9** | | |
| Cl | M = Pd **2**, Pt **14** | | | | | **6** | | | | **10** | | |
| Br | M = Pd **3**, Pt **15** | | | | | **7** | | | | **11** | | |
| I | M = Pd **4**, Pt **16** | | | | | **8** | | | | **12** | | |
|  | | | | | | | | | | | | |
| **Table 2.** Solubility for **4**, **7**, **11**, and **12** in liquid haloalkanes, maximum ESPs (VS(r)max, kcal·mol–1) on the Hal and H atoms in solvents, their dipole moment (μ), and dielectric constant. | | | | | | | | | | | |
| Solvent | | Solubility, mg/mL | | | | | Vs(r)max,[b] kcal**·**mol–1 | | Dipole moment, μ | | Dielectric constant, (T, °C) |
| **4** | **7** | **11** | **12** | | Hal | H |
| **C2H4Cl2** | | 1 | 9 | 11 | 1 | | –0.3 | 24.6 | 1.48 | | 10.42(20) |
| **CH2Cl2** | | 1 | 16 | 20 | 3 | | 2.6 | 32.9 | 1.6 | | 8.93(20) |
| **CHCl3** | | 1 | 26 | 32 | 5 | | 10.4 | 39.5 | 1.04 | | 4.81(25) |
| **CDCl3** | | 1 | 26 | 32 | 5 | | 10.4 | 39.5 | 1.04 | | 4.81(25) |
| **CDCl3**[a] | | 1 | 30 | 35 | 5 | | 10.4 | 39.5 | 1.04 | | 4.81(25) |
| **CH2Br2** | | 3 | 37 | 37 | 18 | | 13.7 | 29.9 | 1.43 | | 7.77(10) |
| **CCl4** | | 2 | 7 | 4 | 2 | | 16.0 | – | 0 | | 2.24(20) |
| **CH2I2** | | 10 | 46 | 77 | 79 | | 23.1 | 27.4 | 1.08 | | 5.316(25) |
| [a] For all experiments except this, 5 vol.% of acetone-*d*6 were added for the NMR lock purpose; [b] Vs(r)max for all solvents, except for C2H4Cl2 and CDCl3, were calculated in our previous work.[[4](#_ENREF_6)] | | | | | | | | | | | |

Solvation properties of various haloalkanes were initially tested by measuring the solubility of representative complexes **4**, **7**, **11**, and **12** (Table 2, SI: Figures S1–3). An approach based on quantitative 1H NMR spectroscopy measurements[[5](#_ENREF_7)] in the presence of hexamethyldisiloxane as an internal standard was preferred.

Amongst all haloalkane solvents studied, diiodomethane, CH2I2, demonstrated the best solvation properties determined by the highest solubility of all model compounds. Thus, the solubility of **4**, **7**, **11**, and **12** in CH2I2 was up to an order of magnitude larger when compared to that in commonly used CHCl3. In addition, similar trends were established for isomerically pure **7**, **11**, and **12** and complex **4** that exists as an isomeric mixture allowing exclusion of the influence of *cis*/*trans* isomerization on solubility.

Given CH2I2 demonstrated the greatest solvation properties, it was chosen for further experiments on the comparative solubility of all isocyanide complexes **1**–**16** (Table 3); results were compared to CDCl3, a commonly used organic solvent for NMR spectroscopy. In addition, CDCl3 has comparable polarity to that of CH2I2 (dipole moment, μ: 1.04 for CDCl3 vs 1.08 for CH2I2), matching the contribution of solvent polarity to solubility of organometallics studied. For all complexes **1**–**16** excluding **10**, CH2I2 remains the solvent with superior solvating properties towards both platinum (**14**–**16**) and palladium (**1**–**4**) derivatives. The solubility of complexes increases upon the transition from *cis*-chloro complexes (**1**–**4**) to *trans*-bromo (**5**–**8**) and, to a greater degree, *trans*-iodo derivatives (**9**–**12**). Although *trans*-complexes have a symmetric ligand arrangement at metal, it is known that those in solutions are significantly distorted when compared to the solid state.[[6](#_ENREF_9)] Isocyanide ligands, i.e. those in **5**–**12** are not monoatomic; they can easily bend and that will lead to the appearance of the dipolar moment.

Placement of the secondary halogen atom into the structure of the isocyanide ligands alters the solubility of **1**–**16** (Table 3). For both palladium (**1**–**4**) and platinum (**13**–**16**) *dichloride* complexes, upon going from unsubstituted phenyl- to a *p*-chlorophenyl isocyanide, the solubility is significantly increased. For palladium *dibromide* (**5**–**8**) and *diiodide* (**9**–**12**) complexes, an opposite effect was observed: the solubility is significantly dropped on going from unsubstituted phenyl- to a *p*-chlorophenyl isocyanide. We have also noted the variation in solubility in the row of complexes containing different halogen-substituted isocyanides (*p*-chloro- vs *p*-bromo- vs *p*-iodophenyl isocyanides, e.g. **2**–**4**, **6**–**8** or **10**–**12**) although the exact effect was not clear. For instance, in complexes **10**–**12** solubility decreases in CHCl3, while it grows in CH2I2.

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| **Table 3.** The solubility and isomeric ratios of **1**–**16** in CHCl3 and CH2I2. | | | | |
| Complex | | | Solubility, mg/mL | |
| Hal | X | Complex | **CDСl3** | **CH2I2** |
| Cl  (M = Pd) | H | **1** | 8 | 9 |
| Cl | **2** | 15 | 31 |
| Br | **3** | 6 | 29 |
| I | **4** | 1 | 10 |
| Cl  (M = Pt) | H | **13** | 7 | 7 |
| Cl | **14** | 13 | 61 |
| Br | **15** | 20 | 72 |
| I | **16** | 2 | 20 |
| Br | H | **5** | 65 | 94 |
| Cl | **6** | 72 | 73 |
| Br | **7** | 30 | 46 |
| I | **8** | 2 | 12 |
| I | H | **9** | 157 | 215 |
| Cl | **10** | 82 | 19 |
| Br | **11** | 35 | 77 |
| I | **12** | 5 | 79 |

To further attest the scope of this approach and usefulness of CH2I2 as solvent for NMR studies, we evaluated solubilities in CDCl3 – taken for comparison as the most common NMR solvent – and in CH2I2 of various kinetically inert metal complexes including square-planar *cis* and *trans* non-electrolyte species bearing halide ligands and also halide-free complexes of different configuration (see Table S3). For the vast majority of platinum- and palladium halide species (entries 1–16), the solubility in CH2I2 was found to be notably higher than that in CDCl3. Halide complexes of other metals (entries 19–21) as well as those without halide- but with acetylacetonate ligands (entries 17–18) demonstrate a similar trend. It is noteworthy that lone pairs of metal-bound *acac* ligands exhibit a pronounced tendency to form XB with suitable XB donors.[[7](#_ENREF_11)] So far we found only one exception from the observed solubility trend when we tested metal species with aromatic ring ligands exhibiting rotational freedom (entries 24–31). We assume that the known[[8](#_ENREF_12)] X–H/π (X = C, N, O) interactions with the acidic H atom of chloroform[[9](#_ENREF_14)] contribute towards a better solubility of those species in this solvent.

Intrigued by our findings on different solvation properties of structurally and chemically related haloalkanes, we attempted to rationalize them. Insofar as one can reasonably exclude the effect of different polarity of haloalkanes studied on the solubility of model compounds, we focused our attention on weak interactions such as halogen bonding.[[10](#_ENREF_15)]

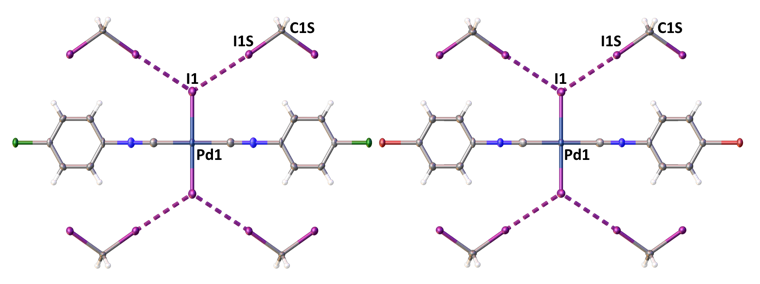
The phenomenon of halogen bonding has recently attracted great attention due to relevance of XBs to pharmaceutical chemistry and drug design,[[11](#_ENREF_16)] polymer and materials science,[[12](#_ENREF_18)] organocatalysis[[13](#_ENREF_20)] and crystal engineering.[[14](#_ENREF_21)] XB is defined as a non-covalent interaction between a localized positive region on a halogen atom in the extension of the covalent bonds (σ-hole) and electron donor species serving as XB acceptors. From this perspective, an emergence of XB between halogen-containing organometallics (as a solute) and solvent or *vice versa* can have an impact on solvation. However, a quantitative effect of XBs on solubility of organometallics has never been verified.

Haloalkanes, apart from positive H centers responsible for HBs, feature an alternative type of partially positive charge centers, *viz*. the *σ*-holes[[15](#_ENREF_23)] of covalently bound halogen atoms capable of non-covalent interactions. We have previously showed[[4](#_ENREF_6), [16](#_ENREF_24)] that the values of the electrostatic potential of the *σ*-holes (VS(r)max), and subsequently the ability to form XBs, depend on the nature and number of halogen atoms in the structure of haloalkanes. The value of VS(r)max on halogen atom grows in the row Cl < Br < I and with increase in electron-withdrawing ability of the substituent by a halogen atom, viz. a number of halogen atoms at the C atom for haloalkanes. Note that DFT calculations of electrostatic potentials (ESPs) at M06-2X/CEP-121G theory level revealed that CH2I2 exhibits the largest positive potential on the halogen *σ*-holes (23.1 kcal**·**mol–1) among all studied haloalkanes (Table 2).

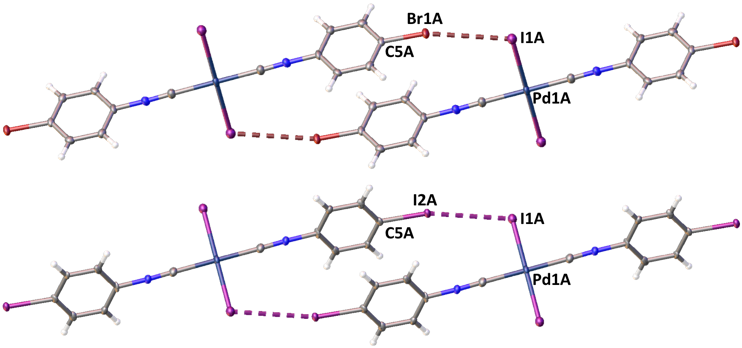
For all the complexes, the relationship between the positive potential on the halogen atom (Vs(r)max)and solubility as a rule increases symbiotically with *σ*-hole donating ability of a solvent (Figure S1, SI), except for CCl4. Tetrachloromethane possesses a high positive potential on the chlorine atom, but a null dipolar moment being the only non-polar solvent among those studied. Highest solubility of model compounds was observed for CH2I2 as a solvent with the largest maximum positive potential on the halogen *σ*-holes, *i.e.* it is 10 times higher (10 mg/mL) for **4** and *ca*. 79 times (79 mg/mL) for **12** when compared against C2H4Cl2 as solvent with the lowest halogen *σ*-hole donating properties (Vs(r)max = –0.3 kcal**·**mol–1). Generally, when the quantity of halogen atoms present is increased and their polarizability (greater *σ*-hole) is increased (Cl < Br < I), better solubility of complexes is more likely due to the formation of solvent–complex XBs in solution. Apparently, the acidity of H atoms (represented by the maximum positive potential on the H, Table 1, Figure S2) does not play a significant role in the solvation process. At this point, one can reasonably suggest that the emergence of XBs between molecules of complex and solvent plays the key role in the dissolution process.

Since non-covalent interactions can hardly be studied in solution, we examined those in the XRD structures of some of our complexes. This canonical approximation is widely used to evaluate the XB situation and properties of solvates for different compounds. Halogen···halogen interactions can be assigned to one of two types on basis of their geometry.[[17](#_ENREF_27)] Contacts of the type 1 are mainly of dispersion nature, whereas those of the type 2 are driven by electrostatic interactions between the polar and equatorial regions. In all contacts described below, the Hal···Hal distances are less than the sum of their Bondi vdW radii,[[18](#_ENREF_28)] while the corresponding angles C−Hal···Hal and Hal···Hal–Pd are in the range 160−180° and 90−120°, respectively (Tables S7–9). In accord with the IUPAC criteria, these interactions are recognised as the type 2.[[10](#_ENREF_15)] Two solvates with CH2I2 (**10·**2CH2I2and **11·**2CH2I2, Figure 1) and two individual iodo complexes (**11** and **12**,Figure 2) were evaluated; ESP distribution for complexes **10**–**12** (Figure 3, Table 4) was also calculated. According to the computations, the iodides ligated to palladium have negative ESP on the whole of their surface and can act only as XB acceptors. At the same time, the halogen atoms in isocyanide ligands have areas with positive ESP corresponding to *σ*-hole position which makes these halogens potential XB donors. Complexes **10** and **11** form the CH2I2 isomorphic solvates upon crystallization from their CH2I2 solutions. In **10·**2CH2I2 (Figure 1, left) and **11·**2CH2I2 (Figure 1, right), the H2C(I)–I•••I–Pd XBs between each molecule of complex and four molecules of CH2I2 were found. The calculated energy of each solvent-complex XB was 2.2–2.5 kcal/mol, and their contribution to the lattice energy in each case appears to be the most significant.

In both **10** and **11**, Vs(r)max value on the halogen atom in the isocyanide ligand is lower than that for iodine in CH2I2 making it a better XB donor for Pd-bound iodide.

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**Figure 1.** The H2C(I)–I•••I–Pd XBs in **10**·2CH2I2 (left) and **11**·2CH2I2 (right).

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**Figure 2.** The C–X2•••I–Pd (X2 = Br, I) XBs between two complex molecules in **11** (top) and **12** (bottom).

Crystals of **11** grown from the less *σ*-hole donating solvent, CHCl3 (Vs(r)max = 10.4 kcal**·**mol–1) contain only individual molecules of the complex with the intermolecular C–Br•••I–Pd XBs (Figure 2, top structure). Energy of C–Br•••I–Pd XBs interaction in this crystal is lower and such non-covalent contacts are less numerous when compared to the H2C(I)–I•••I–Pd XBs in solvate **11·**2CH2I2. This leads to an assumption that in the presence of CH2I2 the system prefers to form solvate. However, in less *σ*-hole donating solvents a competition between complex–complex and solvent–complex XBs could occur during dissolution process. Using a more *σ*-hole donating solvent (CH2I2, Vs(r)max = 23.1 kcal**·**mol–1) leads to an increase in the number of solvent-complex XBs and good solubility, whereas in CDCl3 (Vs(r)max = 10.4 kcal**·**mol–1) the complex–complex interactions (C–Br•••I–Pd XBs, Vs(r)max(CNC6H4–**Br**) = 19.8 kcal**·**mol–1) is more preferable and works towards a precipitation of complex. These results agree with the changes in solubility of **11**, vis.from 35 mg/mL in CDCl3 to 70 mg/mL in CH2I2.

For **12**,crystallization from even the strongest *σ*-hole donating solvent as CH2I2 does not lead to any solvates and the crystals contain only individual molecules of the complex. They are isomorphic to **11** (Figure 2, bottom) and possess a similar pattern of intermolecular XBs C–I•••I–Pd (energy 2.2–2.5 kcal/mol). In this case, emergence of complex–complex XBs C–I•••I–Pd is preferable to solvent-complex XBs H2C(I)–I•••I–Pd presumably due to higher positive ESP on *p*-iodide substituents in isocyanide ligands of **12** than on iodine in CH2I2, viz. 28.7 kcal**·**mol–1 vs. 23.1 kcal**·**mol–1 (Figure 3). This tendency of palladium complexes with *p*-iodo substituted isocyanides to form strong intermolecular complex-complex interactions could explain why they have the poorest solubility of the isocyanide derivatives studied.

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| **Table 4.** The solubility of **10**–**12** in CDCl3 and CH2I2 and maximums electrostatic potentials (VS(r)max, kcal·mol–1) on the X in **10**–**12** and halogen in haloalkanes. | | | | | |
| Complex | Solubility, mg/mL | | Vs(r)max, kcal·mol–1 | | |
| CDCl3 | CH2I2 | XC6H4 | CDCl3 | CH2I2 |
| **10** | 82 | 19 | 8.4 | 10.4 | 23.1 |
| **11** | 35 | 79 | 19.8 |
| **12** | 5 | 77 | 28.7 |



**Figure 3**. ESP distribution in **12** (X = I, Hal = I) (M06-2X/CEP-121G level of theory). Blue color – negative ESP, red color – positive ESP.

To conclude, we scrutinized the solvation properties of a number of haloalkane solvents against a series of organometallic species. Using NMR measurements, we established that CH2I2 demonstrated the best solvation properties among all haloalkanes studied; solubility values for organometallics were improved by up to *an order of magnitude* when compared to the commonly used CHCl3. Since no correlation between the polarity of haloalkanes and the solubility of all model complexes was observed, we looked for an alternative explanation. We anticipated that better solvation properties of CH2I2 are related to a dramatic growth of the *σ*-hole donating ability of this solvent when compared to others, and that results in the formation of strong solvent-(metal complex) halogen bonding. The emergence of these uniquely strong XBs in diiodomethane and its inertness towards organometallics make this solvent a good candidate for NMR solvent-of-choice, in particular, for the acquisition of insensitive spins, where the concentration of an analyte is crucial. Whereas a number of methods to suppress an undesired solvent signal in 1H NMR are available,[[19](#_ENREF_29)] a deuterated version of CH2I2 might be prepared,[[20](#_ENREF_30)] if necessary. The strength of XBs is influenced by the introduction of additional halogens to the organometallic species. Herein, we demonstrated that strength of XBs and subsequently the solubility decreases with the rise of the positive potential on halogen moieties placed on isocyanide ligands due to the formation of more favourable *intermolecular* complex-complex XBs. Further studies on understanding the role of XBs and their application in organometallic chemistry, are currently underway in our group.

Acknowledgements

These studies were funded by the Russian Foundation for Basic Research (grant 16-33-60123 mol\_a\_dk for MAK). Solid state studies and quantum chemical calculations were supported by the Russian Foundation for Basic Research (projects 18-29-04006 and 16-03-00441). KVL thanks the University of Liverpool for support. Measurements were performed at Center for Magnetic Resonance, Center for X-ray Diffraction Studies, Center for Chemical Analysis and Materials Research, and Chemistry Educational Centre (all belonging to Saint Petersburg State University).

**Keywords:** halogen bonding • solvation• organometallics • haloalkanes • isocyanide complexes

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**Entry for the Table of Contents**

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| COMMUNICATION | | | | |
| Unique solvation properties of diiodomethane towards halide-containing organometallics are associated with its enhanced σ-hole donating ability leading to stronger solvent-(metal complex) halogen bonding. |  |  |  | M. A. Kinzhalov,\* M. V. Kashina,  A. S. Mikherdov, E. A. Mozheeva, A. S. Novikov, A. S. Smirnov,  D. M. Ivanov, M. A. Kryukova,  A. Yu. Ivanov, S. N. Smirnov,  V. Yu. Kukushkin, K. V. Luzyanin\*  Page No. – Page No.  Solubility of halide-containing organometallics is dramatically enhanced in diiodomethane: can the solvent•••complex halogen bonding be held responsible? |
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