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Thermochemical Evidence for Strong Iodine Chemisorption by ZIF-8

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Supporting Information

ABSTRACT: For the first time, using aqueous solution calorimetry, we clearly identify the chemisorption of an unusually strong iodine charge-transfer (CT) complex within the cages of a metal−organic framework. Specifically, we studied the sorption of iodine gas in zeolitic imidazolate framework-8 (ZIF-8, Zn(2-methylimidazolate)$_2$). Two iodine-loaded ZIF-8 samples were examined. The first, before thermal treatment, contained 0.17 I_2/Zn on the surface and 0.59 I_2/Zn inside the cage. The second sample was thermally treated, leaving only cage-confined iodine, 0.59 I_2/Zn. The energetics of iodine confinement per I_2 (relative to solid I_2) in ZIF-8 are $\Delta H_{ads} = -41.47 \pm 2.03$ kJ/(mol I_2) within the cage and $\Delta H_{ads} = -18.06 \pm 0.62$ kJ/(mol I_2) for surface-bound iodine. The cage-confined iodine exhibits a 3-fold increase in binding energy over CT complexes on various organic adsorbents, which show only moderate exothermic heats of binding, from −5 to −15 kJ/(mol I_2). The ZIF-8 cage geometry allows each iodine atom to form two CT complexes between opposing 2-methylimidazolate linkers, creating the ideal binding site to maximize iodine retention.

The unusually strong binding of iodine by the metal−organic framework (MOF) zeolitic imidazolate framework-8 (ZIF-8, Zn(2-methylimidazolate)$_2$)[1] has been qualitatively well documented.[2−4] Iodine is well known to form modestly stable charge-transfer (CT) complexes with aromatic carbon molecules, and iodine forms a CT complex with two ZIF-8 linkers, 2-methylimidazolate.[5] However, the energetic magnitude of iodine−framework binding in ZIF-8 is unknown, and it is unclear whether the strong I_2 retention is due to kinetic or thermodynamic factors or a combination of the two. To better understand the energetics of iodine binding in ZIF-8, aqueous solution calorimetry was used to examine the nature of the interactions both on the surface and within the cages.

Much focus in the literature has been on greenhouse gas capture (e.g., CO_2, CH_4).[6−9] There is also a great need and industrial push for the selective capture and eventual long-term storage of fission gases from the nuclear energy arena. Radioactive iodine (namely the isotope ^{129}I, which has a half-life of ~10^7 years) presents a unique challenge because iodine is a mobile and soluble species that is easily absorbed by humans and other animals and is concentrated in the thyroid. Currently silver-exchanged zeolites are the preferred sorbent, and recently the iodine capture mechanism in silver-exchanged mordenite has been described.[10−12] Yet the relatively low sorption capacity and high cost of Ag-loaded zeolites limit their wide-scale implementation.[13] Activated carbon offers an inexpensive option for a high-surface-area, high-capacity sorbent; however, beyond 200 °C activated carbon becomes ineffective, and in environments with high humidity or NO_x gases its performance deteriorates.[13,14]

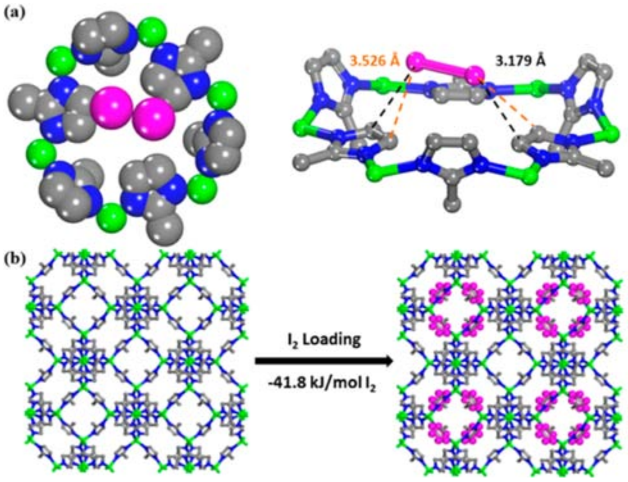

Figure 1. (a) Space-filling (left) and ball-and-stick (right) representation of the six-membered-ring window in ZIF-8, showing the preferential I_2 interaction with opposing 2-methylimidazolate linkers for the cage-bound I_2. (b) Favorable iodine loading energetics and location of molecular iodine binding sites within the ZIF-8 framework. H atoms are omitted for clarity; zinc, green; carbon, gray; nitrogen, blue; iodine, fuchsia.

In this context, MOFs, a relatively new class of porous hybrid organic−inorganic materials, have been shown to address some aspects of the thermal and chemical limitations of activated carbon. Previous studies on ZIF-8 have shown the framework to have a high sorption capacity for I_2, up to 125 wt%: only 25 wt% I_2 binds to the surface, while ~100 wt% I_2 is efficiently contained within the sodalite cages of ZIF-8.[2−4] The cage-trapped I_2 is securely confined until framework decomposition at ~300 °C. Simple thermal or pressure treatments on the iodine-loaded ZIF-8 can induce amorphization, kinetically trapping the bound iodine within the structure.[3,4] ZIF-8 was purposely selected, as its pore opening is nearly identical to the cross section of molecular iodine and it has high surface area

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and thermal and chemical stability, all important considerations for use in industrial conditions. The robustness of ZIF-8 (and most ZIF frameworks) can be attributed to its thermodynamic stability with respect to its dense assemblages: zinc oxide and crystalline 2-methylimidazolium.[15]

The use of specific porous materials has often been dependent on sorption material characteristics such as size selectivity into a pore opening, chemical bonding with framework sites such as metal centers or acid sites, or geometric "pockets" that hold the gas molecule preferentially. Strong chemisorption over physisorption is difficult to predict and is often determined only by trial and error. The ability to identify and characterize physisorption vs chemisorption and then use that information as a predictive tool in combination with structural determinations will greatly aid a large variety of industrial gas separation needs. Yet reliable heats of adsorption as a function of loading are lacking. Experimental heats of adsorption have been extensively studied by measuring isosteric heats of adsorption (Q_{st}).[16] This approach, which involves fitting several isotherms at different temperatures to a polynomial in order to determine Q_{st}, has two drawbacks: First, it is a complex, multistep process which incorporates many uncertainties into the final energetics. Second, the resulting Q_{st} is only an average heat of adsorption across the isotherm and cannot accurately describe systems that have complicated adsorption processes in which the energetics may be a function of coverage and temperature. Our group has developed methods recently to address some of these limitations. Direct gas adsorption calorimetry allows the direct measurement of binding heats for each gas dose along the entire isotherm.[17] This method was applied for the first time to a MOF, CD-MOF-2, to study CO_2 heats of adsorption.[18,19] For adsorbates which form solid complexes with their host from condensed-phase reactants, such as iodine-loaded ZIF-8, room-temperature solution calorimetry can be used to study binding energies at specific loadings.[20] Herein we used solution calorimetry to determine the unusually strong heat of binding of iodine to ZIF-8, comparing this unique calorimetric finding to the energetics of other iodine CT complexes and iodine sorbents.

ZIF-8 used in this study was obtained from Sigma-Aldrich under the trade name Basolite Z1200. Prior to iodine loading, the ZIF-8 material was activated at 300 °C for 4 h. Radiological iodine was not used in this study. The I_2 loading process was carried out as previously reported.[7] The iodine uptake was measured gravimetrically and confirmed by elemental analysis (Table 1).

Table 1. Iodine Loadings of ZIF-8

		I_2 per Zn		
sample	I_2 loading, mass %	total	cage	surface
u-ZIF-8	85.6 ± 5.0	0.76	0.59	0.17
t-ZIF-8	66.0 ± 2.0	0.59	0.59	0.00

To monitor the binding energies of the surface-adsorbed versus cage-bound I_2, two distinct iodine-loaded ZIF-8 samples were studied: (1) an untreated (as-loaded) iodine ZIF-8 sample (u-ZIF-8), containing both surface-sorbed and cage-trapped I_2, and (2) a thermally treated ZIF-8 sample (t-ZIF-8), heated to 125 °C for 1 h to remove the surface-bound I_2. Details about sample loading levels are given in Table 1.

Room-temperature solution calorimetry was used to experimentally obtain the enthalpy of dissolution (ΔH_s) for each component to be used in the thermodynamic cycle (Table 2). A unique biphasic solvent system comprised of 25 mL of 5 M HCl and 10 mL of $CHCl_3$ was developed for calorimetry (Supporting Information). Details describing the instrument, calibration method, and experimental apparatus have been presented elsewhere.[21] Experimental ΔH_s values are presented in Table 3. All uncertainties of the ZIF-8 materials, calorimetric or otherwise, are the standard error of the averaged experimental results.

The enthalpies of solution ΔH_s for the pristine ZIF-8 framework, iodine-loaded frameworks u-ZIF-8 and t-ZIF-8, and elemental I_2 have been measured. The heat of adsorption (ΔH_{ads}) of iodine by pristine ZIF-8 is defined by the heat of formation of reaction 1. The thermodynamic cycle (Table 2)

$$\text{ZIF-8(cr)} + (x + y)\text{I}_2\text{(cr)} \rightarrow [\text{ZIF-8}\cdot x\text{I}_2]\cdot y\text{I}_2 \qquad (1)$$

was constructed to elucidate the energetics of the iodine−framework binding, as described by reaction 1. It is important to note that we reference iodine from the solid phase in order to exclude enthalpies from changes of state and include only the iodine−framework interaction energies. Experimental ΔH_s values for all calorimetry measurements are given in Table 3 for cage- and surface-bound I_2, respectively. Loading can be found in Table 1.

The energetics of iodine binding per Zn shown in reaction 1 are −27.48 ± 3.62 kJ/mol for u-ZIF-8 and −24.47 ± 3.44 kJ/mol for t-ZIF-8. The thermally treated t-ZIF-8, containing only cage-confined I_2, has a less exothermic total enthalpy of adsorption than u-ZIF-8, as u-ZIF-8 contains both cage- and surface-bound I_2. The difference between their ΔH_{ads} represents the energetics of iodine binding to the ZIF-8 surface per mole of Zn, giving a binding energy of −3.07 ± 3.62 kJ/mol. This indicates that surface iodine interacts weakly with the surface, whereas the cage-bound iodine stabilizes the ZIF-8 framework by −24.74 ± 3.44 kJ/(mol Zn).[26,27]

As the main focus is the heat of adsorption per I_2 to ZIF-8, examining the binding enthalpy per I_2 is more relevant. The normalized surface and cage enthalpies per I_2 give ΔH_{ads} = −18.06 ± 0.62 kJ/mol for surface-bound iodine and −41.47 ± 2.03 kJ/mol for cage-confined iodine (Table 3). Comparing the ΔH_{ads} per I_2 to other iodine−organic complexes confirms strong chemisorption of iodine within the ZIF-8 cage. All ΔH_{ads} values shown in Table 4 are the heats of adsorption of solid I_2 to the carbon-based sorbent, as shown by reaction 2.

$$\text{sorbent(s)} + x\text{I}_2\text{(cr)} \rightarrow [\text{sorbent}\cdot x\text{I}_2]\text{(s)} \qquad (2)$$

Interestingly, the I_2 bound within the cage of ZIF-8 shows a 4-fold binding energy increase over the heat of confinement of molecular iodine within activated carbon materials AX-21 and ACG-60 (Table 4). Iodine on the surface of ZIF-8 is only weakly bound. This is highlighted by the ease of iodine removal from the ZIF-8 surface, which occurs at lower temperatures (125 °C). The ease of iodine release on the ZIF-8 surface is attributed to surface iodine interacting with only one imidazole and not confined. In contrast, the strongly bound iodine within the cage forms two independent CT complexes and is not released until framework collapse (300 °C).

Table 2. Thermodynamic Cycle Used To Determine ΔH_{ads}

reaction[a]	enthalpy[b]
ZIF-8(cr) → $Zn^{2+}(aq) + 2mIm^{-}(aq)$	$\Delta H_1 = \Delta H_s$ (pristine ZIF-8)
$(x + y)[I_2(cr) \rightarrow I_2(aq)]$	$\Delta H_2 = (x + y)\Delta H_s$ (iodine)[c]
$Zn^{2+}(aq) + 2mIm^{-}(aq) + (x + y)I_2(aq) \rightarrow [\text{ZIF-8}\cdot xI_2]\cdot yI_2$	$\Delta H_3 = -\Delta H_s$ (iodine-loaded ZIF-8)
ZIF-8(cr) + $(x + y)I_2(cr) \rightarrow [\text{ZIF-8}\cdot xI_2]\cdot yI_2(cr) = \Delta H_{adj}$	**$\Delta H_1 + \Delta H_2 + \Delta H_3 = \Delta H_{ads}$**

[a] ZIF-8 = $Zn(mIm)_2$, where mIm^- = 2-methylimidazolate. [b] All ΔH_s values can be found in Table 3. [c] Iodine values x and y refer to cage- and surface-bound I_2, respectively. Loading can be found in Table 1.

Table 3. Thermodynamic Parameters of All Samples Studied by Calorimetry

compound	formula	ΔH_s, kJ/(mol Zn)	ΔH_{ads}, kJ/(mol Zn)	ΔH_{ads}, kJ/(mol I_2)
iodine	I_2	23.64 ± 0.64[a]		
ZIF-8 (dg)	$Zn(mIm)_2$	−133.47 ± 0.74		
u-ZIF-8	$[Zn(mIm)_2\cdot 0.59I_2]\cdot 0.17I_2$	−86.25 ± 1.19	−27.54 ± 3.62	−59.53 ± 2.65
t-ZIF-8	$[Zn(mIm)_2\cdot 0.59I_2]$	−93.72 ± 2.32	−24.47 ± 3.44	−41.47 ± 2.03
ZIF-8 (cage)	$[Zn(mIm)_2\cdot 0.59I_2]$		−24.47 ± 3.44	−41.47 ± 2.03
ZIF-8 (surface)	$[Zn(mIm)_2]\cdot 0.17I_2$		−3.07 ± 3.62	−18.06 ± 0.62

[a] Unit for ΔH_s of I_2 is kJ/(mol I_2).

Table 4. Energetics of Solid Iodine Binding in ZIF-8 and Various Organic Sorbents

substrate	ΔH_{ads}, kJ/(mol I_2)	K_{ads} (350 K)[a]	I_2 loading, g/g
ZIF-8 (cage)	−41.5 ± 2.0	4.45×10^6	0.66[b]
ZIF-8 (surface)	−18.1 ± 0.6	502	0.19[b]
coal tar pitch[c]	−15.1	179	0.87
hexamethylbenzene[d]	−14.3 ± 0.5	136	1.56
1,3,5-trimethylbenzene[c]	−12.5 ± 0.2	73.4	2.11
carbon (AX-21)[e]	−10.1 ± 1.0	32.2	2.96
carbon (ACG-60)[f]	−7.8	14.6	2.08
benzene[d]	−7.8 ± 0.1	14.7	3.25
perylene[g]	−5.4 ± 0.2	6.40	1.51

[a] Equilibrium constant K_{ads} was calculated using ΔH_{ads} per I_2 at 150 °C, as this is a typical operational environment. [b] Loading of samples (g/g) measured by calorimetry; maximum loadings for ZIF-8 (g/g) are 1.00 (cage) and 0.25 (surface). [c] Ref 22. [d] Ref 23. [e] Ref 14. [f] Ref 24. [g] Ref 25.

The thermochemistry of several iodine−organic CT complexes has previously been reported (see Table 4). Calorimetric studies by McKechnie et al.[25] on small-molecule iodine CT complexes shows the exothermic enthalpies of the CT interaction (equivalent to ΔH_{ads}) to be in the range −5 to −15 kJ/(mol I_2). Work by Joens[23] on methylated benzene complexes with I_2 found a linear dependence between the heat of adsorption and the number of methyl groups on benzene. The ΔH_{ads} values ranged between −5.4 kJ/(mol I_2) for benzene and −14.3 kJ/(mol I_2) for hexamethylbenzene. For each additional methyl group added to the benzene ring, the favorable interaction between the aromatic center and iodine increased approximately 1 kJ/mol. An increase in the exothermic adsorption is expected, as methyl is an electron-donating group to aromatic systems. Thus, more electron density exists within the aromatic system, leading to formation of a stronger CT complex. Though the methyl group in the ZIF-8 linker, 2-methylimidazolate, does contribute to the electronic density of the imidazolate aromatic system, this effect is minor and likely does not play a major role in the iodine binding, nor does it explain the 3- to 4-fold increase in the ΔH_{ads} shown by iodine in the ZIF-8 cage when compared to other iodine CT complexes.

ZIF-8 demonstrates an unusual preference toward molecular iodine over other MOFs. Previous studies on iodine confinement within MOFs have focused primarily on creating a conductive network.[28−30] Zeng and co-workers have studied iodine−framework conductivity both from iodine uptake from solution[28] and incorporation of iodine as a templating agent into the hydrothermal reaction.[30] Hertzch et al. examined incorporating iodine into a porous cyclophosphazene framework both from solution and from a gaseous state.[29] In all studies the frameworks were shown to be poor retainers of iodine, quickly degassing beyond 150 °C; thus, a weak iodine−framework CT complex is likely forming. Why is ZIF-8 different? Experimentally, a maximum of six iodine molecules can be confined within each individual cage in ZIF-8. Iodine is adsorbed on one of two distinct crystallographic I_2 binding sites inside the ZIF-8 cage, though both have similar binding environments, placing a single I_2 molecule between the 4,5 position of two 2-methylimidazolate linkers. In this study, the cage ΔH_{ads} represents the average enthalpy of the two sites, which are likely very similar in energy.[2] Nevertheless, iodine confined within ZIF-8 cages is chemisorbed through strong CT complex interactions.

The small cage in the ZIF-8 framework, 11.6 Å in diameter, provides an ideal environment for the capture of iodine. Previous thermochemical studies of confinement energetics between guest molecules and porous silica host showed a strong dependence on pore size.[31] Immersion calorimetry of silica frameworks of varying one-dimensional (1-D) pore size between water, ethanol, and triethylamine solutions found that the material with the smallest accessible cavity has the strongest host−guest stabilization interaction. The smaller pore lends itself to increased interaction between host and guest, in essence making the nature of the interaction more 3-D in character rather than a 2-D surface−guest interaction. Thermochemically, the increased contact means more stabilization per guest within the cavity, which can increase until the guest molecule can no longer enter the pore.

The relatively small cage and pore of ZIF-8 compared to iodine may be the key to understanding the highly exothermic heat of adsorption. Crystallographically, the ZIF-8 cage provides the optimum spacing between aromatic imidazolate linkers to allow diatomic iodine to position itself, albeit canted, into an ideal CT geometry at both ends of the I_2 molecule. Iodine−aromatic CT complexes typically show I···C distances of ∼3 Å,[5] in agreement with X-ray diffraction studies of iodine loading in ZIF-8, where the shortest I···C contacts are in the range 3.179−3.526 Å.[2] The constricted positioning of I_2 between two binding sites allows for more efficient guest−host interaction. Comparing the ΔH_{ads} of surface-bound iodine, -18.1 ± 0.6 kJ/(mol I_2), to that of cage-bound iodine, -41.5 ± 2.0 kJ/(mol I_2), reveals that cage-bound iodine is adsorbed approximately twice as strongly, suggesting that surface I_2 is bound to a single imidazole, whereas the cage-confined iodine is bound to two imidazoles, as confirmed crystallographically. The iodine CT interaction of cage-confined iodine appears to be symmetrical with each imidazole linker, likely a critical feature which retains iodine within ZIF-8 until the framework collapses.

Intermolecular I_2−I_2 interactions are likely present and may contribute to the overall I_2 stabilization. Although these interactions cannot be separated from the framework−I_2 interactions on the basis of the present study, we believe the latter are the stronger and more favorable interactions.

For the first time, using aqueous solution calorimetry, we clearly identify the strong chemisorption of a gas molecule in the cages of a MOF framework. In this study, we focus on iodine (I_2) within the ZIF-8 sodalite cages. The cages of ZIF-8 strongly bind iodine within the framework, while I_2 bound on the ZIF-8 surface mirrors binding energies of traditional iodine−organic CT complexes. ZIF-8 binds iodine 4 times more strongly than activated carbon, the traditional high-capacity iodine adsorbent. The strong interaction is driven by ideal confinement conditions within the ZIF-8 cage, allowing the formation of an exceptionally strong CT complex involving two iodine−organic bonds per I_2 molecule. The small pore aperture to the cage combined with strong I_2 cage binding leads to confinement of iodine up to framework collapse at 300 °C. In a broader sense, this thermodynamic analysis of iodine−ZIF-8 binding offers clues for designing effective functional MOFs for specific applications which are centered on guest−host interactions. Furthermore, these thermodynamic findings offer additional support to the use of ZIF-8 for radioactive iodine capture. This methodology can be readily applied to the study and design of highly selective MOFs for a wide variety of targeted gas molecules, including greenhouse gases such as CH_4 and CO_2, other fission gas molecules such as Kr and Xe, and both pure streams and industrially relevant systems with complex mixtures of competing gases.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Calorimetry methods. This information is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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