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Iodine Adsorption

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Adsorption of I_2 by Macrocyclic Polyazadithiophenolato Complexes Mediated by Charge-Transfer Interactions**

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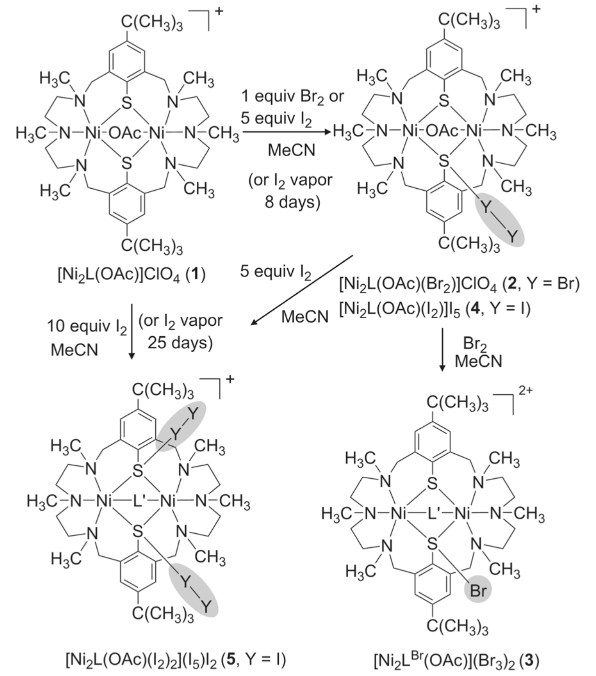
***Abstract:** The macrocyclic complex [Ni_2(L)(OAc)]ClO_4 (**1**) adsorbs up to 17 molar equivalents (>270 wt%) of iodine, although it does not exhibit permanent porosity. Vibrational spectroscopic and crystallographic studies reveal that two I_2 molecules are captured by means of thiophenolate→I_2 charge-transfer interactions, which enable the diffusion and sorption of further I_2 molecules in a polyiodide-like network. The efficient sorption and desorption characteristics make this material suitable for accommodation, sensing, and slow release of I_2.*

The search for new charge-transfer (CT) complexes of the halogens is an attractive research area, given their importance for many practical applications such as batteries for pacemakers,[1] drugs for wound healing and infection treatment,[2] charge carriers in dye-sensitized solar cells (DSSCs), and supercapacitors to name but a few.[3] Thus, a variety of new CT complexes have been reported in recent years,[4] particularly polyhalides[5] of the lighter and more reactive halogens.[6,7] More exotic halogen CT adducts such as those involving extremely good electron-pair donors such as alcoholates and thiolates have received less attention,[8] presumably due to their lower stability and tractability, and only a few compounds have been characterized. In fact, thiolate–dihalogen adducts (RS^-→Hal_2, Hal = I, Br) are instable with respect to disproportionation, and have never been isolated in their free form, but they can be accessed when the thiolate anion is coordinated to a metal ion.[9]

In previous work we reported a unique thiolate→Br_2 CT complex [Ni_2L(OAc)(Br_2)](ClO_4) (**2**; Scheme 1), trapped in the coordination sphere of the macrocyclic complex [Ni_2L(OAc)](ClO_4) (**1**).[10] Complex **2** was expected to form a bis(Br_2) adduct [Ni_2L(OAc)(Br_2)$_2$]$^+$ as well, but disproportionation took place to give a sulfenyl bromide complex [Ni_2L^{Br}(OAc)]$^{2+}$ (**3**). We now show that such a bis(CT) adduct is accessible with the weaker Lewis acid I_2. We further demonstrate the remarkable ability of **1** to adsorb large amounts of I_2 from the gas phase, and that the RS^-→Hal_2 CT interactions play a crucial role in the uptake process. The sorption of I_2 in porous systems such as starch, zeolite MFI,[11] organic zeolites,[12] and metal–organic frameworks is well known,[13] but is without precedence for metal thiolate complexes.[8,14]



Scheme 1. Structures and syntheses of complexes **1**–**5**.

The bis(I_2) adduct [Ni_2L(OAc)(I_2)$_2$](I_5)I_2 (**5**) can be reproducibly obtained in roughly 80% yields by reaction of the mono(I_2) adduct [Ni_2L(OAc)(I_2)](I_5) (**4**)[15] with a fivefold excess of I_2 in acetonitrile (Scheme 1). The same product is also directly accessible from [Ni_2L(OAc)](ClO_4) (**1**), but this requires 10 equiv of I_2. Exposure of the perchlorate salt **1** to iodine vapors for 25 days followed by recrystallization from

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MeCN also leads to **5**. Notice that the bis(CT) adducts are obtained as polyiodide salts. This can be traced to disproportionation of I_2 in MeCN,[16] followed by adduct formation, and anion exchange according to Equations (1a)–(1c).

$$CH_3C{\equiv}N + I_2 \rightarrow [CH_3C{\equiv}N{-}I]^+ + I^- \tag{1a}$$

$$2\,I_2 + I^- \rightarrow I_5^- \tag{1b}$$

$$[Ni_2L(OAc)](ClO_4) + 2\,I_2 + I_5^- \rightarrow [Ni_2L(OAc)(I_2)_2](I_5) + ClO_4^- \tag{1c}$$

The lower solubility of the polyiodide salts is attributed to secondary CT interactions (see the crystal structure below). Compounds **4** and **5** are air stable, paramagnetic (Ni^{II} (d^8, $S = 1$)),[15] crystalline solids, and are readily distinguished by IR and UV/Vis spectroscopy ($\nu(OAc) = 1585\ cm^{-1}$ (**4**), $1578\ cm^{-1}$ (**5**); $n\rightarrow\sigma^*$, $\sigma\rightarrow\sigma^* = 362$, 292 nm (**4**), 362, 284 nm (**5**).

The crystal structure determination of **5**·MeCN confirmed the presence of the bis(I_2) CT adduct. The asymmetric unit contains two crystallographically independent but chemically identical $[Ni_2L(OAc)(I_2)_2]^+$ cations (Figure 1) and two I_5^- ions, along with two I_2 and two MeCN molecules of crystallization. The RS→I–I linkages are all linear, and the I–I distances are longer than in free I_2 (2.667(2) Å)[17] in agreement with charge transfer from the thiolate to the I_2. The S–I distances are also longer than the value of 2.37 Å for a covalent RS–I bond.[18,19]

As shown by Tebbe et al., the I–I bond lengths and angles in iodine-rich polyiodides are often characteristic and can be used to define the constituting species.[4] In $[(C_5H_5)_2Fe]_3I_{29}$,[4] for example, the anionic I_{29}^{3-} substructure can be decomposed to I_3^-, I_5^- units, and bridging iodine molecules, which are connected by cross-linking secondary interactions. In the present compound, similar cross-linking interactions are present between the V-shaped I_5^- anions, the $[Ni_2L(OAc)(I_2)_2]^+$ cations, and the cocrystallized I_2 molecules as illustrated in Figure 2. Only few $RS\rightarrow I_2$ CT adducts are known. One nickel thiolate complex $NiL'{-}I_2$ ($H_2L' = N,N'$-bis(2-mercaptomethylpropane)-1,5-diazacyclooctane) has been described by Darensbourg et al.[9] A dinuclear Mo_2S_2 complex with two $S^{(sulfido)}\rightarrow I_2$ linkages has also been reported.[20]

In view of the high affinity of **1** for I_2, it was of interest to examine possible adduct formation between 1 and gaseous I_2 [Eq.(2)]. Therefore, a powdered, microcrystalline sample of

$$\underset{\mathbf{1}}{[Ni_2L(OAc)](ClO_4)} + n\,I_{2,g} \rightarrow \underset{\mathbf{1}(I_2)n}{[Ni_2L(OAc)](ClO_4)(I_2)n} \tag{2}$$

1 (30 mg) was placed in a chamber and exposed to I_2 vapor at 294 K.[21] The gradual color change from pale-green to black, a substantial increase (ca. 270%) in the mass of the sample (Figure 3), and conversion to an amorphous state (Figure SI-1) clearly confirmed adsorption and uniform penetration of the sample by I_2. The I_2 content increased gradually with time and eventually approached the equilibrium value $n_{sat} \approx 10.2$ mol I_2/mol (**1**), corresponding to an iodine adsorption of 2.697 g(I_2)/g(**1**), a value much higher than the 0.3–1.2 $g\,g^{-1}$ range typically observed for microporous adsorbents and activated carbon.[22–24] This is particularly intriguing, given that **1** does not exhibit permanent porosity (according to the N_2 adsorption isotherms at 77 K, BET surface area $A_{BET} < 1.5\ m^2\,g^{-1}$, Figure SI-2).

The above findings suggested that penetration of I_2 into **1** is accompanied by the generation of openings in the structure to allow the I_2 molecules to thermally jump from one position to a neighboring one, thereby enabling Fickian-type diffusion similar to that of diatomic gases in amorphous polymers matrices.[23] For this reason the sorption of I_2 by **1** was studied as a function of temperature. Figure 3 shows the data at 40, 50, and 60 °C. Two trends are apparent. First the equilibrium solubility of iodine (n_{sat}) increases slightly with temperature, from 11.1(1) at 21 °C to 16.46(1) mol(I_2)/mol(**1**) at 60 °C. Secondly, the rate of the I_2 adsorption increases significantly with temperature. The time ($\tau_{1/2}$) required to reach half of the saturation value (n_{sat}) dropped more than tenfold from about 300 h at 21 °C to 30 h at 60 °C.

There are not many solids whose properties can be compared with those of **1**. The sorption of I_2 in amorphous polymer foams has been investigated theoretically.[25] Here, the unidirectional, isothermal diffusion within a polymer film of thickness L is described by Fickian second law.[26] We tried to model the sorption data of **1** in terms of the long-time ($n/n_{sat} > 0.4$) approximation [Eq. (3)] of this model.

$$n_t = n_{sat}\left(1 - \left(\frac{8}{\pi^2}\right)\exp\left(\frac{-\pi^2 Dt}{L^2}\right)\right) \tag{3}$$

In each case a good fit was possible suggesting that the sorption is indeed diffusion controlled following Fickian kinetics.

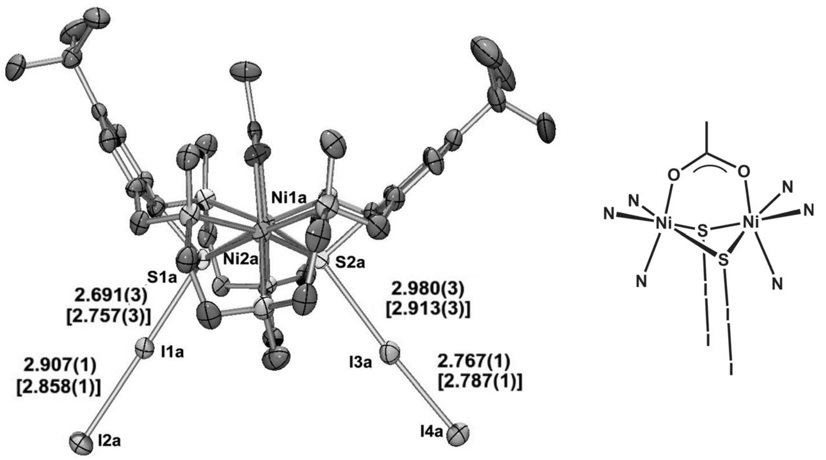

Figure 1. Left: Structure of the CT adduct $[Ni_2L(OAc)(I_2)_2]^+$ (molecule A) in crystals of **5**·MeCN (50% thermal ellipsoids, H atoms omitted, bond lengths in Å (those in square brackets for molecule B)). Right: Illustration of the core structure of the $[Ni_2L(OAc)(I_2)_2]^+$ cation.

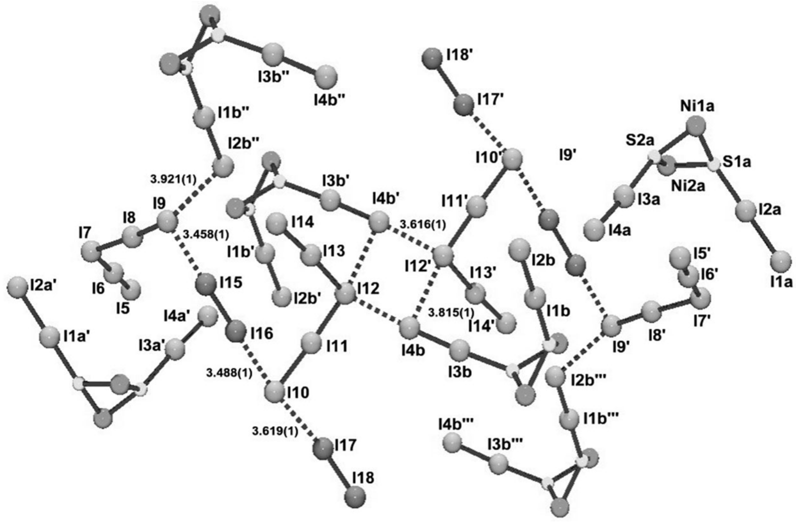

Figure 2. Section of the polyiodide network in crystals of **5**·MeCN. C, H, and N atoms are omitted for clarity. Intermolecular I···I contacts are represented as dashed lines. Cocrystallized I_2 molecules: I15-I16, I17-I18. Selected bond lengths/Å: I5-I6 2.811(2), I6-I7 3.034(2), I7-I8 3.129(2), I8-I9 2.805(2), I10-I11 2.944(2), I11-I12 2.8658(16), I13-I14 2.7388(15), I15-I16 2.715(2), I17-I18 2.724(4). Symmetry codes used to generate equivalent atoms: $-x$, $2-y$, $-z$ ('), $1-x$, $2-y$, $-z$(''), $-1+x$, $+y$, $+z$ (''').

The increase of the sorption rate can be rationalized in terms of the large (ca. 20-fold) increase of the iodine vapor pressure.

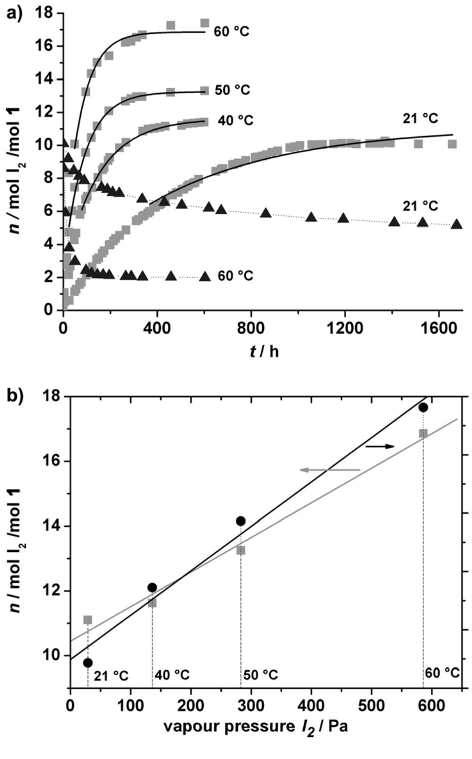

Figure 3. a) Plot of the number (n) of adsorbed (gray squares) and desorbed molecules of I_2 (black triangles) per mol of **1** as a function of time under isothermal and isobaric conditions at 21, 40, 50, and 60 °C. The solid lines are the least-squares fit according to Equation (3).
b) Plot of the saturation values n_{sat} and effective diffusion constants D_{eff} against the I_2 vapor pressure. The solid lines represent linear regression fits of the data, that is, $n_{sat} = 10.4(3) + 0.0107(9) \cdot p(I_{2,gas})$; $D_{eff} = 1.9(10) \cdot 10^{-4}\,h^{-1} + 0.0030(3) \cdot 10^{-3} \cdot p(I_{2,gas}) \cdot h^{-1}\,Pa$.

Both n_{sat} and $D_{eff} = D/L^2$ were found to be linearly dependent upon the iodine vapor pressure; however, the diffusion is much smaller than in rubbery polymers.[23,27] Given the higher flexibility of the polymer chains this is not surprising.[28]

When the I_2-loaded samples are exposed to air atmosphere, a weight loss due to I_2 desorption occurs (Figure 3 a). The release of I_2(g) is slow at 20 °C and does not reach completion during the time scale of the experiment (2 months). Raising the temperature to 60 °C, on the other hand, leads to a rapid weight loss. The saturation stage is reached in about six days and corresponds to a final content of two molecules of I_2 per formula unit of **1**. The IR spectrum of this material shows a band at 1579 cm^{-1} (ν_{as}(OAc)) strongly suggesting that these residual I_2 molecules are due to the bis(I_2) adduct $[Ni_2L(OAc)(I_2)_2](ClO_4)$. This is further supported by thermogravimetric analysis performed on a sample with the composition $[Ni_2L(OAc)(I_2)_2](I_2)ClO_4$ (obtained after exposure of **1** to I_2 vapors for eight days). This compound decomposes in two steps (75–180 °C: 14.2 %, 232 °C: 37.8 %), which can be explained by the sequential evaporation of two different kinds of I_2 molecules (first step: release of one "free" enclathrated I_2 molecule, calcd. 14.8 %; second step: release of two CT-bonded I_2 molecules, calcd. 29.6 %). The low tendency of the enclathrated I_2 molecules to evaporate is indicative of secondary CT bonding interactions of the $RS{\rightarrow}I_2{\cdots}(I_2)_n$ kind similar to those authenticated in the crystal structure of **5**·MeCN. Thus, in the present case the reversible solid–gas equilibrium is in fact governed by the CT adduct $[Ni_2L(OAc)(I_2)_2]ClO_4$, whose polarizable molecular surface acts as a kind of nucleation seed to stimulate the adsorption of molecular iodine at room temperature. Desorption from the solid occurs only slowly at room temperature, but is promoted by heat.

We finally analyzed the sorption of I_2 by IR and Raman spectroscopy.[29] Figure 4 shows IR spectra of three samples (I–III) withdrawn from a sorption experiment after 2 d, 4 d, and 25 d, corresponding to a content of one (sample I), two (sample II), and eight molecules of I_2 (sample III) per formula unit of **1**, respectively. The spectrum of pure **1** is shown for comparison.

A successive red-shift of the antisymmetric carboxylate stretching mode ν_{as}(OAc) is clearly discernible until a I_2/**1** ratio of 2:1 (i.e. sample II) is reached. Beyond this ratio the carboxylate stretching mode remains constant. Notice that the carboxylate stretching frequencies for adducts **4** and **5** are also red-shifted upon formation of CT adducts. This strongly suggests that the sorption process is indeed accompanied by the formation of a thiolate→I_2 adduct.[29] The loss of crystallinity during the sorption process can be rationalized in this way. The formation of the linear S→I–I CT linkages most likely induces steric strain, prevents a tight packing of the molecules, and creates voids for the inclusion of further I_2 molecules.

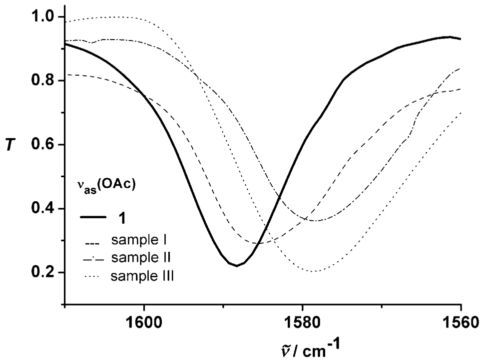

Figure 4. Section of the FTIR spectra of solid **1** and of three samples with I_2/**1** compositions of 1:1, 2:1, and 4:1 prepared by exposing **1** to iodine vapor for 48, 96, and 600 h, respectively, under isothermic and isobaric conditions (294 K, $p_i(I_2) = 29$ Pa).

In conclusion, the macrocyclic amino-thiophenolate complex **1** forms a stable bis(I_2) CT adduct, whose $RS \rightarrow I_2$ linkages can engage in secondary I⋯I bonding interactions. The intriguing chemistry of these compounds is attributed to the special ability of nickel thiolates to form Lewis acid–base adducts through use of the available lone pairs on sulfur and the widely nonpolar but polarizable molecular surface of the nickel complex which aids in the stabilization of elemental iodine (comparable to iodine in benzene). The efficient sorption and desorption characteristics make this material suitable for accommodation, sensing, and slow release of I_2 and even the removal of radioactive $^{129}I_2$.[12]

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Keywords: adsorption · charge-transfer complexes · iodine · structure elucidation · thiophenolates

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[24] Under our experimental conditions, the iodine adsorption capacity of $MgSO_4$, $CaCl_2$, and $Ni(OAc)_2{\cdot}4H_2O$ are 17, 300, and 87 mg g^{-1} (at 298 K, $p_i(I_2) = 45$ Pa, 1600 h).

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[27] One can roughly estimate the diffusion constant D [cm^{2}s^{-1}]: If L is taken as the distance from the surface to the center of the microcrystalline sample (~0.2 cm), then D (21 °C) = 0.00027 (h^{-1}) × (0.2 cm)^2/3600 (s h^{-1}) = 3×10^{-9} cm^{2}s^{-1}; D(60 °C) = 0.0019 (h^{-1}) × (0.2 cm)^2/3600 (s h^{-1}) = 2×10^{-8} cm^{2}s^{-1}. However, these values should considered to be indicative rather than definitive.

[28] I_2 sorption has been observed for other metal complexes supported by the N_6S_2 macrocycle $[M_2L(\mu\text{-}L')]ClO_4$ (e.g. M = Ni^{II}, L′ = O_2COMe, $n_{sat}^{294\,K} = 10.3$; M = Zn^{II}, L′ = OAc, $n_{sat} = 15.0$; M = Co^{II}, L′ = OAc, $n_{sat} = 7.2$). It is concluded that it is a general property of thiolato-bridged metal complexes.

[29] A comparison of the infrared spectra of $[Ni_2L(OAc)](ClO_4)$ (**1**) and $[Ni_2L(OAc)(I_2)_2](I_2)_x(ClO_4)$ (sample III) shows small shifts of the (triply spit) ν_3 and ν_4 vibrations of the ClO_4^- ion (Figure SI-4). This suggests that the iodine also interacts with the ClO_4^- ions. The Raman spectrum (Figure SI-5) of sample III shows strong peaks at 170, 231, and 233 cm^{-1} which are attributed to the I–I and RS–I_2 stretching vibrations. W. Kiefer, H. Herbstein, *J. Raman Spectrosc.* **1973**, *1*, 417–431.