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# Tiara-like Complexes acting as Iodine Encapsulating Agents: The Role of M I Interactions in $[M(\mu\text{-SCH}_2\text{CO}_2\text{Me})_2]_8\text{I}_2$ (M = Ni, Pd, Pt) Inclusion Compounds

Miguel-Armando Ponce-Vargas, Alvaro Munoz-Castro

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5 Tiara-like Complexes acting as Iodine  
6 Encapsulating Agents. The Role of M···I  
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14 Interactions in  $[M(\mu\text{-SCH}_2\text{CO}_2\text{Me})_2]_8\subset\text{I}_2$   
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19 (M=Ni, Pd, Pt) Inclusion Compounds  
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24 *Miguel Ponce-Vargas<sup>a\*</sup>, Alvaro Muñoz-Castro<sup>b\*</sup>*

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27 <sup>a</sup> Institut des Sciences Chimiques de Rennes, UMR 6226 CNRS-Université de Rennes 1,  
28 263 Avenue du Général Leclerc, 35042 Rennes Cedex, France.

29 E-mail: miguel-armando.ponce-vargas@univ-rennes1.fr

30 Phone: +33 (0) 2.23.23.69.73

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33 <sup>b</sup> Grupo de Química Inorgánica y Materiales Moleculares, Universidad Autónoma de  
34 Chile, El Llano Subercaseaux 2801, Santiago, Chile.

35 E-mail: alvaro.munoz@uautonoma.cl  
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44 ABSTRACT

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47 A proposed series of tiara-like complexes  $[M(\mu\text{-SCH}_2\text{CO}_2\text{Me})_2]_8$  (where M = Ni, Pd, Pt)  
48 are here studied through DFT methodologies prompted by the synthesis of the palladium  
49 parent and their potential application in iodine encapsulation from spent nuclear fuel.  
50 Their hollow structure with a suitable cavity size, and the presence of several transition-  
51 metal centers capable to directly interact with an I<sub>2</sub> molecule through noncovalent  
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1 forces, make them attractive inclusion agents. Herein, an Energy Decomposition  
2 Analysis reveals that forces responsible for keeping the guest molecule in the inner  
3 cavity are mainly electrostatic; a remarkable feature given, in principle, the neutral  
4 nature of both the host and guest species, offering us an interesting study case where the  
5 electronic cloud distortion of the binding sites and iodine atoms can be estimated and  
6 related to the intensity of the host-guest interactions. Our results shed light into the  
7 application of the nickel tiara-like host as an alternative to the reported [Pd( $\mu$ -  
8 SCH<sub>2</sub>CO<sub>2</sub>Me)<sub>2</sub>]<sub>8</sub> system. This research can be useful for further evaluation of nickel-  
9 based iodine sequestering agents prior to engaging in explorative synthesis efforts.  
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2 INTRODUCTION  
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6 The effective capture and storage of radioiodine is of paramount importance in public  
7 safety given its high mobility and the long half-life of the  $^{129}\text{I}$  isotope<sup>1,2</sup>. Therefore, the  
8 development of different approaches towards the encapsulation of  $\text{I}_2$  has become the  
9 primary goal of multiple research teams devoted to materials sciences<sup>3,4</sup>. Nowadays, the  
10 strategy to capture  $\text{I}_2$  released from nuclear exhaust gas usually involves the iodine  
11 precipitation in solution by using porous solids including zeolites<sup>2,5,6</sup>, coordination  
12 polymers<sup>7</sup>, hybrid porous materials<sup>8,9</sup>, nanocomposites<sup>10</sup>, and metal-containing  
13 systems<sup>11</sup>. In this last group, metallacycles appear as promising candidates due to the  
14 vast number of hollow geometries they are able to offer<sup>12,13,14</sup>, allowing different size  
15 cavities suitable for iodine. Moreover, the presence of metal centers capable of  
16 interacting with the iodine molecule through noncovalent forces represents a clear  
17 advantage over their pure organic counterparts. The host-guest capabilities of  
18 metallacycles have been already demonstrated, in particular towards small molecules<sup>15</sup>  
19 and anions<sup>16</sup>. With respect to extended metal-containing systems, in addition to the  
20 widely used silver-containing mordenites<sup>1</sup>, other effective  $\text{I}_2$  inclusion materials such as  
21 Zn(II)-metal-organic frameworks<sup>17</sup>, Zn(II)-coordination polymers<sup>9</sup> and supramolecular  
22 networks constructed by one-dimensional  $\text{M}[(\text{ebic})_2]_n$  linear chains (where  $\text{M} = \text{Zn}, \text{Co}$   
23 and  $\text{Hebic} = 2\text{-ethyl-}1H\text{-benzo[d]imidazole-5-carboxylic acid}$ )<sup>18</sup> have been hitherto  
24 reported.

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51 The rationalization of the forces established between metal-containing systems and  
52 halogens is a current subject of research with the aim of obtaining novel iodine  
53 sequestering agents. In this regard, the intensity of noncovalent interactions can be  
54 related to the electronic cloud distortion experienced by the binding sites, i.e. the metal  
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2 centers, in order to gain a deeper understanding of the forces governing the iodine  
3 encapsulation. Similar studies related to halogen bonding<sup>19,20</sup>, amino acids dimers<sup>21</sup>, *S*-  
4 heterocycles-diiodine complexes<sup>22</sup>, and water molecules<sup>23,24</sup> have been conducted, where  
5 an explanation of the noncovalent forces supported on electronic cloud distortions in  
6 terms of multipoles, is proposed.  
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10 Following our interest in metallacycle host-guest capabilities<sup>25,26</sup>, here we study through  
11 density functional theory (DFT) methodologies a series of tiara-like octanuclear  
12 complexes  $[M(\mu\text{-SCH}_2\text{CO}_2\text{Me})_2]_8$  (where M = Ni, Pd, Pt) and their corresponding iodine  
13 inclusion compounds. The palladium and platinum systems have been recently  
14 synthesized by Ura and coworkers<sup>14,27</sup>. It is the formally neutral character of the tiara-  
15 like metal containing complex and the iodine guest that prompts us to study these  
16 inclusion compounds, where the electronic cloud distortion of the binding sites and  
17 iodine atoms leading to multipole-multipole forces is to a large extent responsible for  
18 keeping the guest in the host cavity. To conduct this research we employ a noncovalent  
19 interactions analysis (NCI)<sup>28,29</sup> in order to identify the binding sites; an Energy  
20 Decomposition Analysis (EDA)<sup>30,31</sup> to clarify the nature of the noncovalent forces; a  
21 Natural Population Analysis (NPA)<sup>32</sup> to determine if a significant charge transfer  
22 between the host and the guest occurs; and a Multipole Analysis<sup>33</sup> to estimate the  
23 electronic cloud deviations occurring at the binding sites with the iodine incorporation.  
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25 Additionally, DFT calculations were also performed on simplified models with methyl  
26 groups and hydrogen atoms instead of the methoxycarbonylmethyl arms, in order to  
27 clarify the role played by the latter in the coupling forces. The aim of this work is to  
28 contribute with the development of novel iodine capture materials through a  
29 rationalization of the encapsulation process in metal-containing systems.  
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## COMPUTATIONAL DETAILS

Relativistic density functional theory<sup>34</sup> calculations were carried out by using the ADF code<sup>35</sup>, via the scalar ZORA Hamiltonian. An all electron triple- $\zeta$  Slater basis set including a polarization function (STO-TZP) was employed within the generalized gradient approximation (GGA) of Becke and Perdew (BP86)<sup>36,37</sup>. The good performance of the BP86 functional has been demonstrated in the study of equilibrium bond lengths of transition-metal diatomic molecules<sup>38</sup>, intermolecular hydrogen bonds in a series of sandwich double-decker tetradiazepinoporphyrazine-based lanthanide complexes<sup>39</sup>, and in the rationalization of noncovalent interactions of cadmium(II) coordination compounds<sup>40</sup>. Geometry optimizations were conducted via the analytical energy gradient method implemented by Verluis and Ziegler<sup>41</sup>. The Grimme dispersion correction was incorporated in order to properly account for weak London forces<sup>42</sup>.

A Noncovalent Interactions Analysis (NCI), as proposed by Yang and coworkers, was conducted by using the NCIPLOT-3.0<sup>28</sup> and NCImilano codes, the later using the electron density from ADF calculations<sup>29</sup>. Furthermore, an Energy Decomposition Analysis was carried out following the Morokuma-Ziegler scheme<sup>30,31</sup>, and complemented by a NPA Analysis<sup>32</sup>. Finally, the Atomic Multipole Moment Analysis proposed by Swart and coworkers<sup>33</sup>, was used to study in deep the electronic cloud variation at the binding sites and iodine atoms. For all isosurfaces and figures the software packages Chemcraft<sup>43</sup> and Visual Molecular Dynamics (VMD)<sup>44</sup> were used.

## RESULTS AND DISCUSSION

The ester-substituted systems subject of this study were recently synthesized by Ura and coworkers<sup>20</sup> via reactions of  $[\text{MCl}_2(\text{MeCN})_2]$  ( $\text{M} = \text{Pd}, \text{Pt}$ ) with *m*- $\text{C}_6\text{H}_4(\text{CMe}_2\text{SCH}_2\text{CO}_2\text{Me})_2$  leading to  $[\text{M}(\mu\text{-SCH}_2\text{CO}_2\text{Me})_2]_8$ , hereafter referred as **1-Pd<sub>8</sub>** and **1-Pt<sub>8</sub>**. The palladium complex can react with  $\text{I}_2$  in  $\text{CHCl}_3$  at room temperature to generate the inclusion compound **1-Pd<sub>8</sub>⊂I<sub>2</sub>**. To obtain a detailed picture of the noncovalent forces established between the iodine guest and the tiara-like hosts we extend the series also covering the hypothetical systems **1-Ni<sub>8</sub>**, **1-Ni<sub>8</sub>⊂I<sub>2</sub>** and **1-Pt<sub>8</sub>⊂I<sub>2</sub>**. Additionally, we replace the methoxycarbonylmethyl arms by methyl groups (**2**) and hydrogens (**3**) in order to determine the influence of the ester substituents in the iodine encapsulation.

All the ester-substituted complexes can be adjusted to a  $D_2$  symmetry given the ellipsoidal shape of their inner cavity defined by eight metal centers  $\text{M}(\text{II})$  ( $\text{M} = \text{Ni}, \text{Pd}, \text{Pt}$ ) bridged by sulphur atoms. We label these metal centers as M1, M2 and M3 starting from that contained in the largest symmetry axis of the ellipsoidal cavity. The results are presented in Table 1 and Figure 1. It seems that the inclusion of the iodine guest does not alter in a great extent the size of the cavity as evidenced by the small variation of  $\text{M}\cdots\text{M}$  distances and angles. On the other hand, the typical iodine bond length (2.667 Å)<sup>45</sup> is enlarged to 2.989 Å in **1-Ni<sub>8</sub>⊂I<sub>2</sub>**, 2.903 Å in **1-Pd<sub>8</sub>⊂I<sub>2</sub>** and 2.880 Å in **1-Pt<sub>8</sub>⊂I<sub>2</sub>** suggesting that noncovalent interactions occur between the iodine atoms and the M1 centers that could lead to a further dissociation of  $\text{I}_2$ . The comparison of van der Waals radii sum<sup>46</sup> and  $\text{M}\cdots\text{I}$  distances also suggest that a certain degree of orbital overlap occurs between M1 and the guest, with values of  $\text{M1}\cdots\text{I}$  of 2.879 Å in **1-Ni<sub>8</sub>⊂I<sub>2</sub>**, 3.153 Å

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2 in **1**-Pd<sub>8</sub>⊂I<sub>2</sub>, and 3.204 Å in **1**-Pt<sub>8</sub>⊂I<sub>2</sub>, smaller than those corresponding to the van der  
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4 Waals radii sums (3.220 Å, 3.370 Å and 3.340 Å, respectively). With respect to M2⋯I,  
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6 calculated distances are longer than van der Waals radii sums, with the exception of **1**-  
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8 Ni<sub>8</sub>⊂I<sub>2</sub> where a shorter distance is found (3.083 Å), that can be ascribed to stronger  
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10 interactions. Recently, Devatour-Vinot and coworkers determined by a combining  
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12 spectroscopic and computational study that I<sub>2</sub> molecules directly interact with the Ni(II)  
13  
14 ions of a Ni(pz)[Ni(CN)<sub>4</sub>] lattice displaying M⋯I distances of 3.42 Å<sup>9</sup>.

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16 DFT calculations at the MPW1PW91/LANL2DZ (Pd), DGDZVP (I), 6-31G (S,H) level  
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18 were previously carried out by Ura and coworkers for a hypothetical hydrogen-  
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20 substituted [Pd(μ-SH)<sub>2</sub>]<sub>8</sub>⊂I<sub>2</sub> tiara-like compound providing M⋯I distances close to  
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22 those obtained in this work<sup>27</sup>.

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24 In order to clarify the role of the metal centers as binding sites and to determine if the  
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26 sulphur atoms surrounding the I<sub>2</sub> also play a relevant role in keeping the guest in the  
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28 cavity center, we carried out a Noncovalent Interaction Analysis (NCI)<sup>28,29</sup>, which is  
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30 based on a 2D plot of the reduced density gradient *s*, and the electron density  $\rho$ , where *s*  
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32 can be expressed as

$$s = \frac{1}{2(3\pi^2)^{1/3}} \frac{|\nabla\rho|}{\rho^{4/3}}$$

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34 When non-covalent interactions occur, there is a crucial change in *s*, producing density  
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36 critical points. Then, an isosurface considering only those values of *s* associated to the  
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38 critical points is generated evidencing the regions where noncovalent forces arise. To  
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40 determine the type of interaction, the second eigenvalue of the electronic density  
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42 Hessian ( $\lambda_2$ ) is invoked, where more than weak stabilizing interactions, such as hydrogen  
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44 bonds, are characterized by  $\lambda_2 < 0$ , non-bonded interactions such as steric repulsion by  
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46  $\lambda_2 > 0$ , and weak interactions by  $\lambda_2 \approx 0$ . These  $\lambda_2$  values are denoted over the isosurface,  
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2 by using a color scale. In the ester-substituted complexes NCI analysis (Figure 2) the  
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4 blue regions of the isosurface denote that more than weak interactions arise between the  
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6 metal centers M1 and the iodine atoms. On the other hand, between M2 and the iodine  
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8 atoms, the intensity of noncovalent interactions seems to be lower, as denoted by the  
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10 turquoise region, while weak London forces between M3 and the iodine molecule are  
11  
12 evidenced by the green region of the isosurface suggesting a more important role of M1  
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14 in keeping the iodine molecule in the host cavity. The NCI analysis also reveals that  
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16 sulphur atoms do not interact with I<sub>2</sub> to the same extent as the metal centers.  
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21 The nature of the host-guest interactions between the tiara-like host and the iodine guest  
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23 can be explored in deep through the Energy Decomposition Analysis (EDA) proposed  
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25 by Morokuma<sup>30,31</sup> which separates the total interaction energy in different terms such as  
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27 electrostatic, Pauli repulsion, and orbital overlapping, thus clarifying the nature of the  
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29 interactions arising in several systems<sup>47,48,49,50</sup>. In this analysis, the interaction between  
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31 the frozen charge densities is accounted by the electrostatic interaction  $\Delta E_{elec}$ , which is  
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33 calculated by subtracting the Coulomb integral of the fragments from that corresponding  
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35 to the overall system. The product of density fragments, which is normalized but violates  
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37 the Pauli principle, is antisymmetrized and renormalized to give an intermediate state.  
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39 The energy difference between the states before and after the antisymmetrization-  
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41 renormalization is called Pauli repulsion,  $\Delta E_{Pauli}$ , and can be related to destabilizing  
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43 forces between the fragments. Finally, the fragment orbitals are relaxed to yield the final  
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45 state corresponding to the inclusion system. The energy decrease caused from such  
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47 orbital mixing is identified as the orbital interaction,  $\Delta E_{orb}$ . Adding  $\Delta E_{elec}$ ,  $\Delta E_{Pauli}$ , and  
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49  $\Delta E_{orb}$  we obtain the total interaction energy  $\Delta E_{int}$  of the fragments. To overcome the  
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51 basis set superposition error (BSSE), the counterpoise method proposed by Boys and  
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53 Bernardi is employed<sup>51</sup>, denoting in this case BSSE values of about 4.15 kcal mol<sup>-1</sup>. The  
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1 dispersion interaction is included according to the Grimme pairwise dispersion  
2 correction<sup>42</sup> where an attractive energy term summed over all atomic pairs is  
3 incorporated, taking into account the weak forces associated to instantaneous  
4 fluctuations of fragment electronic densities. Finally, the energy difference between the  
5 initial geometries of the fragments and those belonging to the inclusion systems is  
6 denoted as preparation energy,  $\Delta E_{prep}$ .  
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15 The EDA results presented in Table 2 reveals that in the ester-substituted series, all  
16 systems present almost the same total interaction energy, with values of  $-56.61 \text{ kcal mol}^{-1}$   
17 for **1**-Ni<sub>8</sub>⊂I<sub>2</sub>,  $-60.34 \text{ kcal mol}^{-1}$  for **1**-Pd<sub>8</sub>⊂I<sub>2</sub>, and  $-58.73 \text{ kcal mol}^{-1}$  for **1**-Pt<sub>8</sub>⊂I<sub>2</sub>,  
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The EDA analysis for the ester-substituted systems also indicates that the highest preparation energy is obtained for **1**-Pt<sub>8</sub>⊂I<sub>2</sub> ( $350.43 \text{ kcal mol}^{-1}$ ) denoting that more pronounced structural variations occur with the encapsulation of the guest in this case. The orbital contribution in **1**-Ni<sub>8</sub>⊂I<sub>2</sub> ( $-95.44$ ) evidences a higher extent of orbital overlap for this complex probably due to the smaller M...I distances. This higher orbital contribution in **1**-Ni<sub>8</sub>⊂I<sub>2</sub> allows a more effective charge transfer during the inclusion process as is reflected in the NPA results (See discussion below). On the other hand, the electrostatic contribution increases as the metal centers of the tiara-like host present more localized orbitals being  $-72.04 \text{ kcal mol}^{-1}$  for **1**-Pt<sub>8</sub>⊂I<sub>2</sub>,  $-73.89 \text{ kcal mol}^{-1}$  for **1**-Pd<sub>8</sub>⊂I<sub>2</sub>, and  $-131.38 \text{ kcal mol}^{-1}$  for **1**-Ni<sub>8</sub>⊂I<sub>2</sub>.

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2 The dispersion energy according to the Grimme correction<sup>42</sup> increases in line with the  
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4 volume of the metal binding sites with values of -37.80 kcal mol<sup>-1</sup> in **1**-Ni<sub>8</sub>C<sub>12</sub>, -47.62  
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6 kcal mol<sup>-1</sup> in **1**-Pd<sub>8</sub>C<sub>12</sub>, and -49.28 kcal mol<sup>-1</sup> in **1**-Pt<sub>8</sub>C<sub>12</sub>. The opposite occurs with the  
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8 Pauli term accounting for repulsion forces, that reaches its maximum value in **1**-Ni<sub>8</sub>C<sub>12</sub>,  
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10 a fact that could be attributed to the shorter M...I distances that enhance the steric  
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12 repulsions.  
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16 The replacement of the alternately located methoxycarbonylmethyl arms by methyl  
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18 groups leads to a decrease in preparation energy, which now ranges from 128.66 kcal  
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20 mol<sup>-1</sup> in **2**-Ni<sub>8</sub>C<sub>12</sub> to 161.70 kcal mol<sup>-1</sup> in **2**-Pt<sub>8</sub>C<sub>12</sub>, suggesting that structural variations  
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22 occurring in **1** could be associated to the ester arms rearrangements. The subsequent  
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24 replacement of methyl substituents by hydrogens results in a more pronounced decrease  
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26 of such energy now ranging from 75.28 kcal mol<sup>-1</sup> in **3**-Ni<sub>8</sub>C<sub>12</sub> to 79.78 kcal mol<sup>-1</sup> in **3**-  
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28 Pt<sub>8</sub>C<sub>12</sub>. Conversely, the replacement of the ester arms does not influence significantly  
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30 the orbital and electrostatic contributions. The same occurs with the Pauli term where the  
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32 incorporation of the methyl groups exerts a small influence. However, when we go  
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34 towards the hydrogen-substituted complexes, a steep decrease of Pauli repulsion occurs,  
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36 now ranging from 190.37 kcal mol<sup>-1</sup> in **3**-Ni<sub>8</sub>C<sub>12</sub> to 98.22 kcal mol<sup>-1</sup> in **3**-Pt<sub>8</sub>C<sub>12</sub>. These  
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38 results indicate that steric effects in the ester-substituted series can be mainly attributed  
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40 to the methylene groups attached to the sulphur atoms.  
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48 The nature of the side arms can also affect the host-guest capabilities of the studied  
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50 structures, by preventing access to the binding sites provided by the M<sub>8</sub> backbone. In this  
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52 regard, it has been shown earlier by Higgins III and coworkers, that the related [Pd<sub>8</sub>(S-  
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54 *n*Pr)<sub>16</sub>] complex is not able to encapsulate I<sub>2</sub> among other neutral molecules<sup>52</sup>, in contrast  
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56 to results obtained with **1**-Pd<sub>8</sub>, by Ura and coworkers<sup>20</sup>. This reflects that variation of  
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2 steric effects related to the ligands could also be a good strategy towards a fine tuning of  
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4 host capabilities provided by the multimetallic array.  
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8 Looking for a deeper understanding of the electrostatic contribution to total interaction  
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10 energy, we study the electronic cloud distortion experienced by the metal centers in  
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12 terms of dipole moments and quadrupole moments, according to the methodology  
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14 proposed by Swart and coworkers<sup>33</sup> where the local electrostatic potential is mainly  
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16 determined by the charge distribution around the respective atom, or within the atomic  
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18 multipole expansion, by the atomic multipoles near to that point. This charge analysis  
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20 offers an accurate description of the electrostatic potential from the charge distribution in  
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22 molecules by writing the total density as a sum of atomic densities expressed in terms of  
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24 atomic functions, which in turn are used to define a set of atomic multipoles. The results  
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26 of the atomic multipole analysis are presented in Table 4, where it is clear that before the  
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28 iodine molecule inclusion, the dipole moments of the metal centers exhibit an almost  
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30 negligible distortion, as reflected by values under 0.12 D that can be attributed to their  
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32 slightly distorted square planar coordination sphere. With the incorporation of I<sub>2</sub> a  
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34 noticeable variation of the metal centers dipoles is observed, especially in the M1  
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36 centers. Thus, in **1**-Pd<sub>8</sub>⊂I<sub>2</sub> the M1 dipole reaches its highest value of 0.737 D, followed  
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38 by 0.344 D in **1**-Ni<sub>8</sub>⊂I<sub>2</sub> and 0.260 D in **1**-Pt<sub>8</sub>⊂I<sub>2</sub>, well above to those observed for M2  
39  
40 and M3. A correspondence between the magnitude of M1 dipoles and those related to  
41  
42 the iodine atoms is observed, although with lower magnitudes for the later ones, i.e.  
43  
44 0.223 D in **1**-Pd<sub>8</sub>⊂I<sub>2</sub>, 0.177 D in **1**-Pt<sub>8</sub>⊂I<sub>2</sub>, and 0.150 D in **1**-Ni<sub>8</sub>⊂I<sub>2</sub>. The graphical  
45  
46 representation of the atomic dipoles also evidences the proper head-to-tail orientation for  
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48 the M1 and iodine dipoles leading to the dipole-dipole forces (Figure 3), also present in  
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50 the methyl-substituted and hydrogen substituted series (Figure S1).  
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2 In the methyl-substituted (**2**) and hydrogen-substituted (**3**) series, we can also observe  
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4 low magnitude electronic dipoles for the metal centers before the guest encapsulation,  
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6 where only the platinum centers of the hydrogen-substituted series overcome the barrier  
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8 of 0.12 D. In almost all cases, the guest incorporation leads to electronic rearrangements  
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10 in which M1 presents the highest dipole value, with the exception of **2**-Pt<sub>8</sub>⊂I<sub>2</sub> and **3**-  
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12 Pt<sub>8</sub>⊂I<sub>2</sub> where M2 centers exhibit the maximum dipole moments of 0.132 D and 0.131 D,  
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14 respectively.  
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18 In addition to dipole-dipole forces, the quadrupole-quadrupole interactions also play a  
19  
20 relevant role in electrostatic forces. Bearing this in mind, we calculate the atomic  
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22 quadrupole tensors for the metal centers and the iodine atoms. Then, we determine the  
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24 anisotropy of such tensors in order to quantify the degree of electronic cloud  
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26 distribution. Also we plot the quadrupole tensors in order to acquire a deeper knowledge  
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28 in the electronic rearrangement occurring at the binding sites with the I<sub>2</sub> incorporation.  
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31 Results are presented in Table 5.  
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35 In the ester-substituted series the quadrupole anisotropy is more pronounced for the M2  
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37 centers with values of -7.721 B for **1**-Pd<sub>8</sub>⊂I<sub>2</sub>, -5.910 B for **1**-Pt<sub>8</sub>⊂I<sub>2</sub> and 1.025 B for **1**-  
38  
39 Ni<sub>8</sub>⊂I<sub>2</sub>. On the other hand, the iodine atoms experience a quadrupole distortion in line  
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41 with that observed in the dipoles case, with the maximum anisotropy value of 4.212 B  
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43 for **1**-Pd<sub>8</sub>⊂I<sub>2</sub>, followed by 4.062 B for **1**-Pt<sub>8</sub>⊂I<sub>2</sub>, and 3.335 B for **1**-Ni<sub>8</sub>⊂I<sub>2</sub>.  
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47 The graphical representation of the quadrupole moment tensors allows us to notice that a  
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49 different distribution is obtained in **1**-Ni<sub>8</sub>⊂I<sub>2</sub>, where the positive lobes of the metal  
50  
51 centers point towards the center of the cavity avoiding the opposite-sign interaction with  
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53 the negative lobe of the iodine quadrupole. Conversely, in **1**-Pd<sub>8</sub>⊂I<sub>2</sub> and **1**-Pt<sub>8</sub>⊂I<sub>2</sub> the  
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55 metal negative lobes point towards the center of the cavity leading to an effective match  
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2 between the negative lobe of M1 and the iodine positive lobe. Also, this distribution  
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4 allows a closer distance between M2 negative lobes and iodine positive lobes in good  
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6 agreement with the higher M2 quadrupole anisotropy values found for the palladium and  
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8 platinum systems. The same quadrupole distributions are obtained with the methyl-  
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10 substituted (**2**) and hydrogen-substituted systems (**3**) (Figure S2). Hence, the multipole  
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12 results evidence a more relevant role played by the dipole-dipole and quadrupole-  
13  
14 quadrupole interactions in **1**-Pd<sub>8</sub>C<sub>12</sub> and **1**-Pt<sub>8</sub>C<sub>12</sub> in comparison to **1**-Ni<sub>8</sub>C<sub>12</sub>.  
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18 A series of hypothetical hydrogen-substituted complexes (**3**) enables us to carry out a  
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20 Natural Population Analysis to obtain a deeper understanding of the charge transfer  
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22 occurring during the guest inclusion. The optimized structures of **3** present M...I  
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24 distances in good agreement to those corresponding to the ester-substituted frameworks  
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26 (Table S1). The NPA results presented in Table 3 suggest that an electronic charge  
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28 transfer from the metal centers to the iodine guest occurs, which is more pronounced in  
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30 **3**-Ni<sub>8</sub>C<sub>12</sub> -in line with the higher orbital contribution obtained in the EDA- with an  
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32 average charge of +0.40 |e| for each metal center and an overall charge of -1.14 |e| for I<sub>2</sub>.  
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34 In Pd<sub>8</sub>C<sub>12</sub> and Pt<sub>8</sub>C<sub>12</sub> the electronic transfer leads to lower M charges of +0.30 |e| and  
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36 +0.19 |e|, respectively and an overall charge of -0.70 |e| for I<sub>2</sub> in both cases. The NPA  
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38 analysis also evidences that sulphur atoms do not experience an important charge  
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40 transfer with the guest incorporation.  
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## CONCLUDING REMARKS

The Energy Decomposition Analysis reveals that **1-Ni**<sub>8</sub>, **1-Pd**<sub>8</sub> and **1-Pt**<sub>8</sub> thiolate complexes are capable to establish noncovalent interactions with the iodine molecule to a similar extent as evidenced by the total interaction energies of their corresponding inclusion systems (-56.61 kcal mol<sup>-1</sup>, -60.34 kcal mol<sup>-1</sup>, and -58.73 kcal mol<sup>-1</sup>, respectively). In all of them, the electrostatic contribution arises as the most important term representing about 45% of total interaction, a remarkable feature considering the formally neutral character of both the host and the guest. The nickel system presents the higher orbital contribution in line with a major amount of charge transferred during the encapsulation process. Interestingly, a rise of multipole-multipole forces occur in **1-Pd**<sub>8</sub>⊂I<sub>2</sub> and **1-Pt**<sub>8</sub>⊂I<sub>2</sub>, as revealed by the higher electronic cloud deviation experienced by the metal centers, in terms of dipole magnitudes (M1) and quadrupole anisotropies (M2). Moreover, a correspondence between the electronic cloud deformation degree of the metal centers and that concerning the iodine atoms is found.

The studied systems constitute promising iodine sequestering agents. Thus, our results shed light into the interesting application of the nickel tiara-like host [Ni( $\mu$ -SCH<sub>2</sub>CO<sub>2</sub>Me)<sub>2</sub>]<sub>8</sub> as an alternative to the reported [Pd( $\mu$ -SCH<sub>2</sub>CO<sub>2</sub>Me)<sub>2</sub>]<sub>8</sub> complex. This can

be useful for further evaluation of nickel-based iodine encapsulating systems prior to engaging in explorative synthesis efforts.

## ACKNOWLEDGEMENTS

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## TABLES AND FIGURES

**Table 1:** Selected structural parameters of the studied systems (Å and degrees).

	1-Ni <sub>8</sub>	1-Ni <sub>8</sub> Cl <sub>2</sub>	1-Pd <sub>8</sub>		1-Pd <sub>8</sub> Cl <sub>2</sub>		1-Pt <sub>8</sub>		1-Pt <sub>8</sub> Cl <sub>2</sub>
			Exp. <sup>a</sup>	Theor.	Exp. <sup>a</sup>	Theor.	Exp. <sup>b</sup>	Theor.	
M1...M1	8.612	8.747	8.719	9.051	-	9.209	8.754	9.049	9.288
M2...M2	8.002	8.085	8.233	8.677	-	8.753	8.801	8.812	8.908
M3...M3	7.332	7.396	8.231	8.307	-	7.924	8.434	8.518	8.083
< M2-M1-M2	121.2	126.7	131.3	130.2	-	130.1	134.7	132.1	131.1
< M1-M2-M3	134.8	135.3	133.9	135.1	-	132.2	136.2	134.6	131.7
< M2-M3-M2	143.1	142.6	136.4	139.6	-	145.3	137.0	138.8	145.4
M1...I	-	2.879	-	-	3.099	3.153	-	-	3.204
M2...I	-	3.083	-	-	3.402	3.449	-	-	3.536
M3...I	-	3.989	-	-	4.198	4.219	-	-	4.291
I-I	-	2.989	-	-	2.762	2.903	-	-	2.880

a. Experimental data from reference 27

b. Experimental data from reference 15



**Table 2:** Energy Decomposition Analysis (EDA) (kcal mol<sup>-1</sup>) for the octanuclear tiara-like complexes.

	1-Ni <sub>8</sub> Cl <sub>2</sub>		1-Pd <sub>8</sub> Cl <sub>2</sub>		1-Pt <sub>8</sub> Cl <sub>2</sub>	
$\Delta E_{prep}$	301.69		308.54		350.43	
$\Delta E_{orb}$	-95.44	36.07%	-53.09	30.41%	-50.68	29.47%
$\Delta E_{elec}$	-131.38	49.65%	-73.89	42.32%	-72.04	41.88%
$\Delta E_{disp}$	-37.80	14.28%	-47.62	27.27%	-49.28	28.65%
$\Delta E_{Pauli}$	208.01		114.26		113.27	
$\Delta E_{int}$	-56.61		-60.34		-58.73	
	2-Ni <sub>8</sub> Cl <sub>2</sub>		2-Pd <sub>8</sub> Cl <sub>2</sub>		2-Pt <sub>8</sub> Cl <sub>2</sub>	
$\Delta E_{prep}$	128.66		130.15		161.70	
$\Delta E_{orb}$	-97.32	36.58%	-54.32	30.77%	-51.44	29.80%
$\Delta E_{elec}$	-132.81	49.91%	-76.60	43.39%	-73.96	42.84%
$\Delta E_{disp}$	-35.95	13.51%	-45.62	25.84%	-47.24	27.36%
$\Delta E_{Pauli}$	206.66		117.35		115.43	
$\Delta E_{int}$	-59.42		-59.19		-57.21	
	3-Ni <sub>8</sub> Cl <sub>2</sub>		3-Pd <sub>8</sub> Cl <sub>2</sub>		3-Pt <sub>8</sub> Cl <sub>2</sub>	
$\Delta E_{prep}$	75.28		65.89		79.78	
$\Delta E_{orb}$	-81.21	35.42%	-41.38	27.59%	-39.30	27.46%
$\Delta E_{elec}$	-120.00	52.34%	-69.41	46.28%	-63.31	44.23%
$\Delta E_{disp}$	-28.06	12.24%	-39.18	26.13%	-40.53	28.31%
$\Delta E_{Pauli}$	190.37		105.29		98.22	
$\Delta E_{int}$	-38.90		-44.68		-44.92	

**Table 3.** Natural population analysis (NPA, a.u.) of the hydrogen-substituted metallacycle complexes. M1 corresponds to the metal center closest to an iodine atom.

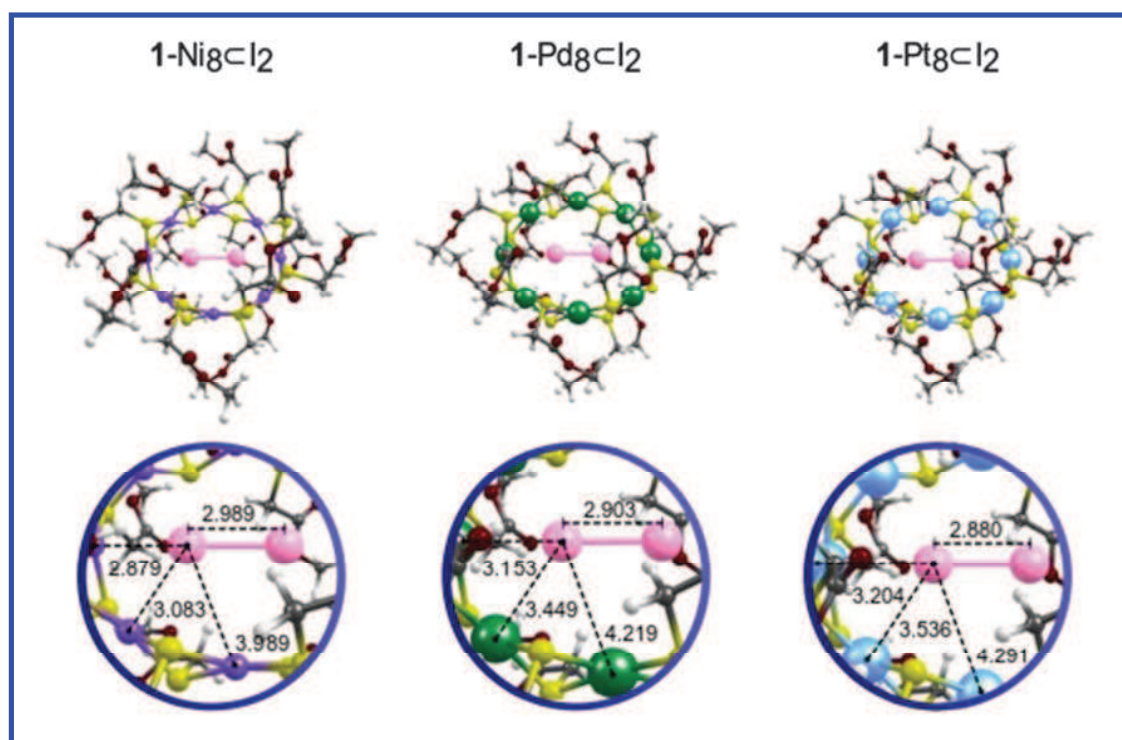
	<b>3-Ni<sub>8</sub></b>	<b>3-Ni<sub>8</sub>Cl<sub>2</sub></b>	<b>3-Pd<sub>8</sub></b>	<b>3-Pd<sub>8</sub>Cl<sub>2</sub></b>	<b>3-Pt<sub>8</sub></b>	<b>3-Pt<sub>8</sub>Cl<sub>2</sub></b>
M 1	0.35	0.41	0.29	0.31	0.17	0.20
M 2	0.35	0.40	0.29	0.31	0.17	0.19
M 3	0.35	0.38	0.29	0.29	0.17	0.17
I	-	-0.57	-	-0.35	-	-0.35
S 1 (H in)	-0.33	-0.32	-0.29	-0.28	-0.24	-0.23
S 1 (H out)	-0.33	-0.31	-0.29	-0.28	-0.24	-0.23
S 2 (H in)	-0.33	-0.32	-0.29	-0.28	-0.24	-0.22
S 2 (H out)	-0.33	-0.32	-0.29	-0.29	-0.24	-0.24

**Table 4:** Electronic dipole vectors for metal and guest atoms (Debyes). M1 corresponds to the metal center closest to an iodine atom.

	<b>1-Ni<sub>8</sub></b>	<b>1-Ni<sub>8</sub>Cl<sub>2</sub></b>	<b>1-Pd<sub>8</sub></b>	<b>1-Pd<sub>8</sub>Cl<sub>2</sub></b>	<b>1-Pt<sub>8</sub></b>	<b>1-Pt<sub>8</sub>Cl<sub>2</sub></b>
M1	0.114	0.344	0.007	0.737	0.046	0.260
M2	0.047	0.046	0.031	0.056	0.068	0.091
M3	0.076	0.100	0.010	0.220	0.039	0.001
I	-	0.150	-	0.223	-	0.177
	<b>2-Ni<sub>8</sub></b>	<b>2-Ni<sub>8</sub>Cl<sub>2</sub></b>	<b>2-Pd<sub>8</sub></b>	<b>2-Pd<sub>8</sub>Cl<sub>2</sub></b>	<b>2-Pt<sub>8</sub></b>	<b>2-Pt<sub>8</sub>Cl<sub>2</sub></b>
M1	0.006	0.206	0.041	0.309	0.110	0.121
M2	0.006	0.019	0.041	0.028	0.110	0.132
M3	0.006	0.023	0.041	0.060	0.110	0.108
I	-	0.153	-	0.270	-	0.193
	<b>3-Ni<sub>8</sub></b>	<b>3-Ni<sub>8</sub>Cl<sub>2</sub></b>	<b>3-Pd<sub>8</sub></b>	<b>3-Pd<sub>8</sub>Cl<sub>2</sub></b>	<b>3-Pt<sub>8</sub></b>	<b>3-Pt<sub>8</sub>Cl<sub>2</sub></b>
M1	0.019	0.229	0.059	0.279	0.136	0.085
M2	0.016	0.020	0.059	0.042	0.133	0.131
M3	0.015	0.036	0.059	0.044	0.128	0.127
I	-	0.137	-	0.220	-	0.114

**Table 5.** Anisotropy of the electronic quadrupole tensors for the representative metal and guest atoms (Buckingham). M1 corresponds to the metal center aligned with the iodine molecule.

	<b>1-Ni<sub>8</sub></b>	<b>1-Ni<sub>8</sub>Cl<sub>2</sub></b>	<b>1-Pd<sub>8</sub></b>	<b>1-Pd<sub>8</sub>Cl<sub>2</sub></b>	<b>1-Pt<sub>8</sub></b>	<b>1-Pt<sub>8</sub>Cl<sub>2</sub></b>
M 1	0.630	0.744	-3.701	-3.362	-3.002	-2.943
M 2	1.016	1.025	-7.203	-7.721	-5.591	-5.910
M 3	0.750	0.791	-3.635	3.023	-3.028	-3.063
I	-	3.335	-	4.212	-	4.062
	<b>2-Ni<sub>8</sub></b>	<b>2-Ni<sub>8</sub>Cl<sub>2</sub></b>	<b>2-Pd<sub>8</sub></b>	<b>2-Pd<sub>8</sub>Cl<sub>2</sub></b>	<b>2-Pt<sub>8</sub></b>	<b>2-Pt<sub>8</sub>Cl<sub>2</sub></b>
M 1	0.543	0.593	-3.780	-4.054	-3.302	-3.187
M 2	0.851	0.855	-6.546	-6.778	-5.902	-6.041
M 3	0.543	0.628	-3.780	-3.900	-3.302	-3.455
I	-	3.162	-	4.268	-	4.110
	<b>3-Ni<sub>8</sub></b>	<b>3-Ni<sub>8</sub>Cl<sub>2</sub></b>	<b>3-Pd<sub>8</sub></b>	<b>3-Pd<sub>8</sub>Cl<sub>2</sub></b>	<b>3-Pt<sub>8</sub></b>	<b>3-Pt<sub>8</sub>Cl<sub>2</sub></b>
M 1	0.678	0.681	-3.192	-3.777	-2.945	-3.003
M 2	1.107	1.017	-5.379	-6.058	-5.220	-5.549
M 3	0.687	0.756	-3.186	-3.527	-2.958	-3.123
I	-	3.584	-	4.319	-	4.283



**Figure 1.** Optimized geometries of the inclusion compounds (distances in Å)

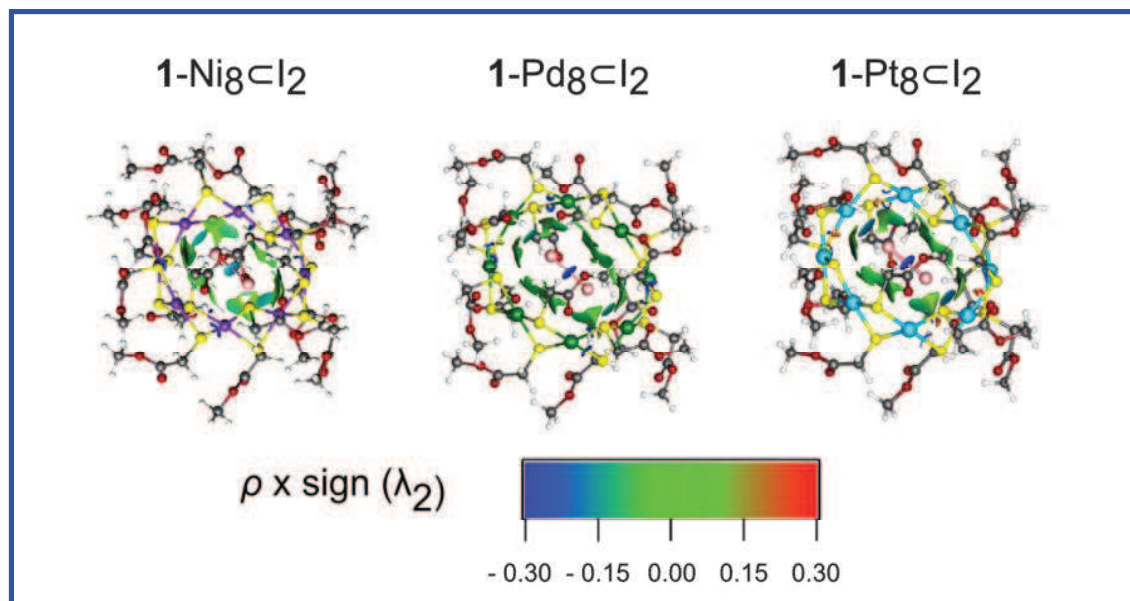


Figure 2. NCI Analysis of the studied systems.

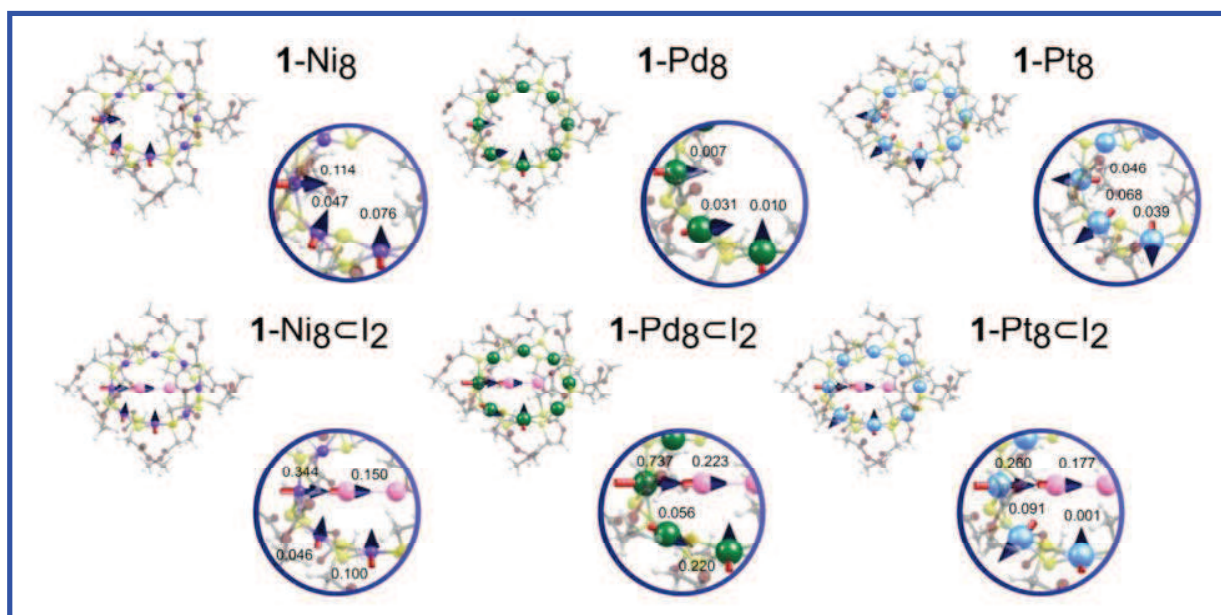
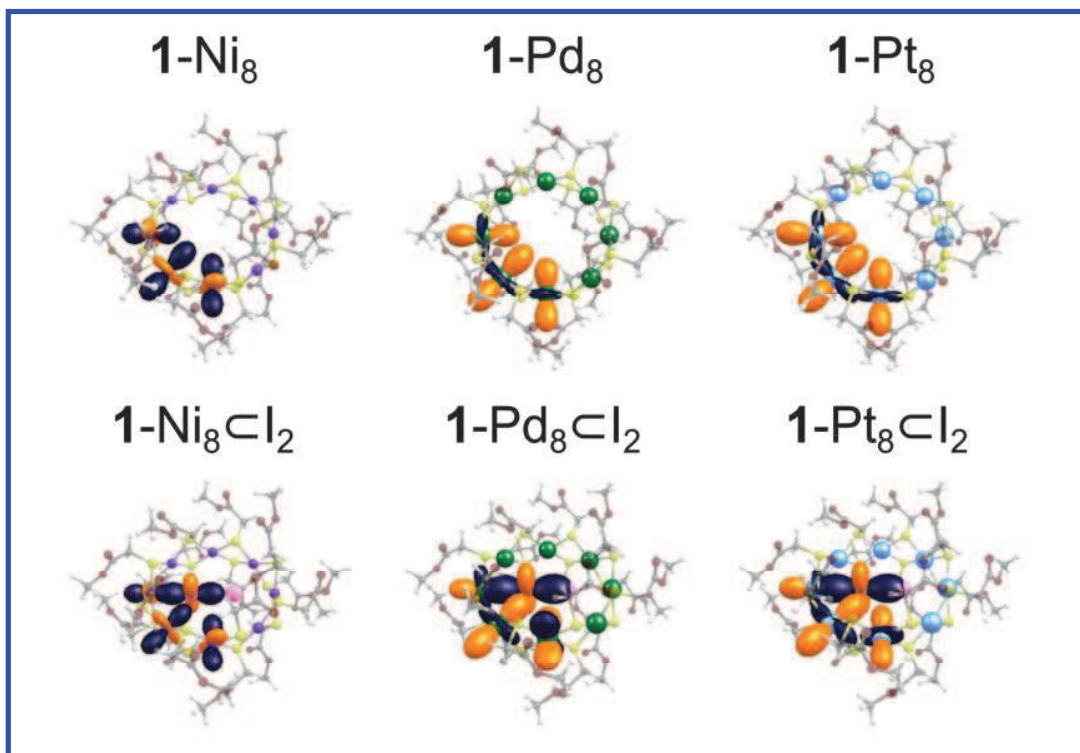


Figure 3. Graphical representation of the electronic dipole vectors of the studied systems where the blue arrowhead denotes the negative region (Debyes).



**Figure 4.** Graphical representation of the electronic quadrupole tensors of the studied systems (orange lobes denote negative regions and the blue ones, positive regions).

#### SUPPORTING INFORMATION AVAILABLE

Selected calculated distances (Å) and angles (degrees), graphical representation of the dipole vectors, and graphical representation of the quadrupole moments tensors for the methyl-substituted (**2**) and the hydrogen-substituted (**3**) series are available free of charge at <http://pubs.acs.org>.

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