

Comparison of extended-Hückel and ab initio calculations in predicting the hapticity of benzene in silica-supported Ni^I complexes

Jean-Michel Garrot, Christine Lepetit *, Michel Che

Laboratoire de Réactivité de Surface, URA 1106 CNRS, Université P. et M. Curie, Tour 54–55, 2ème étage, 4, Place Jussieu, 75252 Paris Cedex 05, France

Abstract

Extended Hückel and ab initio calculations based on the density functional theory were carried out onto the model complexes [(benzene)Ni^I(OH)₃]²⁻ and [(benzene)Ni^I(OH)(OH₂)₂] in order to investigate the bonding mode of benzene to silica-supported Ni^I ions. In these model complexes, the contribution of the silica support is restricted to hydroxyl groups or water molecules. Both calculation methods are consistent in predicting an η²-coordination of benzene that was previously observed by infrared spectroscopy. The calculations allow a better geometrical description of the stable dihapto benzene complexes and are discussed in terms of interaction of molecular orbitals.

Keywords: Nickel; η²-Benzene; Silica surface; Extended Hückel calculations; Density functional theory; Local density approach; Non-local density approach; DMol

1. Introduction

Silica-supported Ni^I-dihapto benzene complexes have been recently evidenced in our laboratory [1]. In these complexes, Ni^I interacts only with two carbon atoms of the benzene ring as evidenced by infrared (IR) spectroscopy. The bathochromic shift of the C–C stretching vibration (–20 cm⁻¹) relative to the free C₆H₆ molecule is consistent with a ring-edge bound complex [2]. Unlike η⁶-arene complexes, little is known about this lower coordination mode of benzene, already observed in Cu^{II}, Ag^I or Os^{II} complexes [2–4].

In order to confirm this unusual hapticity and to better describe its influence on the benzene mol-

ecule, semi-empirical and ab initio calculations were performed onto the model complexes [(benzene)Ni^I(OH)₃]²⁻ and [(benzene)Ni^I(OH)(OH₂)₂], where the contribution of the silica support is restricted to hydroxyl groups or water molecules.

Extended Hückel (EHT) is a simple semi-empirical method [5], already successfully used for studying a large range of inorganic and organometallic compounds. It gives a good initial approximation of the electronic structure of complex molecules but generally fails in predicting reasonable bond lengths. It has also been efficient in predicting the coordination of condensed arenes [6].

Ab initio calculations are however preferred as they provide more reliable geometric and elec-

* Corresponding author. E-mail: CML@CCR.JUSSIEU.FR.

tronic structure, yet they often may not be applied to large scale systems due to high computational cost. Density functional theory (DFT) [7–9] in the non-local approach is now widely accepted as a reliable and efficient ab initio technique [10–12]. It appears as an attractive alternative method to post-Hartree–Fock methods. Its computational efficiency (approximate third power dependence on the number of orbitals N) allows the investigation of larger systems. Moreover, it is a convenient method for transition metal chemistry as electron correlation is included. The software DMol [13,14] incorporates these features and is expected to provide an accurate description of the bonding mode of benzene to monovalent nickel.

In this work, the results of both calculations are compared and discussed.

2. Computational details

The EHT calculations were carried out by using the weighted H_{ij} formula [15]. The parameters used in the present work are listed in Table 1 [16]. The Wolfsberg–Helmoltz constant K was varied from 2.0 to 3.0.

Ab initio fully optimized calculations were carried out with the density functional program DMol available from Biosym Technologies. The molecular orbitals are represented as linear combinations of numerically generated basis functions of double zeta quality and polarization functions have been added. The exchange–correlation energy, described by the von Barth and Hedin potential [17] in the local density approach (LDA), is in some cases improved by gradient-corrected techniques [18]

Table 1
Ni parameters used in the extended Hückel calculations

Orbital	H_{ii} (eV)	ζ_1	ζ_2	C_1^a	C_2^a
3d	–12.99	5.75	2.00	0.5683	0.6292
4s	–8.86	2.1			
4p	–4.90	2.1			

^a Contraction coefficients used in the double-zeta expansion.

3. Results and discussion

3.1. Extended Hückel calculations

Calculations were performed using the model complex $[(\text{benzene})\text{Ni}^{\text{I}}(\text{OH})_3]^{2-}$ in which the geometry of the $[\text{Ni}^{\text{I}}(\text{OH})_3]^{2-}$ fragment is derived from the tetrahedral symmetry of the ‘real’ supported complex, suggested by previous spectroscopic studies [1]. Interatomic distances were taken from literature (benzene, OH) or from recent EXAFS measurements ($d_{\text{Ni-O}} = 1.90 \text{ \AA}$) [19].

In a first approach, the benzene ring is allowed to move without any rotation or distortion above the rigid $[\text{Ni}^{\text{I}}(\text{OH})_3]^{2-}$ fragment, in the Oxy plane located 2 \AA above the nickel center (Fig. 1). The latter value lies in the range of metal–benzene distances observed in arenes complexes [6]. For each position of the center $\text{C}(x,y)$ of the benzene molecule, a potential energy is derived from EHT calculations and a potential energy surface **I** may be constructed.

By rotating the benzene ring by 30° in the Oxy plane and using the same approach as above, a second potential energy surface **II** may be calculated. If both surfaces **I** and **II** are taken into account, then most of the different possible configurations for the coordination of the $[\text{Ni}^{\text{I}}(\text{OH})_3]^{2-}$ fragment to a planar benzene, are considered.

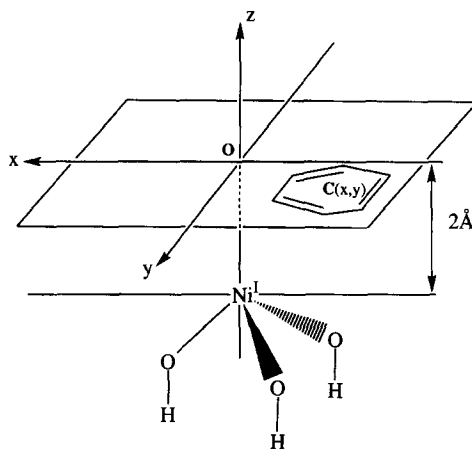


Fig. 1. Geometry of the model complex used for the EHT calculations.

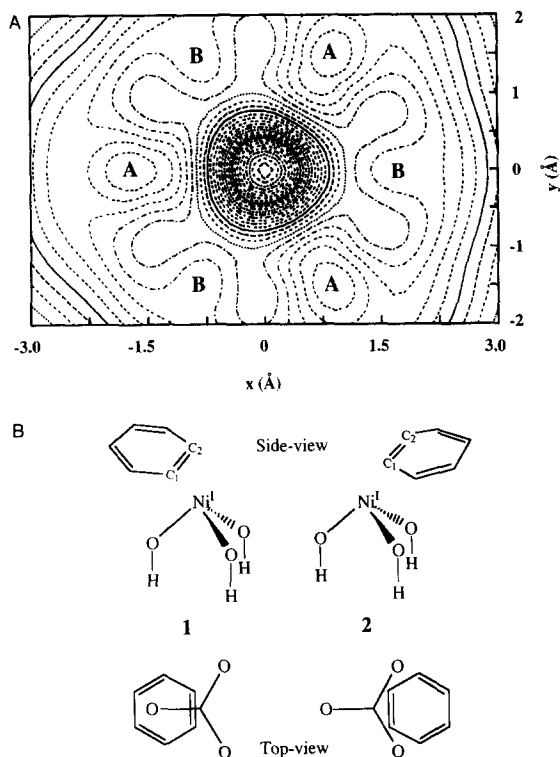


Fig. 2. (A) Contour map corresponding to the potential energy surface I. EHT calculations were performed with $K=2.5$. (B) Stable structures 1 and 2 assigned to minima A and B respectively.

The potential energy surfaces are regular and show three-fold symmetry around the origin of the x and y axes, as it can be seen in Fig. 2A for surface I. When the center C of the benzene ring is located at the origin, i.e., on top of the nickel center, the total energy is maximum (Fig. 2A and Fig. 5) suggesting that η^6 coordination is not favoured.

Surface I (Fig. 2A) exhibits two sets of three symmetry-equivalent energy minima A and B. The corresponding stable structures, respectively 1 and 2, are drawn in Fig. 2B. In these complexes, the nickel center lies closer to the C₁ and C₂ carbon atoms of the ring, suggesting a dihapto-benzene. The corresponding Ni–C bond length of 2.1 ± 0.1 Å lies in the range of the one reported for dihapto-benzene complexes [6].

Similarly, Surface II presents two sets of three equivalent minima assigned to the η^2 -benzene complexes 3 and 4 shown in Fig. 3. The comparison of the corresponding potential energies shows

that complexes 3 and 4 are less stable than 1 and 2. The latter were therefore the only ones taken into account here.

The modeling of the most stable dihapto-benzene complexes 1 and 2 is improved using the same rigid $[\text{Ni}^{\text{I}}(\text{OH})_3]^{2-}$ fragment as above and a tilted benzene ring (angle α) where the two hydrogen atoms attached to the carbon atoms bound to Ni are bent away (angle β). Two new more stable structures 1' and 2' are obtained (Fig. 4). In complex 1', the benzene tilt (5°) and the hydrogen atoms back-bending (15°) are consistent with the reported structures of dihapto-benzene Ag^{I} and Cu^{I} complexes [3,20] obtained from X-ray diffraction studies.

Influence of the Wolfsberg–Helmoltz constant K

By varying the Wolfsberg–Helmoltz constant K from 2.0 to 3.0, the potential energy profile is modified (Fig. 5). The energy maximum becomes steeper whereas from several shallow minima ($K=2.0$) two sharper minima emerge ($K=3.0$). An optimum value of $K=2.5$ was obtained from calculations of EPR g tensors of known Ni^{I} complexes [21] using a previously reported method [22]. The same K value was used in EHT calculations performed on isoelectronic Cu^{II} complexes [22].

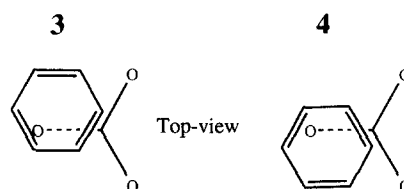


Fig. 3. Structure of the Ni^{I} complexes 3 and 4 corresponding to the minima of the potential energy surface II.

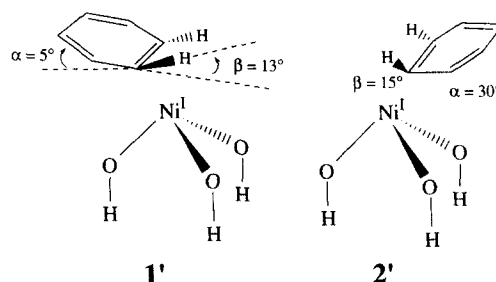


Fig. 4. 1' and 2' structures obtained from refinement of 1 and 2.

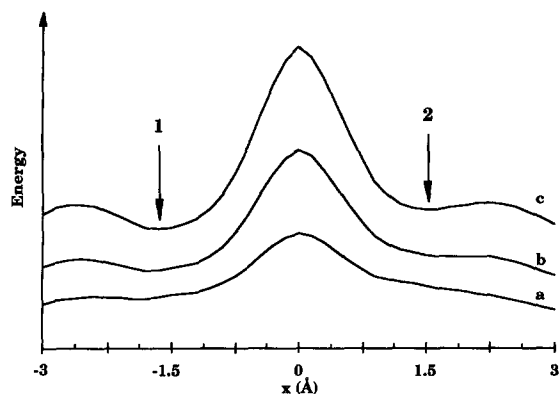


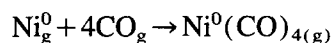
Fig. 5. Influence of K on the potential energy profile: (a) $K=2.0$ (b) $K=2.5$ (c) $K=3.0$.

3.2. DMol calculations

Software calibration

The software was tested with the well-known tetrahedral $\text{Ni}^0(\text{CO})_4$. This study also allowed to tune the convergence parameters for nickel.

Two optimized structures are obtained in T_d and D_{4h} symmetry by energy minimization. As expected, the tetrahedral $\text{Ni}^0(\text{CO})_4$ is more stable than the square-planar isomer. However in the absence of gradient corrections, the calculated nickel–ligand distances are too short (Table 2). Moreover, the gas phase heat of formation of $\text{Ni}^0(\text{CO})_4$ (ΔH_f) produced by the following reaction:



is much higher than the experimental value (Table 2). By contrast, gradient-corrected calculations provide bond lengths and energy values close to the experimental ones, closer than the ones obtained at the Hartree–Fock level (Table 2).

The software was also tested through the comparison with recent calculations carried out for the Ni^+ (η^6 -benzene) complex [25]. Starting from an Ni^+ (η^3 -benzene) complex, the DMol energy minimization predicts a stable Ni^+ (η^6 -benzene). The corresponding structure and binding energy are given in Table 3. There is a good agreement between the results of both calculations, but again, gradient corrections are required in order to obtain

reliable distances and energies values from DMol calculations (Table 3). The binding energy derived from our calculations is lower than the one derived from the SCF-MCPF calculations and lower than the experimental value (Table 3).

Modeling of [(benzene) $\text{Ni}^I(\text{OH})(\text{OH}_2)_2$]

DMol calculations performed onto the model [(benzene) $\text{Ni}^I(\text{OH})_3$] $^{2-}$ complex yield optimized structures with some of the highest occupied orbitals of positive energy. In the case of anions, additional diffuse orbital basis sets are required to perform ab initio calculations. As this is not yet available in the DMol software, calculations were carried out onto the neutral model complex [(benzene) $\text{Ni}^I(\text{OH})(\text{OH}_2)_2$]. Moreover, the modeling of the support by two types of ligands (one hydroxyl group and two water molecules) is expected to be more realistic.

Table 2
Comparison of calculated and measured bond lengths and heats of formation for $\text{Ni}^0(\text{CO})_4$

Calculation method	$d_{\text{Ni-C}}(\text{Å})$	$d_{\text{C-O}}(\text{Å})$	$-\Delta H_f(\text{kcal/mol})$
DMol (LDA)	1.79	1.16	274
DMol (with gradient-corrections)	1.87	1.17	170
SCF ^a			80
Experimental ^b	1.84	1.15	140

^a Self-consistent field: from ref. [23].

^b From ref. [24]: calorimetry measurements.

Table 3
Structures (Å and deg) and binding energies (kcal/mol) for Ni^+ (η^6 -benzene)

Calculation method	$d_{\text{Ni-ring}}$	$d_{\text{C-C}}$	$d_{\text{C-H}}$	H bent (β)	Binding energy
DMol (LDA)	1.55	1.41	1.10	2.6	103
DMol (gradient corrections)	1.69	1.44	1.11	1.1	55
SCF-MCPF ^a	1.75	1.42	1.07	0.0 ^c	59
Experimental ^b					68 ± 5

^a Self-consistent field modified coupled-pair functional, from ref. [25].

^b From ref. [26].

^c Non-optimized.

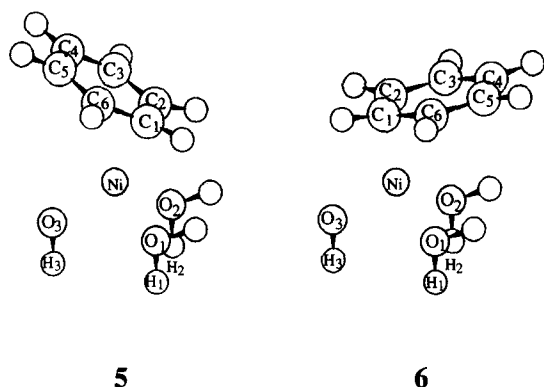


Fig. 6. Stable Ni^I complexes predicted from DMol calculations.

In a first approach, the starting geometry of the [Ni^I(OH)(OH)₂] fragment is the same as in the above EHT calculations. The oxygen atoms lie at the vertices of an equilateral triangle with an O–O distance of 3.08 Å. Three hydroxyl groups (O_{*i*}H_{*i*}, *i* = 1, 2 or 3; Fig. 6) are constrained and maintained perpendicular to the oxygen atoms plane, in order to avoid H bonding which is not relevant here. The Ni atom and the benzene ring as well as the two remaining H atoms of the water molecules are free of constraints.

Such starting hexahapto- or dihapto benzene configurations were examined by energy minimization in the local density approach (LDA). The resulting optimized geometries **5** and **6** are drawn in Fig. 6 and described in Table 4. Both structures involve an η²-benzene in agreement with the above EHT calculations. Complex **5** is more stable by about 5 kJ/mol than complex **6**.

The benzene ligand is almost planar and is tilted (angle α) with respect to the oxygen atoms plane.

The H atoms attached to the carbon atoms interacting with Ni are lifted up out of the ring plane (angle β). The Ni–C distance is close to 2 Å. The α and β values obtained for structures **5** and **6**, are close to the ones respectively derived from EHT calculations for structures **2'** and **1'**; the orientation of the NiO₃ fragment with respect to the ring in structure **5** (**6**) is however reversed as compared to the one in structure **2'** (**1'**).

The benzene ring has a Kekule-type structure in which there is an alternation in the C–C bond lengths (Table 4). The coordinated C–C bond is elongated with respect to free benzene and lie in the range of transition metal–olefin complexes [27]. The same observations were made from X-ray crystallography measurements on η²-arene Os^{II} complexes [28]. The benzene ring is therefore divided into a coordinated ethylene-like fragment and a butadiene-like fragment.

3.3. Discussion of the results

The preferable low hapticity of benzene in the supported Ni^I complexes may be translated in terms of molecular orbitals interactions. The orbital interaction diagrams for [(OH)₃Ni^I(η⁶-benzene)]²⁻ and [(OH)₃Ni^I(η²-benzene)]²⁻ derived from the EHT calculations are compared in Fig. 7. The repulsions between the filled 3d orbitals of the Ni^I(OH)₃ fragment (1e and 1a₁) and the filled π orbitals of benzene (ψ₁, ψ₂ and ψ₃) are lower in the ring-edge bound complex than in the η⁶-benzene one. Moreover, the stabilizing

Table 4

Geometrical parameters of the optimized structures obtained from DMol calculations (LDA) – bond distances in Å and angles in deg

Structure	<i>E</i> _b ^a	α	β	<i>d</i> _{Ni–C₁,Ni–C₂} <i>d</i> _{Ni–C₃,Ni–C₆}	<i>d</i> _{C₁–C₂}	<i>d</i> _{C₂–C₃} <i>d</i> _{C₆–C₁}	<i>d</i> _{C₃–C₄} <i>d</i> _{C₅–C₆}	<i>d</i> _{C₄–C₅}	<i>d</i> _{Ni–O₃} <i>d</i> _{Ni–O₁} <i>d</i> _{Ni–O₂}
5	35.7	30	3	2.01, 2.03 2.67, 2.63	1.41	1.40	1.37	1.39	1.83 2.14 2.15
6	34.3	10	12	1.99 2.71	1.43	1.42	1.38	1.41	1.83 2.11 2.10

^a *E*_b = binding energy in kcal/mol.

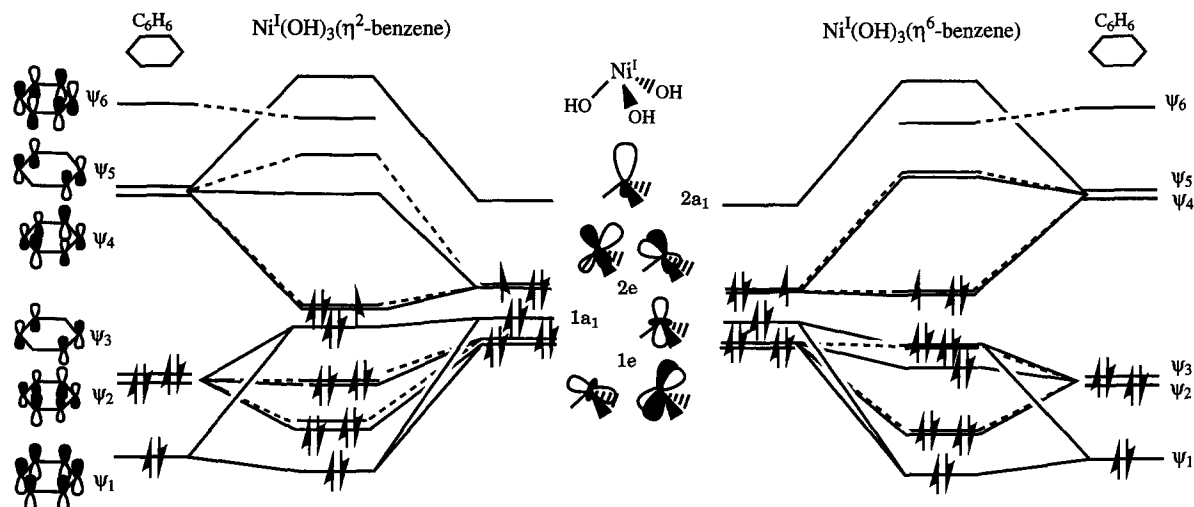


Fig. 7. Comparison of the orbital interaction diagram of $(\text{OH})_3\text{Ni}^{\text{I}}(\eta^6\text{-benzene})$ and $(\text{OH})_3\text{Ni}^{\text{I}}(\eta^2\text{-benzene})$. Solid lines show the interacting symmetrical orbitals whereas dotted lines show the interacting antisymmetrical orbitals. The energy scale is schematic.

interactions, i.e., $\text{SOMO}(\text{Ni}) = 2e$ with $\pi^* - \text{LUMO}(\text{benzene}) = \psi_4, \psi_5$ and $\text{LUMO}(\text{Ni}) = 2a_1$ with $\pi - \text{HOMO}(\text{benzene}) = \psi_2, \psi_3$, are favoured in the η^2 -coordination as compared to the η^6 one.

The η^2 -coordination of benzene is accompanied by an aromaticity loss which has been evaluated to be 75% by Brauer et al. [29] from simple Hückel calculations.

The elongation of the coordinated C–C bond with respect to free benzene results from the π -back-bonding from Ni to benzene which is comparable to the one described in transition metal-olefin complexes [27].

Both calculation methods predict two possible tilting for the benzene ring ($5\text{--}10^\circ$ and 30°), which lie in the range of known dihapto benzene complexes [6].

Lifted up H atoms have been reported for a Ni^0 -anthracene complex [29] as well as for Ni^0 -olefins complexes [30,31]. The sp^3 hybridization of the coordinated carbon atoms is a possible reason for this distortion.

4. Conclusion

EHT and ab initio calculations performed onto the model $[(\text{benzene})\text{Ni}^{\text{I}}(\text{OH})_3]^{2-}$ and $[(\text{benzene})\text{Ni}^{\text{I}}(\text{OH})(\text{OH}_2)_2]$ complexes predict two

stable dihapto benzene complexes consistent with the previous experimental observations. Both predicted stable structures involve: (i) a dihapto benzene, (ii) a benzene ring tilted with respect to the oxygen atoms plane, (iii) H atoms, attached to the two coordinated C atoms, that are bent back with respect to Ni.

The EHT calculations performed here do not permit optimization of interatomic distances. The geometry of the stable dihapto benzene complex is therefore more accurately predicted by the ab initio calculations.

Future work will focus on DMol calculations and improving the modeling of the support by including the contribution of either zeolite fragments or several tetrahedra where the Si valence requirements are satisfied by introducing terminal H or OH species.

We will try to calculate the vibrational frequencies of the Ni^{I} -dihapto benzene in order to compare with our experimental IR spectra.

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