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Schiff base complexes that form sandwich compounds

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Abstract
In this article, we explore the capacity of formed Schiff base complexes to trap metal atoms or ions, using their aromatic ends. The intrinsic geometry of each complex defines the process of substitution. Two cases were studied; one involving a *trans* Schiff base complex and the other considering how a salen ligand, with nickel systems traps chromium. We also assessed the nature of the new bonds and the frontier molecular orbitals.

Keywords Schiff base · Metallocenes · Theoretical calculations

Introduction

Schiff bases are compounds that are able to trap certain types of metal ions, taking advantage of the nitrogen and oxygen terminals, which potentially have the power to generate coordinated covalent bonds [1]. These types of compounds play a specific role and maintain influence in several important chemistry fields, among which can be cited electrochemistry [2], pharmacy [3], and biochemical [4] systems.

The Schiff bases themselves can be classified according to several different definitions, depending on different features such as the geometry adopted around the metal ion [5], intramolecular bonds, or the nature of the intrinsic metal itself [6].

Another important aspect to consider is the organic moiety behind the active terminals. This organic region may be reactive in terms of organic biology and organometallic characteristics [7].

Several kinds of organic ligands are able to trap metal ions, taking advantage of varied bond pathways. Salen compounds [8, 9] have been characterized for their marked ability to coordinate this ionic species by means of their terminal nitrogen and oxygen tailpieces. These constitute particular cases of the ligands cited above, as their characteristic feature is their aliphatic bridge connecting both nitrogen ends, a feature which

provides a measure of rigidity to this particular molecule and causes interesting variations with respect to the general behavior of the Schiff base. However, the possibility that they may have an organometallic association by means of the aromatic rings has not been explored; thus, one of our goals in this work is to explore the possibility that these molecules have two different metal ions trapped within the same ligand.

The aim of this work is thus to study the possibility that some normal coordination Schiff bases partake in the formation of organometallic compounds. This would imply that a common Schiff base coordinated molecule, with a nickel ion trapped by the nitrogen and oxygen ends, participates in a new reaction, resulting in the entrapment of a Cr(0) species by means of its terminal aromatic rings.

We also analyzed a derivative from salen compounds in a similar context. Salen, with its Schiff base should normally be represented as having derivatives of nickel and copper [9]. Thus the possibility of having a nickel substituent, joined by the terminal nitrogen and oxygen point, will be combined with the probability of having an organometallic bond within the same molecule with Cr (0). We also consider a third kind of species, where axially rotating (Pt-salphen)$_2$ frameworks with two salen unities are also considered as Cr(0) trappers, in order to search for stabilization in the proposed "tweezer" structure.

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Methods

All geometries were optimized using a pure DFT method for energy evaluations, applying Becke's gradient corrections

[10] for exchange and Perdew–Wang's for correlation [11]. This is the scheme for the B3PW91 method that forms part of the Gaussian 09 package [12]. This method was chosen because it has demonstrated to yield good results to show semiconductor behavior [13]. All calculations were performed using the 6-31G** basis set. Frequency calculations were carried out at the same level of theory in order to confirm that the optimized structures were at a minimum of the potential surfaces and for the purpose of recording all enthalpy values used in the isodesmic reaction calculation.

Results and discussion

Schiff base case

The first result involves the Schiff base compound that presents the most novel results. This molecule is the result of the hypothetical reaction between a common Schiff base and a Cr(0) atom, and the shapes of these molecules are shown in Fig. 1. The resultant molecule (molecule **1**) contains a Ni ion trapped in the nitrogen-oxygen region and a Cr atom joined in sandwich fashion between the aromatic rings of the tail. It is possible to appreciate the presence of both interactions with metal atoms, although they have different sources and descriptions.

The common interaction among nitrogen and oxygen tails and the nickel atom manifests distorted planarity, caused by the search for the second metal atom coming from the aromatic tails. The distance between the chromium atom and the center of the aromatic ring is 1.55 Å. This short length warranted the presence of a chemical bond, shown in the HOMO of the molecule, which appears in Fig. 2. Interestingly both nickel and chromium participate in this orbital, although the π interaction between the aromatic rings and chromium make the greatest contribution.

Importantly, the distance between nickel and chromium atoms is only 2.3 A, possibly indicating some kind of electronic communication between these two metal atoms. This last feature can be explained, taking into account the 18-electron rule [14]. Also of note is the fact that the HOMO is actually an accidentally double degenerated set, formed from HOMO and HOMO-1 orbitals. The proximity of both of these orbitals should be reminiscent of the real degeneracy found in bis-benzene-chromium [15]. The LUMO is a single MO and also makes the contribution of both metal atoms and the contiguous nitrogen, oxygen, and carbon atoms.

The 18-electron rule declares that an organometallic complex which reaches 18 electrons in its coordination sphere will be able to reach noble gas configuration, with concomitant stability. Several 18-electron rule chromium organometallic complexes have been described and have proven to be very stable species; bis-benzene-chromium is a substance which is known to comply with this rule [16]. In this case, the count considers six electrons from the Cr(0) metal, and six electrons coming from the π-clouds of the benzene rings. Notably, the fragment which supports the Cr(0) atom has two benzene rings that trap it, so that as a matter of principle, the description must be similar to that referring to bis-benzene-chromium.

The main difference between both mentioned species concerns the distortion on molecule **1**. This distortion compels the six-membered rings to loosen their bond with chromium, and subsequently it is possible to find Cr-C distances that vary between 2.11 and 3.66 A (the theoretical bond length in bis benzene-chromium is 2.14 A), and the symmetric and stable configuration of bis benzene-chromium is partially lacking. However, the presence of the Ni-Cr bond represents a very important stabilizing factor.

This particular arrangement engenders a tetra-hapto interaction between the chromium atom and both aromatic rings, meaning that there are only eight electrons forming the pi bond in the organometallic interaction for each aromatic cloud. Considering that Cr(0) has six valence electrons, the count will only reach 14, so that the only way to produce a stable configuration (requiring 16 electrons) is to establish an intermetallic bond with the nickel ion, an interaction which indeed exists. Figure 3 presents the shape of the HOMO-3 molecular orbital, where it is possible to observe the interaction between both metal species. Notably, this orbital is at a distance of 0.490 eV from the HOMO; so this is a relatively achievable function on the part of the frontier molecular orbitals. Besides, the bond length between Ni and Cr atoms is 2.63 Å, a value that is comparable to the average distances, previously suggested by Das [17] (2.38–2.75 Å).

Bond order values for both aromatic rings joined to the chromium atom were determined; the Wiberg bond indices [18] revealed through NBO analysis indicated that distribution by the bond was not uniform and the description in the last paragraphs is corroborated, because the addition of all the values between chromium and one of the rings is only 0.997, whereas for the other one this value is 2.11. Obviously, there is an excess of electrons in one bond compared to the other and not all the carbon atoms on the rings present significant interaction with the metal atom. Besides this, and as suggested, there is an interesting value of 0.353 related to the interaction between nickel and chromium.

Importantly, the short energy gap between the frontier molecular orbitals, which has a value of 0.65 eV, exhibits the behavior of a strong semiconductor or even a mild conductor material [19], a characteristic that will be addressed again in the next section.

Fig. 1 The formation of compound **1** from a Schiff base and a Cr(0) atom
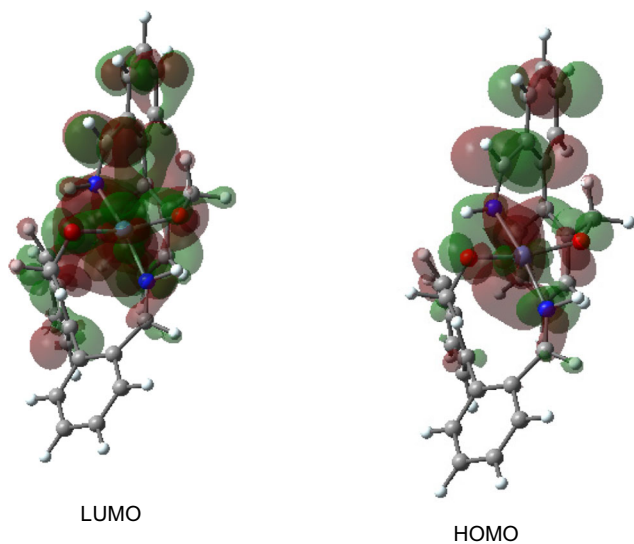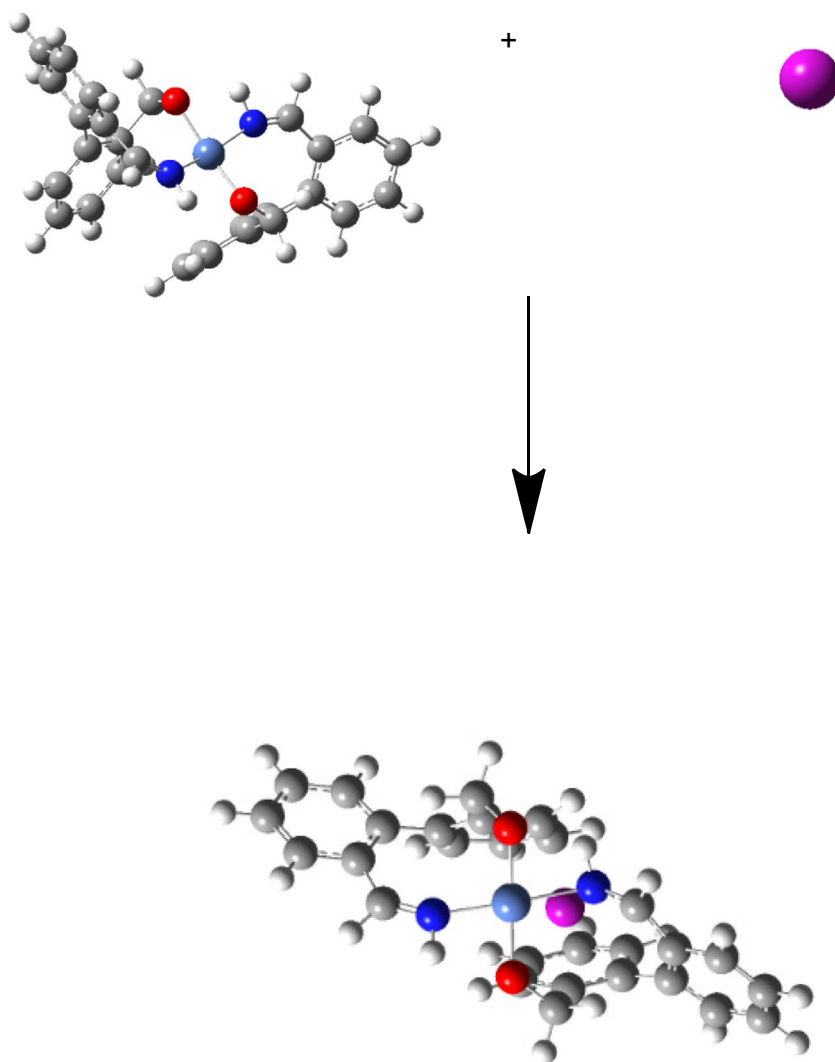

Thermodynamic stability manifests an important characteristic; the isodesmic reaction shown in Scheme 1 was designed to achieve this energy value. This reaction involves bis(benzene)chromium, 1,5-diazabicyclo[3,1,0]hexane, nickel tetracarbonyl and methyl-naphtalene, in order to yield the Schiff base compound being studied, plus
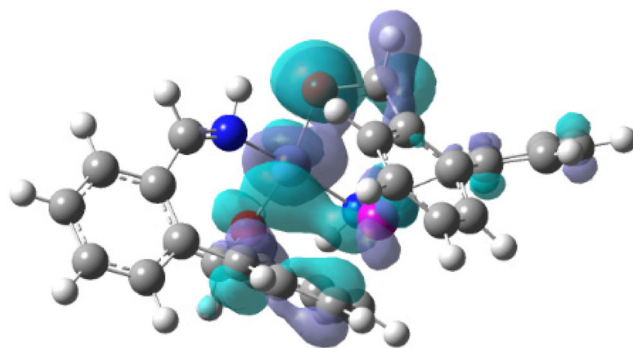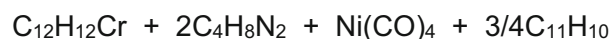

Fig. 2 Frontier molecular orbitals from compound **1**. The *pale blue atom* corresponds to the Ni, whereas the *red-purple* one represents the Cr. The HOMO is the combination of HOMO and HOMO-1, which are accidentally degenerated

Fig. 3 Molecular orbital HOMO-3 illustrating the interaction between Cr and Ni

$$C_{12}H_{12}Cr + 2C_4H_8N_2 + Ni(CO)_4 + 3/4C_{11}H_{10}$$

Fig. 5 Salen-Ni molecule under study

$$C_{28}H_{24}CrN_2NiO_2 + 13/8C_2H_4 + NH_2CH_3 + NO_2$$

Scheme 1 Isodesmic reaction to validate the formation of compound **1**

ethylene, methyl-amine and NO_2, (see Fig. 4 for the shapes of some of these molecules). All of these species were calculated using the DFT b3pw91 method included in the Gaussian package, described in the Methods section. The result for the enthalpy of this reaction is 31.56 kcal/mol. This is a positive but very low value, which can thus be produced by applying a soft thermal procedure.

Salen case

The salen analogue [8] is the other system studied here. In principal, this contrasts with molecule **1** as an obvious new bond forms between the carbon atoms and the nitrogen ligand.

This bridge causes more rigidity than occurs in the case of the simple Schiff base and the substitution is forced to yield a *cis* substitution with the respect to the Ni atom, rather than the *trans* found in molecule **1**.

Figure 5 presents the shape of the isolated salen-Ni system, where direct interaction between the terminal aromatic rings to form a metallocene is obviously impossible. The species manifests greater symmetric geometry, arising from the rigidity of the ligand and the forced *cis* configuration.

In this case, it is therefore impossible for intramolecular interaction to occur, but the greater symmetric geometry (C_2 point group) and the terminal position of the aromatic rings makes it possible for some kind of intermolecular interaction, i.e., a metallocene compound can be formed from two isolated salen molecules. The shape of the resultant molecule (molecule **2**) is shown in Fig. 6.

Fig. 4 Some compounds which participate in the isodesmic reaction. **a** 1,5-diazabicyclo[3,1,0]hexane. **b** Bis-dibenzene-chromium. **c** Methyl-naphtalene
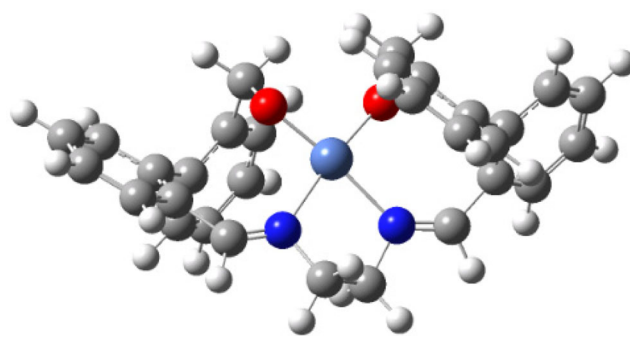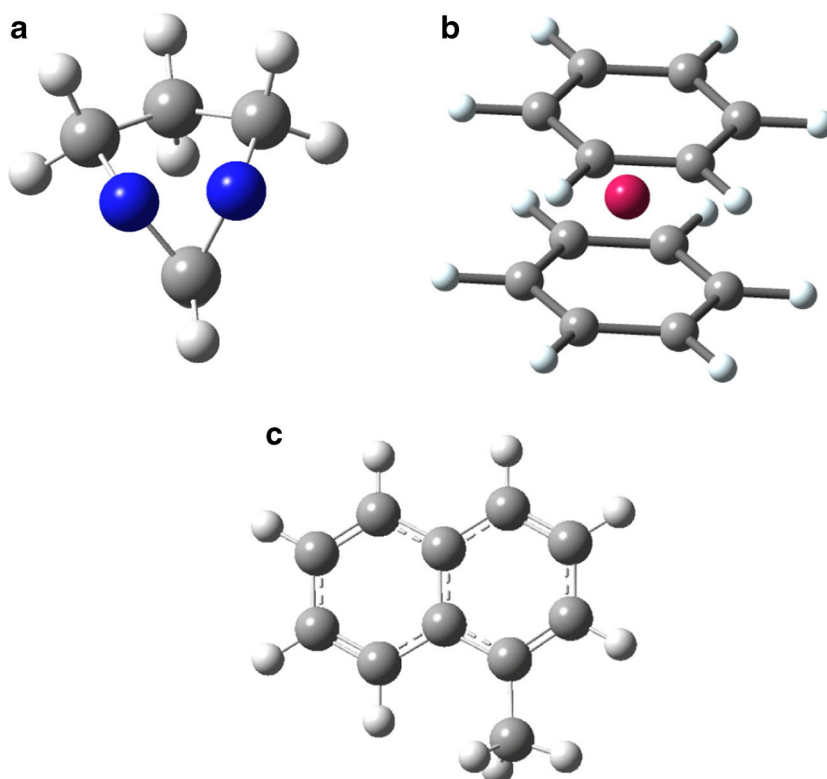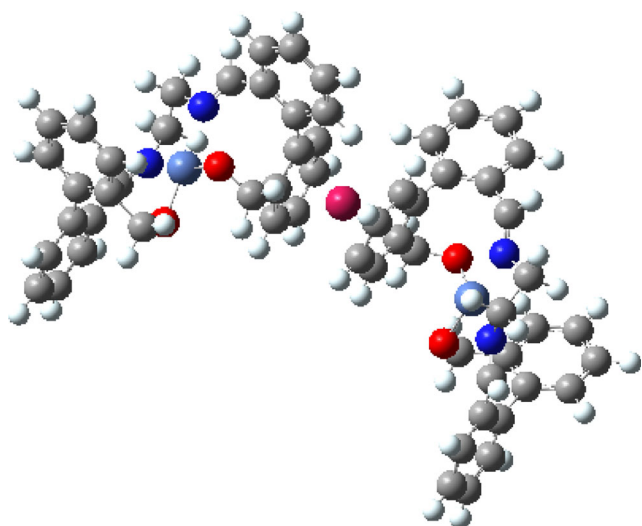

a

b

c

**Fig. 6** Metallocene chromium complex pertaining to the salen compound

The Wiberg bond indices for this case are completely symmetric; the definition of the interaction is said to be the same as for the chromium atom and a deck and its counterpart. In both cases, the value is 1.985, showing the suggested metallocene arrangement.

Obviously in this case it is impossible to find direct interaction between the metallic atoms and this fact is indeed corroborated when the frontier molecular orbitals are analyzed.

The point group (C_2) does not have double degenerated irreducible representations. However, the isolated dibenzene-chromium moiety belongs to the D_6h point group [15], which has four double degenerated irreducible representations. The presence of accidentally double degenerated sets for the HOMO as well as for the LUMO thus represents a legacy of this type. Figure 7 presents the scheme for these functions.

Interestingly, LUMO is a function found mainly on lateral fragments, where the nitrogen and oxygen ends of the tweezer and of the nickel atom itself participate. In another context, the HOMO is localized solely at the center of the molecule, corresponding to the metallocene moiety. The shape of both molecular orbitals is shown in Fig. 8. The absence of interaction between any of the metal atoms is notable.
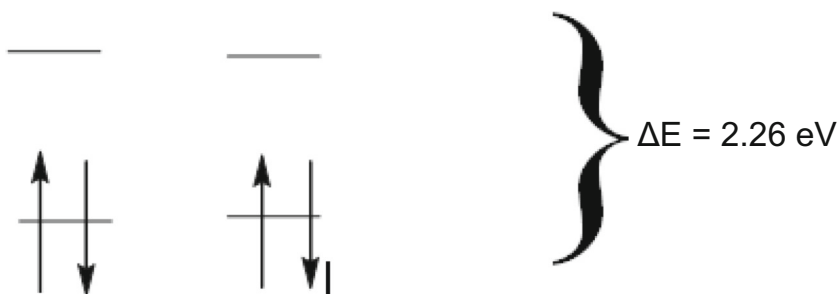
The short band gap between both frontier molecular orbitals is another important feature to highlight and similar to that revealed when the Schiff base complex is analyzed. Its value, shown in Fig. 7, is 2.26 eV, complies with the classification for semiconductor materials. This is an important point to consider when studying both kinds of complexes, as neither dibenzene-chromium nor salen compounds have been reported as semiconductors. However, when both of these are combined, the resultant compounds may have this useful characteristic.

Axially rotating frameworks

These types of substances have been the focus of important studies because they show luminescent characteristics in solution [20]. The shape of an example of these molecules is shown in Fig. 9.

The important feature shown here is that both salphen unities are joined to an aryl bridging group, so that the planar coordinated moieties are forced to adopt a face-to-face conformation. The luminescent as well as cation-detecting capacity of these species has been analyzed by Chan's group [21] and discussed by Kleij and coworkers [8], who make the important point that these molecules are able to interact with other metal ions. Chan and his coworkers show that compounds of this kind can trap Pb(II) ions, a phenomenon which causes rotation between the functional groups and provokes the disruption of the π stacking interaction [21]. This effect is novel and interesting, and indeed in the present study we intend to describe the interaction of molecules of this kind with Cr(0) atoms, as this represents a new kind of electronic interaction.

The shape of the molecule shown in Fig. 9 resembles a tweezer species [22] or a metallocene framework [23]. Therefore the aromatic rings coming from the salphen moieties remain in a frontal position, which appears apt for trapping a metallic ion. However in Fig. 9, it is evident that the aromatic rings are not in symmetrical eclipsed positions, therefore even though only one ring can interact with metallic species, we have designed two modified molecules in which the trapping ability has
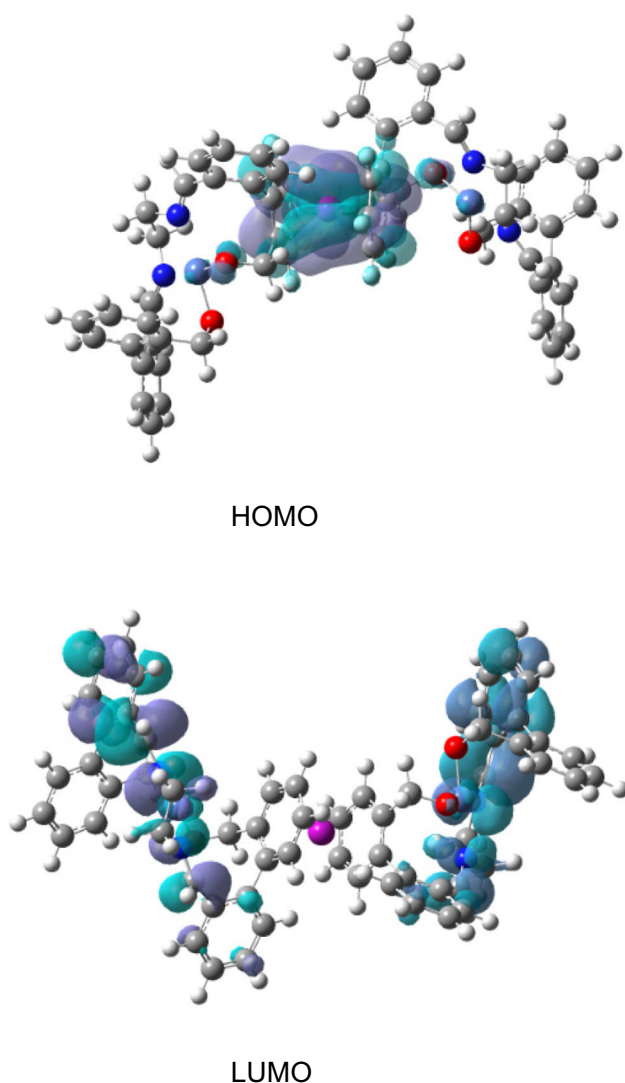
Fig. 7 Frontier molecular orbitals pertaining to the salen compound (**2**)

ΔE = 2.26 eV

HOMO

LUMO

Fig. 8 Frontier molecular orbitals pertaining to the salen compound (**2**)

been reinforced, putting new aromatic rings in the polyaromatic "arms", in order to have new electronic interchange regions.

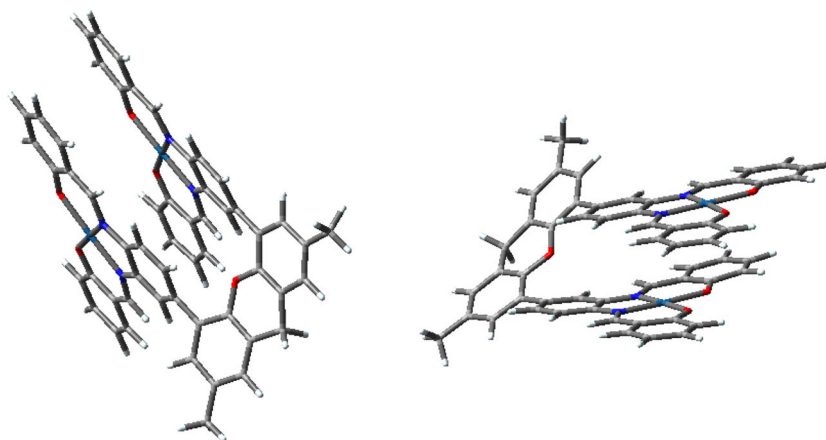**Fig. 9** The axially rotating framework viewed from two different perspectives (compound **3**)

Figure 10 shows the proposed compounds; compound **4** has an additional aromatic ring at only one end of the salphen group, whereas compound **5** has two new rings, one at each end of the salphen moiety. Each one of these compounds is able to trap Cr(0) atoms in a metallocene fashion, as this figure, compound **4** appears to trap one, and compound **5** two.

The molecules in Fig. 10 already have chromium atoms, but the interesting point is to consider how the presence of the chromium atoms changes the electronic behavior of the empty species.

Figure 11 shows the form of the resultant molecule (molecules 5′) when the chromium atoms are removed from the molecule 5, the interesting point being that both "wings" of the set show a tendency to align in parallel fashion, a spatial disposition which may be an obvious consequence of the marked steric effect between both aromatic sets. However, apparently there is an overall π-π stacking interaction both between aromatic wings and indeed on the metal chelate rings, because chelate rings in salphen ligands may be involved in π-stacking interactions independent from the presence of any metal ion [24]. Likewise, an argument to reinforce this proposition is that the frontier molecular orbitals (HOMO and LUMO) occupy one wing each, as also shown in Fig. 11.

The same behavior is observed for molecule **4**, but in this case there is only one Cr atom.

This change in electronic behavior is very interesting, because empty molecules (i.e., molecules without Cr atoms) show almost the same value for the energy gap as that between frontier molecular orbitals (approx. 1.39 eV). This value suggests semiconductor behavior; however, the value dramatically changes to approximately 0.3 eV, corresponding to a conductor species when the new metal atoms are included. The shape of the new molecular orbitals is shown in Figs. 12 and 13. It is possible to see that the Cr orbitals participate in an outstanding

Fig. 10 Designed salphen
compounds, which can trap Cr(0)

4

5
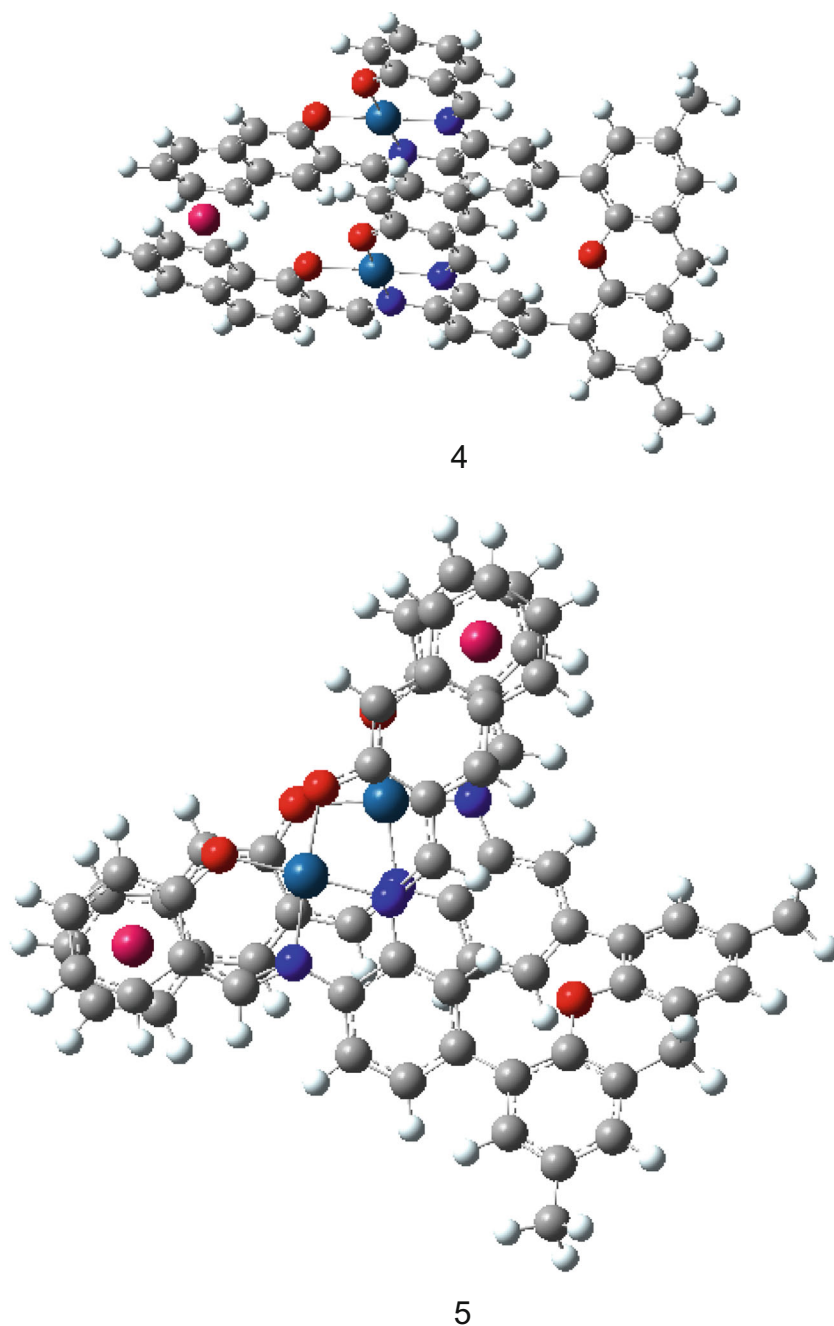
way and indeed electronic communication between both aromatic sets in this situation occurs through the metal centers and is not a π-π stacking interaction. Obviously these molecules manifest greater rigidity than those where no metallocene interaction occurs.

Notably, the occupied molecular orbitals in molecule **5** (Fig. 13) are relatively close, a phenomenon which may relate to the possible luminescent features, as it is possible to have several electronic promotions. These promotions may be derived from UV-visible spectroscopy and from a time-dependent Gaussian calculation

(TD-DFT) and the results from this process are as follows:

Time-dependent Gaussian calculations were carried out on both the free metallic atoms and the chromium substituent species. These results are very interesting and the behavior of the theoretical electronic transitions in the free metal compound appears typical of the non-salen species [20]. Apparently, three electronic transitions within the UV-visible region with: 505.7, 494.8, and 442.4 nm follow the pathway from HOMO and HOMO-1 to LUMO. This description is similar to those
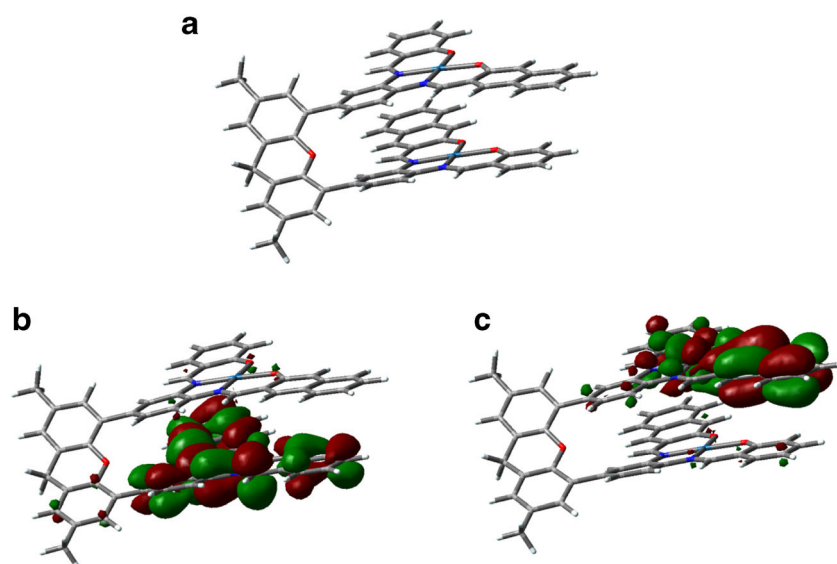
Fig. 11 **a** Shape of molecule 5′; **b** HOMO; **c** LUMO

a

b

c

Fig. 12 LUMO, HOMO, and HOMO-1 of the species with one Cr atom
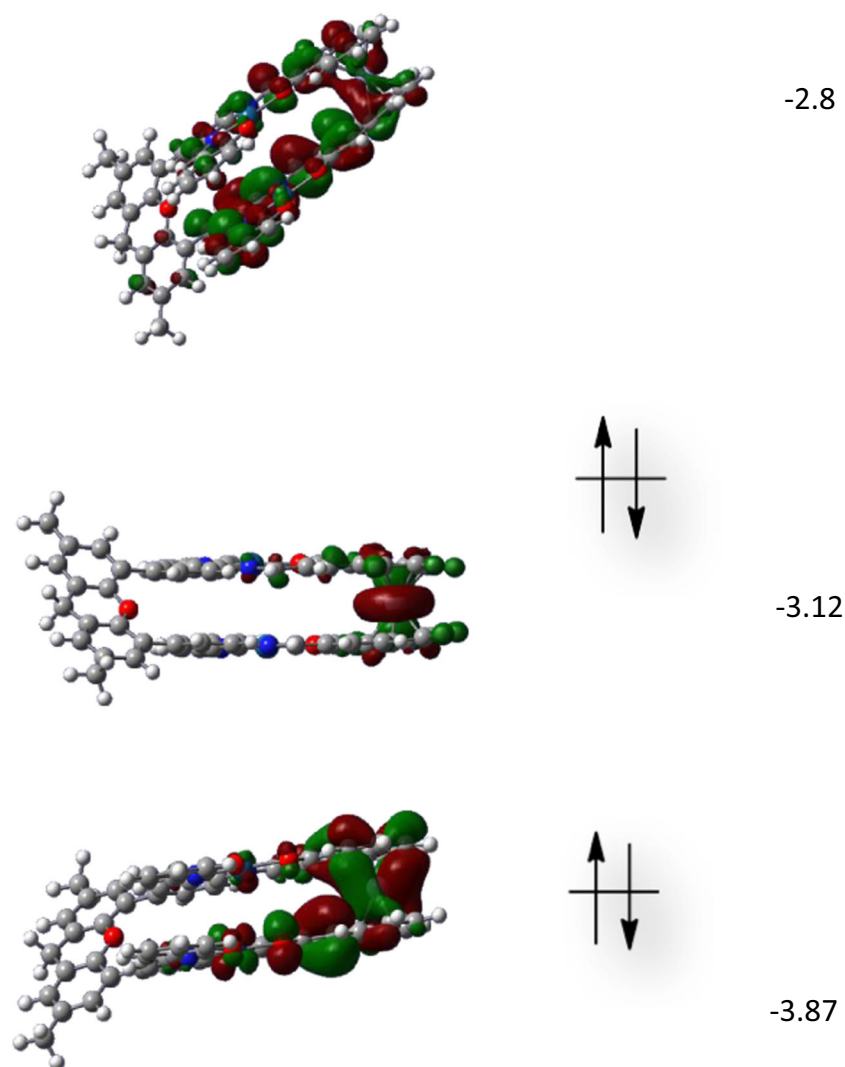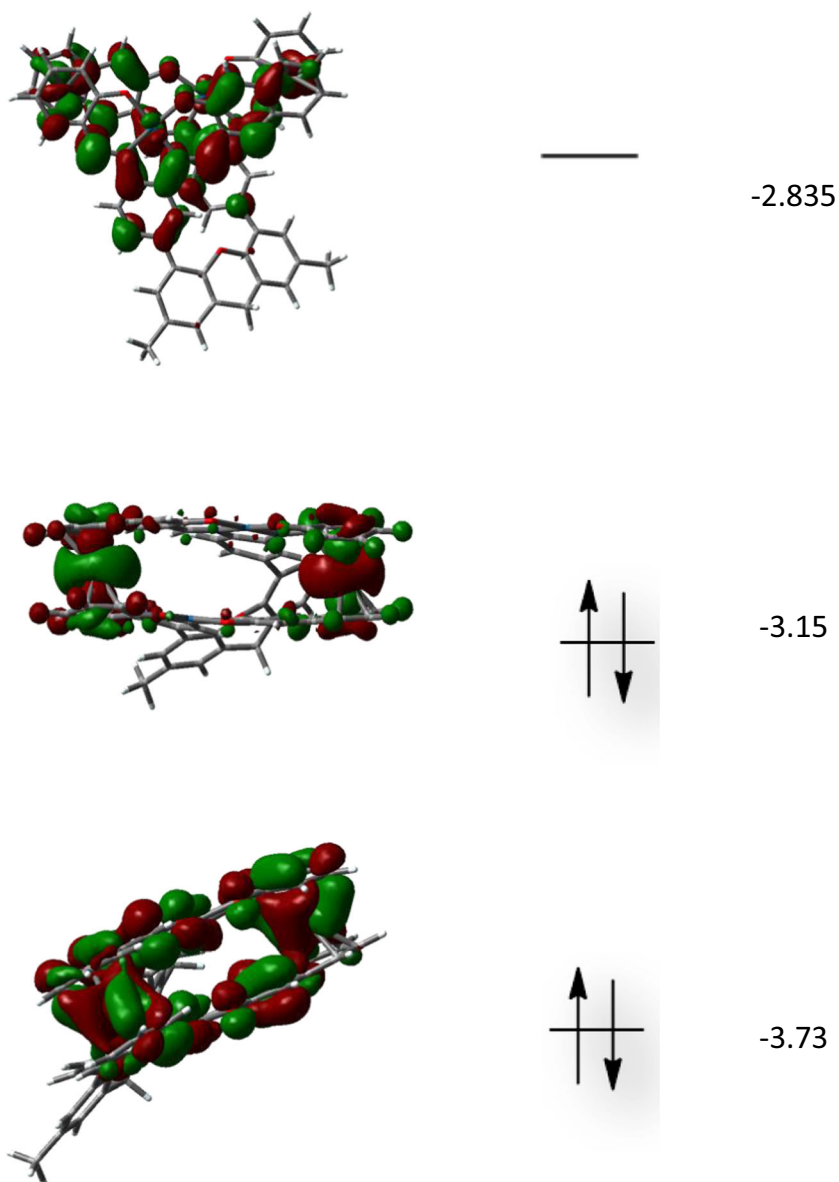

-2.8

-3.12

-3.87

Fig. 13 LUMO, HOMO, and
HOMO-1 of the species with two
Cr atoms

-2.835

-3.15

-3.73

posited for platinum salen complexes which produce luminescent effects, although the transition in this case takes place between both wings of the complex. The situation dramatically changes when the chromium atoms appear in the new complexes. TD calculations show that there are no electronic transitions in the UV-visible region and the nearest transition is found at 787 nm, which is at the border of the IR region. Therefore luminescent behavior is not expected for these new complexes; the reason for the change is that the frontier molecular orbitals for this case are completely occupied by the functions corresponding to the chromium atom and its neighbors.

The inclusion of a second metal atom into the framework of known metallic salen complexes changes electronic behavior and will yield new species with promising conductive and supramolecular characteristics.

Conclusions

Both Schiff base and salen nickel complexes are able to trap chromium atoms, following the metallocene procedure. In the first case, an intramolecular interaction takes place and an interesting electronic communication is established between both metal atoms. In the second case, more rigid geometry prevents the intramolecular inclusion of the chromium atom; however it is possible to design a complex where two salen complexes offer a phenyl end and form a large hybrid

compound in which the chromium atom acts as a bridge. Both suggested species show potentially semiconductor behavior.

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