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Electronic structure of *bis*-azepine transition-metal complexes: A DFT investigation

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ABSTRACT

DFT calculations with full geometry optimizations have been carried out on a series of hypothetical compounds of $M(C_6NH_7)_2$ (M = transition metal) type with an eclipsed and staggered conformations in order to understand their electronic structure. A rationalization of the bonding with respect to the electron count in all the investigated hypothetical complexes is provided. Depending on the electron count and the nature of the metal, the azepine ligands can bind to the metal through the (η^7,η^7), (η^6,η^6), (η^7,η^4), (η^6,η^4), (η^4,η^4), (η^4,η^2) and (η^3,η^3) coordination modes.

1. Introduction

The azepine ligand (C_6NH_7; Azp) is a seven-member ligand which, although less investigated than its related cycloheptatrienyl (C_7H_7; Ch) [1], has been shown to be a ligand of high versatility in organometallic chemistry [2]. Whereas very little is known on the stability and structure of $M(Azp)_2$ transition-metal complexes, the bonding in $M(Ch)_2$ complexes has been investigated in detail for transition metals [3]. In this paper we report a theoretical investigation at the DFT level of the molecular and electronic structures of a series of hypothetical complexes of the type $M(Azp)_2$ (M = transition metal) in order to analyse their stability/viability [4] and to stimulate further investigation. The nature of the metal–ligand bonding will be analysed in neutral $M(Azp)_2$ species as a function of the total number of valence electrons, in a similar way as it is often done by keeping this number constant for different metals in varying the molecular charge [5].

2. Computational details

Density functional theory (DFT) calculations were carried out on the studied compounds using the Amsterdam Density Functional (ADF) program [6], developed by Baerends and coworkers [7]. Electron correlation was treated within the local density approximation (LDA) in the Vosko–Wilk–Nusair parametrization [8]. The non-local corrections of Becke and Perdew were added to the exchange and correlation energies, respectively [9,10].

The numerical integration procedure applied for the calculations was developed by te Velde et al. [7e]. The atom electronic configurations were described by a triple-ζ Slater-type orbital (STO) basis set for H 1s, C 2s and 2p, N 2s and 2p augmented with a 3d single-ζ polarization for C and N atoms and with a 2p single-ζ polarization for H atoms. A triple-ζ STO basis set was used for Ti, V, Cr, Mn, Fe, Co, Ni 3d and 4s, and for Mo 4d and 5s augmented with a single-ζ 4p polarization function for metals of the first row of the periodic table and a single-ζ 5p polarization function for the second row. A frozen-core approximation was used to treat the core shells up to 1s for C, N and 3p for the metal atoms first row [7] For the systems containing atoms in which *Z* is greater than 41, the scalar relativistic (SR) ZORA (zero-order regular approximation) was used (with the optimized valence basis set associated) [11]. Full geometry optimizations were carried out using the analytical gradient method implemented by Verluis and Ziegler [12]. Spin-unrestricted calculations were performed for all the open-shell systems. Frequencies calculations [13] were performed on all the studied compounds to check that the optimized structures are at local minima. In the case of a few compounds, for the sake of simplicity the described structure has a higher symmetry and almost the same energy (within 0.03 eV) than the C_1 geometry which was found to be the energy minimum. The Coulomb

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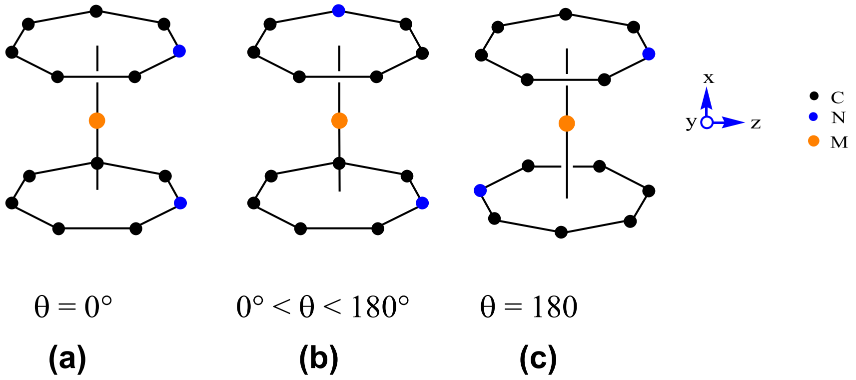


Scheme 1. Conformation structures of M(Azp)$_2$; eclipsed (C_{2v}) (a), gauche (C_2) (b) and staggered (C_{2h}) (c).

potential was evaluated *via* an accurate fitting of the charge density with Slate-type exponential functions centered on the atoms. Representation of the molecular structures and molecular orbitals were done using ADF-GUI [8] and MOLEKEL4.1 [14], respectively.

3. Preliminary considerations

3.1. Electron counting formalism

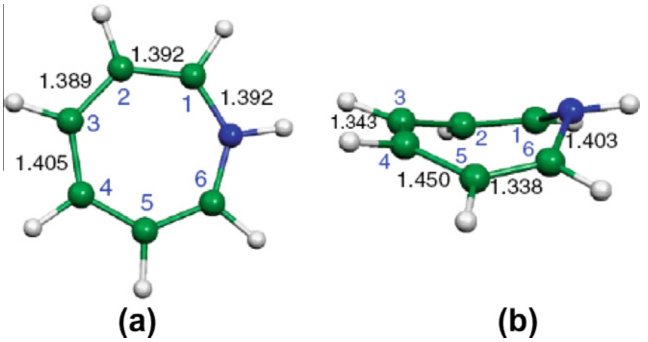
When considered as formally neutral, the azepine ligand is a potential donor of 8 π-electrons but the actual number of electrons really donated to the metal depends on the coordination mode of the metal and consequently can be lower or equal to 8. Therefore, we will use in the two following different electron counts for the investigated M(Azp)$_2$ compounds.

(1) The total number of electrons (TNE) which is indicative of the global electron richness of the molecule. It is the sum of all the electrons which can be potentially donated by the two azepine ligand (i.e. $2 \times 8 = 16$) plus the metal valence electrons in its actual oxidation state (azepine considered neutral). Thus, TNE = $2 \times 8 + n$ for a neutral M(Azp)$_2$ complex, with n being the number of valence electrons of M(0).

(2) The number of metal valence electrons (MVE) which corresponds to the number of electrons really belonging to the metallic sphere. This number takes into account the ligand electrons which are effectively donated to the metal and consequently depends on the metal hapticity. For example in the case of Mo(η^6-Azp)$_2$ where only the 6 carbon atoms of the azepine rings are bonded to M, each Azp ligand behaves as a 6-electron donor, therefore MVE = $6 \times 2 + 6 = 18$, whereas TNE = 22. MVE is necessarily always lower or equal to TNE.

3.2. Geometrical parameters

An important structural characteristic of *bis*-azepine transition-metal complexes is the rotational conformation of the two azepine rings as shown in Scheme 1. For the studied M(Azp)$_2$ systems, the conformation adopted by the two azepine rings can be described by the torsion angle θ defined as [N–Azp$_{\text{cent}}$–Azp$'_{\text{cent}}$–N$'$], where Azp$_{\text{cent}}$ and Azp$'_{\text{cent}}$ are the centroids of the two azepine rings (see S1 in Supplementary information). Thus, $\theta = 0°$ for a totally eclipsed arrangement of the two azepine ligands (C_{2v} ideal symmetry), while a fully staggered arrangement (C_{2h} ideal symmetry) will correspond to a $\theta = 180°$. The intermediate half-way conformation corresponds to the partially eclipsed (gauche) arrangement with $0° < \theta < 180°$ having ideal C_2 symmetry.



Scheme 2. Optimized geometries of dicationic (a) (6 π electrons) and neutral (b) (8 π electrons) Azp with C_{2v} and C_s symmetry, respectively. Atom labelling of azepine ligand considered throughout the paper.

3.3. The free azepine ligand

The free Azp^{2+} cation (6 π electrons) is a planar aromatic species exhibiting a delocalized structure with C_{2v} symmetry, whereas neutral Azp (8 π electrons) adopts a C_s boat structure with significant out-of-plane distortion of the nitrogen atom, with a C(2)–C(6)–C(1)–N dihedral angle of 41° [1,15]. This bending is associated with the existence of single C–N bonds (1.403 Å) and a noticeable single and double C–C bond alternation (1.343 Å for the double bonds and 1.450 Å for the single bonds), associated with a significant HOMO–LUMO gap (2.04 eV at the BP86 level [1]). The optimized bond distances of the free cationic and neutral azepine ligands are given in Scheme 2. It is noteworthy to mention that flattening of the bent neutral Azp does not requires much energy (2.5 kcal/mol at the BP86 level) [1], a value which can be easily overcome by the bonding with a metal atom. The atomic labelling used throughout this paper is depicted in Scheme 2. These data are in agreement with the X-ray structure of a substituted azepine derivative [16].

4. Results and discussion

The obtained results of the studied compounds will be presented according to the increasing order of the total number of electrons (TNE).

4.1. 18-TNE complexes

TNE = 18 implies that each Azp ligand donates all its π electrons to the metal (see Section 3.1) and therefore is heptacoordinated.

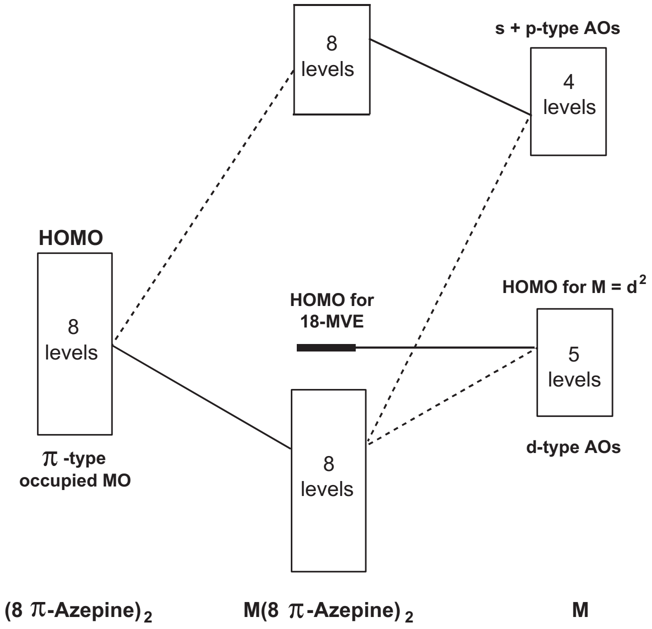


Fig. 1. Simplified MO diagram for a d^2 M(8 π-azepine)$_2$ complex with 18-MVE.

The electronic structure of such an M(η^7-Azp)$_2$ (M = d^2) complex can be described as resulting from interaction between the 9 metal AO's and the 8 combinations of the occupied π-type MO's of the two Azp ligands (see Fig. 1). For completing full coordination of both rings, the 8 occupied MO's ligand combinations need to match with vacant counterparts on M. Among the nine metal AO's, the diffuse s and p orbitals are best suited to strongly interact with ligand orbitals. Four d-type AO's are needed to complete the set of the 8 metal orbitals required for interaction with the ligands. Therefore, only one d-type orbital will remain non-bonding and hold the two electrons provided by the metal. The closed-shell principle is satisfied for such an 18-TNE/18-MVE species for which a significant energy gap is expected, separating the occupied bonding and non-bonding MO's from the vacant metal–ligand antibonding MO's.

Although this crude qualitative description does not take into account the Azp π^* orbitals neither the s/p/d hybridization on the metal, it is in full agreement with the DFT results obtained on the 18-TNE model [Sc(Azp)$_2$]$^+$, (isoelectronic to Mo(η^7-Ch)(η^5-Cp) [2d,2e] and V(η^7-Azp)(η^5-Cp) [1]). Three [Sc(η^7-Azp)$_2$]$^+$ characterized energy minima of C_2, C_{2h} and C_{2v} symmetries were found to lie a very similar energies (Table 1 and Fig. 2). Application of zero-point vibrational energy corrections does not change the stability order. These results suggest easy rotation of the Azp ligands. In the three rotamers, the Azp ligands are slightly distorted and all their atoms are clearly bonded to the metal. Moreover, the C–C distances exhibit long and short bond alternation (Table 1). These structural features indicate that the azepine ligand should be viewed as a coordinated form of type I (Scheme 3). This is in agreement with the formal neutral charge of the azepine ligands. Analysis of the 8 bonding MO's in any of the three rotamers indicates substantial contributions from both metal and azepine rings indicating strong M-Azp covalency. This includes the Sc–N interaction, with an interatomic separation of 2.424 Å and a Mulliken overlap population of 0.094. The calculated net charge of the Sc(I) metal is +0.14, indicating significant ligand to metal donation. This can be traced by the fragment interaction analysis which can be performed with the ADF program [6] and which allows calculating the occupation of the eight π-type combinations of the Azp···Azp fragment in the complex: Those of π_5 (1.70), π_6 (1.66) and π_7 (1.52) are noticeably lower than 2. On the other hand, there is significant backdonation from the metal into the formally vacant π^*_9 and π^*_{10} combinations, with respective occupations 0.52 and 0.24. As one may expect from Fig. 1, the non-bonding metal orbital is mainly of d_δ character (Scheme 4). It is slightly stabilized by a vacant π^*(Azp) combination and is the HOMO-2 of the complex. Finally, it is worth to mention that the calculated [Sc(η^7-Azp)$_2$]$^+$ sandwich model exhibits a different coordination mode than the structurally characterized 18-TNE Ti(η^7-Ch)(η^5-Ch) which is a 16-MVE species [2,3].

4.2. 20-TNE complexes

Going from TNE = 18 to TNE = 20 (d^4 and d^5 metals), results in the occupation of one of the metal–ligand antibonding orbitals in Fig. 1. Partial decoordination should result in order to cancel the

Table 1
Selected computed data for the optimized 18- and 20-TNE [Sc(Azp)$_2$]$^+$ and [TiAzp)$_2$ model complexes.

Azepine hapticity and molecular symmetry	[Sc(Azp)$_2$] $^+$ (S = 0) TNE = 18			Ti(Azp)$_2$ (S = 0) TNE = 20		
	(η^7,η^7) (C_2) (θ = 90°)	(η^7,η^7) (C_{2h}) (θ = 180°)	(η^7,η^7) (C_{2v}) (θ = 0°)	(η^7,η^4) (C_1) (θ = 17°)	(η^7,η^4) (C_s) (θ = 0°)	(η^6,η^6) (C_2) (θ = 55°)
HOMO–LUMO gap (eV)	1.06	1.07	1.08	1.46	1.19	0.98
Relative energy between isomers (kcal/mol)	0	0	1.6	0.0	3.0	6.0
M–N (Å)	2.406	2.393	2.424	2.269	2.173	2.776
M–C(1) (Å)	2.405	2.419	2.426	2.251	2.239	2.410
M–C(2) (Å)	2.427	2.419	2.418	2.286	2.306	2.301
M–C(3) (Å)	2.418	2.424	2.409	2.305	2.271	2.212
M–C(4) (Å)	2.400	2.424	2.409	2.313	2.271	2.261
M–C(5) (Å)	2.401	2.419	2.418	2.285	2.306	2.349
M–C(6) (Å)	2.417	2.419	2.426	2.202	2.239	2.482
M–N′ (Å)	2.427	2.393	2.424	3.227	3.461	2.776
M–C′(1) (Å)	2.405	2.419	2.426	2.464	3.202	2.482
M–C′(2) (Å)	2.401	2.419	2.418	2.202	2.531	2.349
M–C′(3) (Å)	2.400	2.424	2.409	2.156	2.158	2.261
M–C′(4) (Å)	2.418	2.424	2.409	2.382	2.158	2.212
M–C′(5) (Å)	2.427	2.419	2.418	3.062	2.531	2.301
M–C′(6) (Å)	2.405	2.419	2.426	3.443	3.202	2.410
C(2)–C(6)–C(1)–N (°)	176	180	178	169	179	145
C(3)–C(2)–C(5)–C(6) (°)	177	180	178	175	173	179
C(2′)–C(6′)–C(1′)–N′ (°)	176	180	178	151	176	145
C(3′)–C(2′)–C(5′)–C(6′) (°)	177	178	178	170	166	179

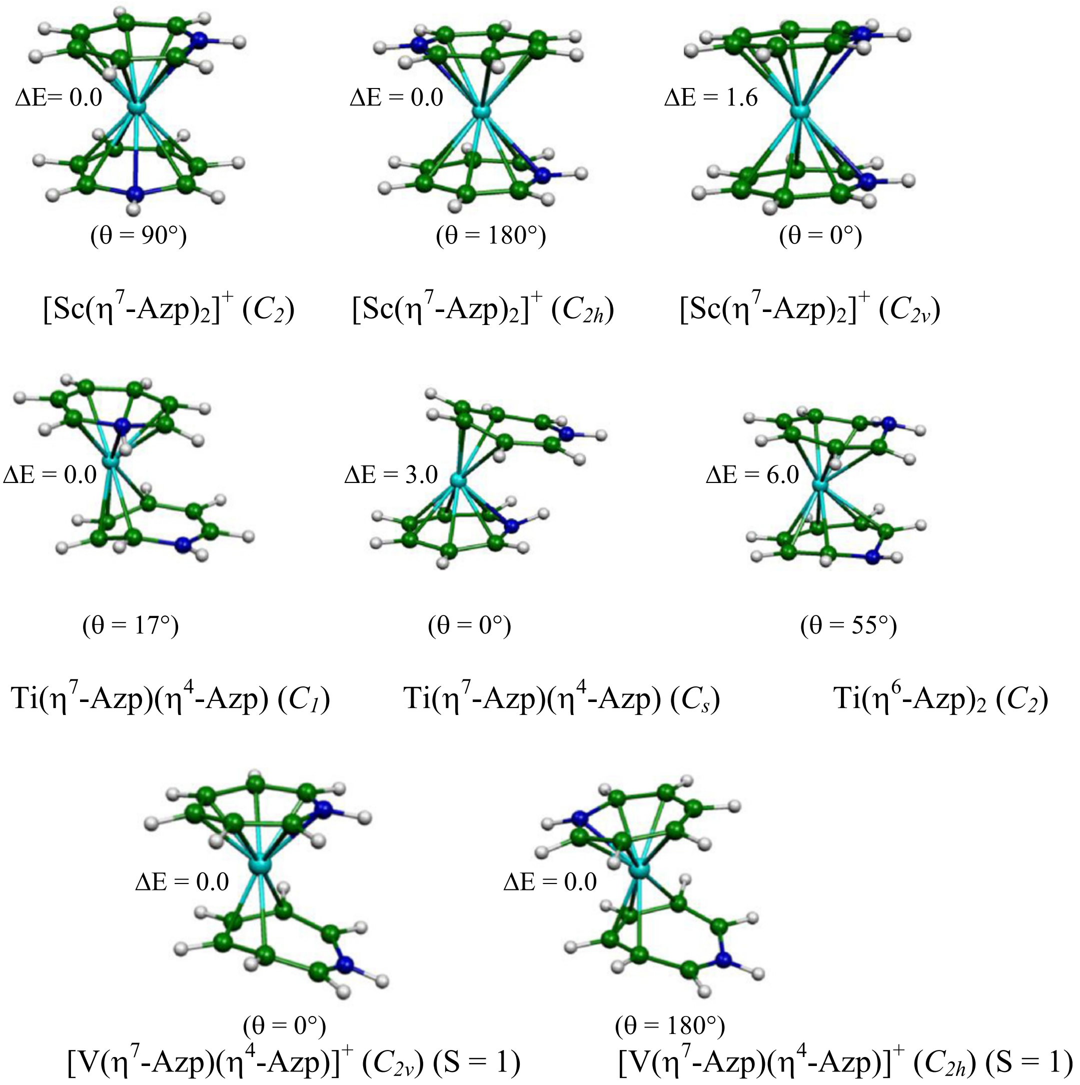
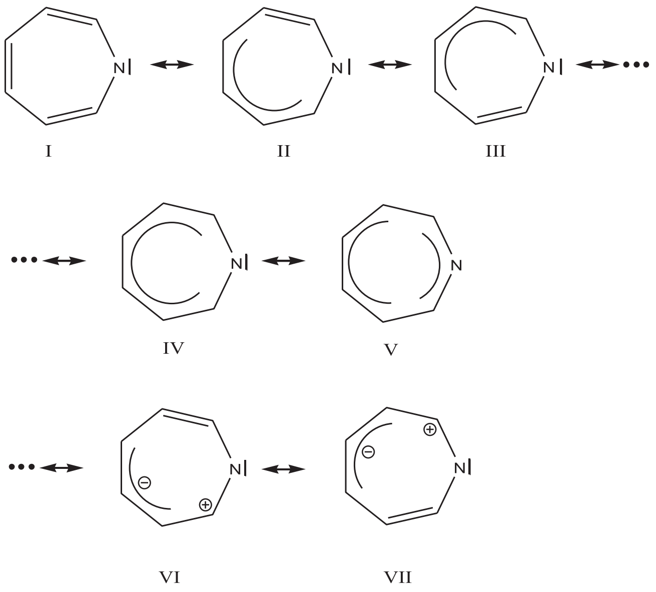


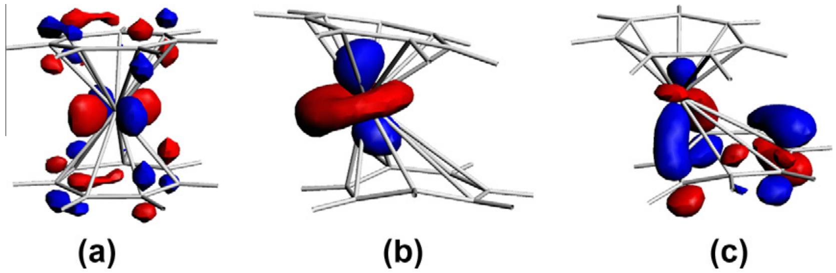
Fig. 2. Optimized geometries for $[Sc(Azp)_2]^+$, $Ti(Azp)_2$ and $V(Azp)_2$. The relative energies between isomers are given in kcal/mol.



Scheme 3. Lewis structures of neutral azepine ligand.

antibonding character of the orbital holding the added electron pair. This is what indeed results from the DFT optimization of the 20-TNE $[Ti(Azp)_2]$ models (isoelectronic to $(CO)_3M(Azp)$ (M = Mo, Cr and W) [17,18] and CpMn(Azp) [1]). In which the N′, C′(1) and C′(2) atoms of one azepine ligand (Azp′) are not bonded to Ti atom, whereas the other azepine ligand (Azp) maintains the η^7 coordination (Fig. 2 and Table 1). Three Ti(η^7-Azp)(η^4-Azp) characterized energy minima of C_1, C_s and C_2 symmetries were found within a range of 6 kcal/mol. However, the expected partial decoordination does not lead to an 18-, but to a 16-MVE count (Azp′ is now a donor of solely 4 electrons). Clearly, the decoordination of the unique N′ atom leading to Ti(η^7-Azp)(η^6-Azp) 18-MVE model is not favored. The search for alternative 18-TNE minima was unsuccessful. This is at variance with the 20-TNE Mo (η^7-Ch)(η^5-Ch) complex in which only one Azp nitrogen atom is not coordinated to the metal [2], and which is consequently a 18-MVE species.

The electron deficiency of Ti(η^7-Azp)(η^4-Azp) is associated with a metallic LUMO (Scheme 4) and the two uncomplexed carbon atoms of the η^4-Azp ring C′(5) and C′(6) having long Ti–C distances of 3.062 and 3.443 Å and negative overlap populations (OPs) of −0.035 and −0.026, respectively, comparable to that encountered in singlet 16-MVE Ti(η^7-C_7H_7)(η^5-C_7H_7) structure [3] and



Scheme 4. The HOMO-2 (a) of $[(Sc(\eta^6\text{-Azp})_2)]^+$ and the LUMO (b) and the HOMO (c) of $Ti(\eta^7\text{-Azp})(\eta^4\text{-Azp})$.

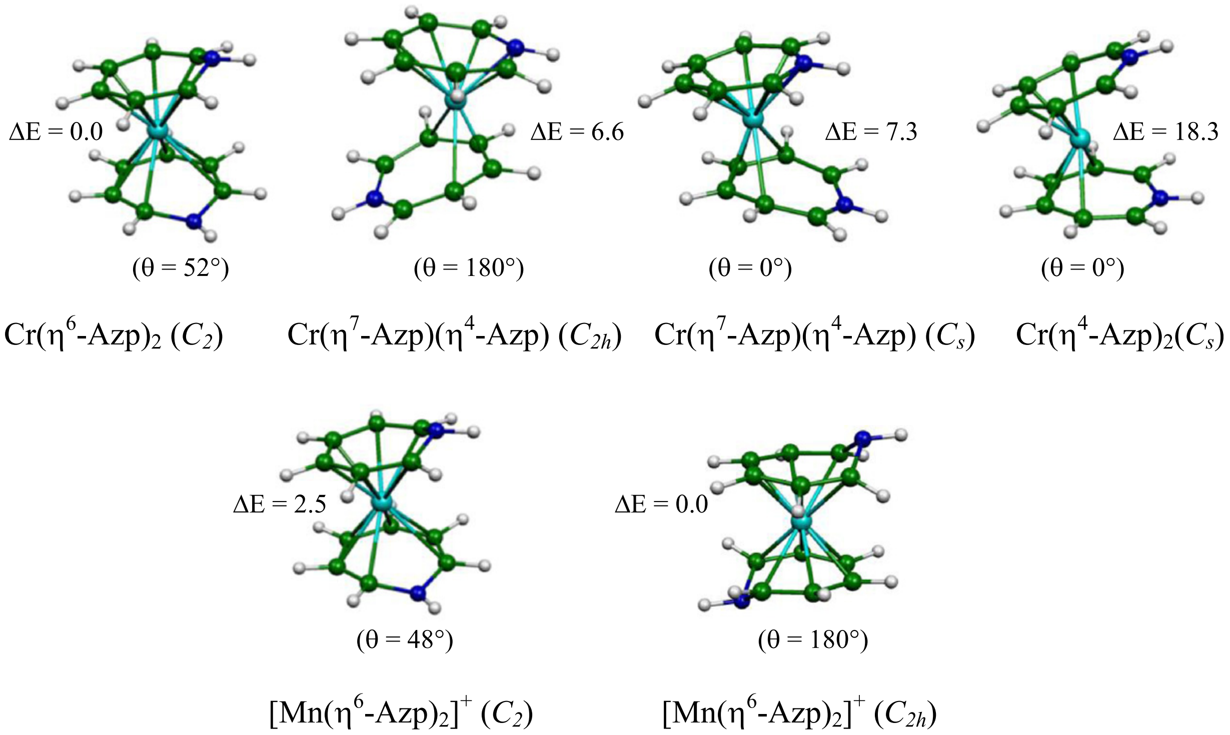


Fig. 3. Optimized geometries for $Cr(Azp)_2$ and $[Mn(Azp)_2]^+$. The relative energies between isomers are given in kcal/mol.

Table 2
Selected computed data for the optimized for 22-TNE $[Cr(Azp)_2]$ model complexes.

Azepine hapticity and molecular symmetry	$Cr(Azp)_2$ ($S = 0$) TNE = 22			
	(η^6,η^6) (C_2) ($\theta = 52°$)	(η^7,η^4) (C_{2h}) ($\theta = 180°$)	(η^7,η^4) (C_s) ($\theta = 0°$)	(η^6,η^6) (C_s) ($\theta = 0°$)
HOMO–LUMO (eV)	1.56	1.04	0.84	0.30
Relative energy between isomers (kcal/mol)	0.0	6.6	7.3	18.3
M–N (Å)	2.690	2.034	2.125	2.777
M–C(1) (Å)	2.312	2.178	2.163	2.586
M–C(2) (Å)	2.245	2.244	2.180	2.233
M–C(3) (Å)	2.202	2.246	2.311	2.059
M–C(4) (Å)	2.222	2.246	2.311	2.066
M–C(5) (Å)	2.255	2.244	2.180	2.251
M–C(6) (Å)	2.332	2.178	2.163	2.612
M–N′ (Å)	2.690	3.388	3.180	2.777
M–C(1′) (Å)	2.332	3.058	3.087	2.586
M–C(2′) (Å)	2.255	2.362	2.354	2.233
M–C(3′) (Å)	2.222	2.158	2.034	2.059
M–C(4′) (Å)	2.202	2.158	2.034	2.066
M–C(5′) (Å)	2.245	2.362	2.354	2.251
M–C(6′) (Å)	2.312	3.058	3.087	2.612
C(2)–C(6)–C(1)––N (°)	150	174	174	173
C(3)–C(2)–C(5)–C(6) (°)	174	177	177	179
C(2′)–C(6′)–C(1)–N (°)	150	174	174	173
C(3′)–C(2′)–C(5′)–C(6′) (°)	174	177	177	179

the related compound [19]. However, the HOMO is bonding metal–ligand level (Scheme 4). Nevertheless the complex displays a large HOMO–LUMO gap (1.46 eV in its global minimum). The η^7 coordinated Azp ring involves strongly all its atoms in the coordination with the metal atom. The Ti–N interaction is clearly bonding, with a short interatomic separation of 2.210 Å and a Mulliken overlap population of 0.085. On the other hand, in the η^4 coordinated Azp′ ligand a long Ti–N′ distance is found (3.277 Å) with a negative overlap population of −0.025. The C–C bond distances (Table 1) indicate delocalization for the six π electrons of Azp, which is consistent with the Lewis structure IV (Scheme 3), while the Lewis structure III is appropriated for Azp′.

The 20-TNE $[V(Azp)_2]^+$ model was also investigated. It was found to exhibit the same η^7, η^4 coordination mode as its neutral Ti relative. However, the corresponding singlet-state HOMO–LUMO gaps found for the C_{2v} and C_{2h} major minima are lower than 0.2 eV. This suggests the possibility for low-lying triplet state. Unsurprisingly, the computed triplet states for the optimized CpV(η^7,η^4-Azp) structures (see Fig. 2) are ∼16 kcal/mol more stable than their corresponding singlet states.

4.3. 22-TNE complexes

The optimized energy minima obtained for the 22-TNE $Cr(Azp)_2$ model (d^6 metal) are shown in Fig. 3 and their major computed data are given in Table 2. The three lowest in energy are all 18-MVE species. The most stable, Cr(η^6-Azp)$_2$ adopts a gauche conformation with $\theta = 52°$. It exhibits a large HOMO–LUMO (1.56 eV), indicative of a very good thermodynamical stability. In this isomer, the nitrogen atoms are not coordinated to the metal (corresponding Mulliken overlap population = −0.109). Consistently, the ligand rings show significant out-of-plane distortion (C(2)–C(6)–C(1)–N = 150°) and the sum of the nitrogen bond angles at nitrogen is equal to 112.5°, indicating sp^3 hybridization. The non-alternating C–C bond distances (Table 2) indicate that the azepine ligand should be viewed as a coordinated form of type IV (Scheme 3).

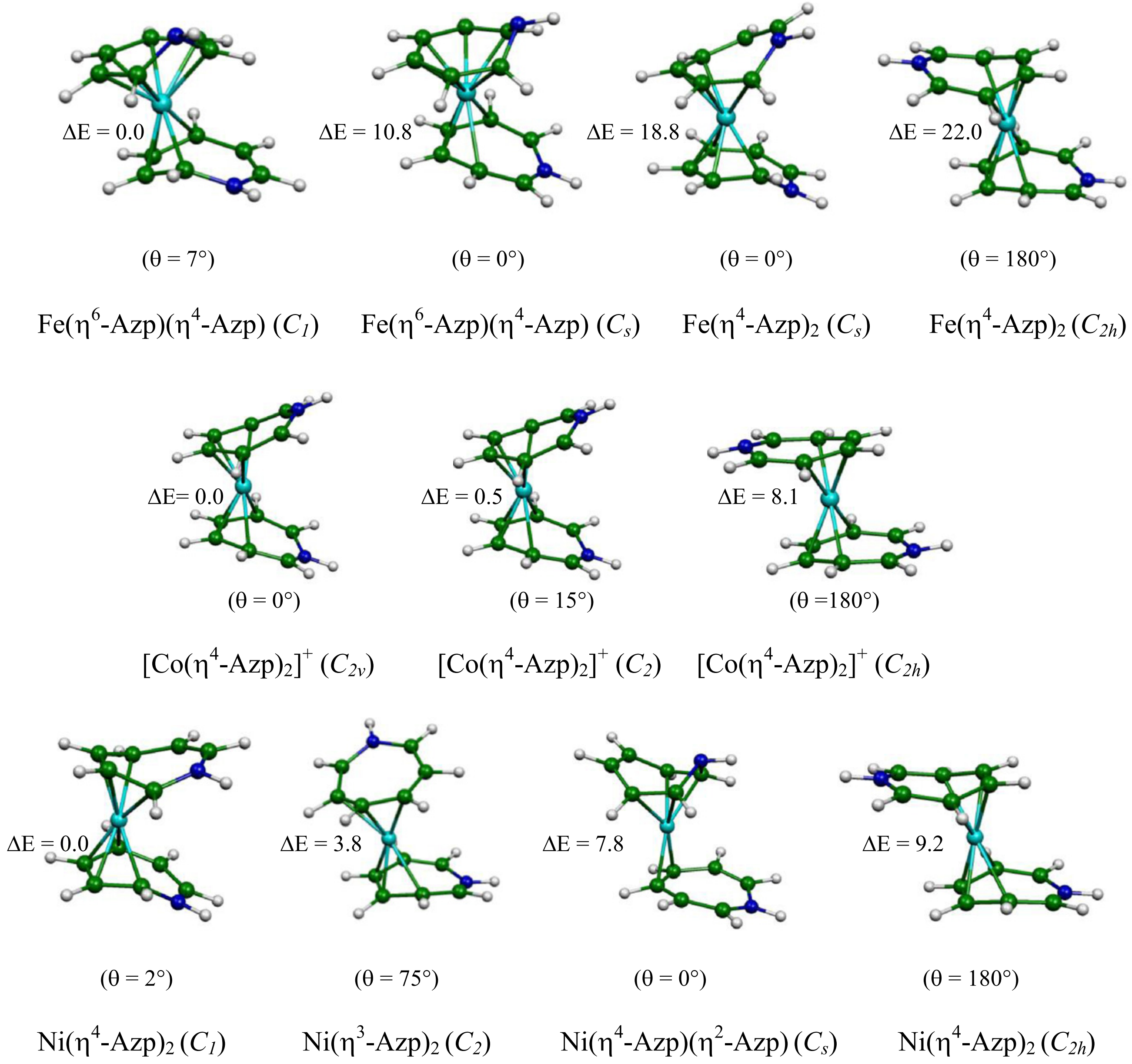


Fig. 4. Optimized geometries for $Fe(Azp)_2$, $[Co(Azp)_2]^+$ and $Ni(Azp)_2$. The relative energies between isomers are given in kcal/mol.

Table 3
Selected computed data for the optimized for 24- and 26-TNE [Fe(Azp)$_2$] and [Ni(Azp)$_2$] model complexes.

Azepine hapticity and molecular symmetry	Fe(Azp)$_2$ TNE = 24				Ni(Azp)$_2$ (S = 0) TNE = 26			
	(S = 0)			(S = 1)				
	(η^6,η^4) (C_1) $(\theta = 7°)$	(η^6,η^4) (C_s) $(\theta = 0°)$	(η^4,η^4) (C_s) $(\theta = 0°)$	(η^4,η^4) (C_{2h}) $(\theta = 180°)$	(η^4,η^4) (C_1) $(\theta = 2°)$	(η^3,η^3) (C_2) $(\theta = 75°)$	(η^4,η^2) (C_s) $(\theta = 0°)$	(η^4,η^4) (C_{2h}) $(\theta = 180°)$
HOMO–LUMO (eV)	2.26	1.67	1.15	–	1.54	1.29	1.53	0.59
Relative energy between isomers (kcal/mol)	0.0	10.8	18.8	22	0.0	3.8	7.8	9.2
M–N (Å)	2.659	2.709	2.965	3.102	2.972	3.411	2.609	3.319
M–C(1) (Å)	2.133	2.163	3.072	2.775	3.284	3.194	2.059	3.030
M–C(2) (Å)	2.076	2.056	2.633	2.202	2.942	2.525	2.118	2.290
M–C(3) (Å)	2.097	2.030	2.085	2.018	2.182	2.001	2.731	1.967
M–C(4) (Å)	2.080	2.030	2.014	2.018	2.002	1.943	2.731	1.967
M–C(5) (Å)	2.048	2.056	1.981	2.202	1.990	2.184	2.118	2.290
M–C(6) (Å)	2.098	2.163	2.098	2.775	2.086	2.956	2.059	3.030
M–N′ (Å)	3.041	3.432	2.965	3.102	2.974	3.411	3.446	3.319
M–C(1′) (Å)	3.048	3.107	3.072	2.775	3.296	2.956	2.671	3.030
M–C(2′) (Å)	3.028	2.340	2.633	2.202	2.959	2.184	1.984	2.290
M–C(3′) (Å)	2.085	1.981	2.085	2.018	2.188	1.943	1.984	1.967
M–C(4′) (Å)	1.985	1.981	2.014	2.018	1.998	2.001	2.671	1.967
M–C(5′) (Å)	1.997	2.340	1.981	2.202	1.986	2.525	3.446	2.290
M–C(6′) (Å)	2.156	3.107	2.098	2.775	2.088	3.194	2.609	3.030
C(2)–C(6)–C(1)–N (°)	119	121	161	162	176	167	167	173
C(3)–C(2)–C(5)–C(6) (°)	179	174.09	162	162.55	147	166	166	160
C(2′)–C(6)–C(1′)–N′ (°)	168	169	161	162	177	167	167	173
C(3′)–C(2′)–C(5′)–C(6′) (°)	151	159	162	162	146	166	166	160

The two other low-energy isomers lie ~7 kcal/mol above the lowest one and exhibit the same Cr(η^7-Azp)(η^4-Azp) coordination mode in which N, C(1) and C(6) of one of the Azp ligand are not bonded to the metal (Fig. 3 and Table 2). They differ only by the rotational orientation of the ligands. Analysis of their electronic structure leads to suggest that the partially coordinated ligand is a 4-electron donor which is best described by the Lewis structure V of Scheme 3. Consistently, the net charge on the non-coordinated N is −0.115.

Surprisingly, no other 18-MVE isomer with different bonding modes, such as for instance Cr(η^7-Azp)(η^5-Azp), could be found. This is reminiscent to isoelectronic 18-MVE species such as the structurally characterized CpCo(η^4-Azp) and (CO)$_3$Fe(η^4-Azp) complexes [20], in which the tetrahapto azepine ligand adopts the same bonding mode as in Cr(η^7-Azp)(η^4-Azp). The less stable isomer Cr(η^4-Azp)$_2$ isomer lies a significantly higher energy (Fig. 3 and Table 2). It is a highly electron-deficient species exhibiting a small HOMO–LUMO gap which is likely not to be viable. Whereas, the positive OPs of 0.065 and 0.053 calculated for the relatively long distances of Cr–C(1) = 2.586 Å and Cr–C(6) = 2.612 Å, respectively, suggest a weak bonding between Cr and these two carbon atoms leading to a possibly Cr(η^6-Azp)$_2$.

The 22-TNE cationic model as d^7 [Mn(Azp)$_2$]$^+$ was also investigated (see Fig. 3). In this compound, only the two [Mn(η^6-Azp)$_2$]$^+$ rotamers shown in Fig. 3 could be identified as true minima. Similarly to the related Cr(η^6-Azp)$_2$, they exhibit a large HOMO–LUMO (1.75 eV) suggesting good stability.

4.4. 24-TNE complexes

Going to the 24-TNE Fe(Azp)$_2$ (d^8 metal) and [Co(Azp)$_2$]$^+$ (d^9 metal) complexes isoelectronic to Ni(Ch)$_2$, the electronic demand of the metal to the ligands for reaching the 18-MVE count is now of 10 electrons. This leads to anticipate the two azepine rings to be differently coordinated. Coordination modes such as (η^7,η^2) or (η^6,η^4) can be expected. In fact, only (η^6,η^4) modes were found to lead to a 18-MVE energy minima (Fig. 4 and Table 3). In the lowest Fe(η^6-Azp)(η^4-Azp) minimum, the N atom of the hexahapto Azp is not coordinated (Lewis Formula IV), while the N, C′(1) and C′(2) atoms of the tetrahapto Azp′ ligand are NOT coordinated (Lewis Formula II). This isomer exhibits a very large HOMO–LUMO gap (2.26 eV). The second Fe(η^6-Azp)(η^4-Azp) minimum (less stable by 10.8 kcal/mol) differs from the previous one in the coordination of the tetrahapto Azp′ in which N, C′(1) and C′(6) are NOT coordinated (Lewis Formula V). Two electron-deficient Fe(η^4-Azp)$_2$ minima (of which one with a triplet ground state) were found a higher energy. Similarly, [Co(Azp)$_2$]$^+$ yielded to a series of [Co(η^4-Azp)$_2$]$^+$ rotamers in which the coordinated Azp ligands correspond to Structure V of Scheme 3. These 16-MVE species are unlikely to be viable.

4.5. 26-TNE complexes

In the case of a 26-TNE species such as d^{10} Ni(Azp)$_2$, the electronic demand of the metal atom for satisfying the 18-electron rule is of 8 electrons. This can be achieved by metal coordination to four C=C bonds in a more or less distorted tetrahedral coordination. This situation was found for the lowest minimum, namely Ni(η^4-Azp)$_2$, in which the two Azp ligands adopt the same coordination mode, being best described by Structure II (Scheme 3). The second minimum is a Ni(η^3-Azp)$_2$ 18-MVE species in which the azepine ligand can be described by Structure VI. This isomer is related to the well-known family of Ni(η^3-allyl)$_2$ complexes [21]. In the third isomer, namely Ni(η^4-Azp)(η^2-Azp), the tetrahapto Azp ligand donates six electrons and the dihapto one donates two electron. The highest minimum is a Ni(η^4-Azp)$_2$ complex in which the Azp ligands can be described by Structure V. Despite its relatively small HOMO–LUMO gap, this singlet state is computed to be more stable than the triplet state by 7.5 kcal/mol. Elsewhere, we note there are no related complexes of the same count for comparison.

5. Conclusion

In this paper we have investigated the coordination ability of two azepine ligands to bind to one transition metal to form a sandwich complex, varying the metal. The bonding in these hypothetical compounds has been rationalized with respect to the electron count. Most of the investigated compounds should be enough “stable” for being isolated (i.e. viable [4]). Depending on the compound total number of electrons and the nature of the metal, the (η^7,η^7), (η^6,η^6), (η^7,η^4), (η^6,η^4), (η^4,η^4), (η^4,η^2) and (η^3,η^3) modes can be adopted by the two azepine ligands. Moreover, several $M(Azp)_2$ compounds were found to have several low-energy isomers, raising the possibility of interconversion between them. Thus, a large variety of $M(Azp)_2$ structures were found, indicating that the azepine ligan behaves differently than the related cycloheptatrienyl ligand. In terms of formal oxidation state, coordinated azepine should be most often considered as being a neutral ligand which adopts significantly bent structures. In general, the staggered conformations lie at higher energy than the eclipsed and semi-staggered ones, except for the scandium model where the three conformations are almost degenerate. In the investigated species, the most favored closed-shell count is 18-MVE except for the Ti and V models which prefer the 16-MVE configuration.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.theochem.2010.05.019.

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