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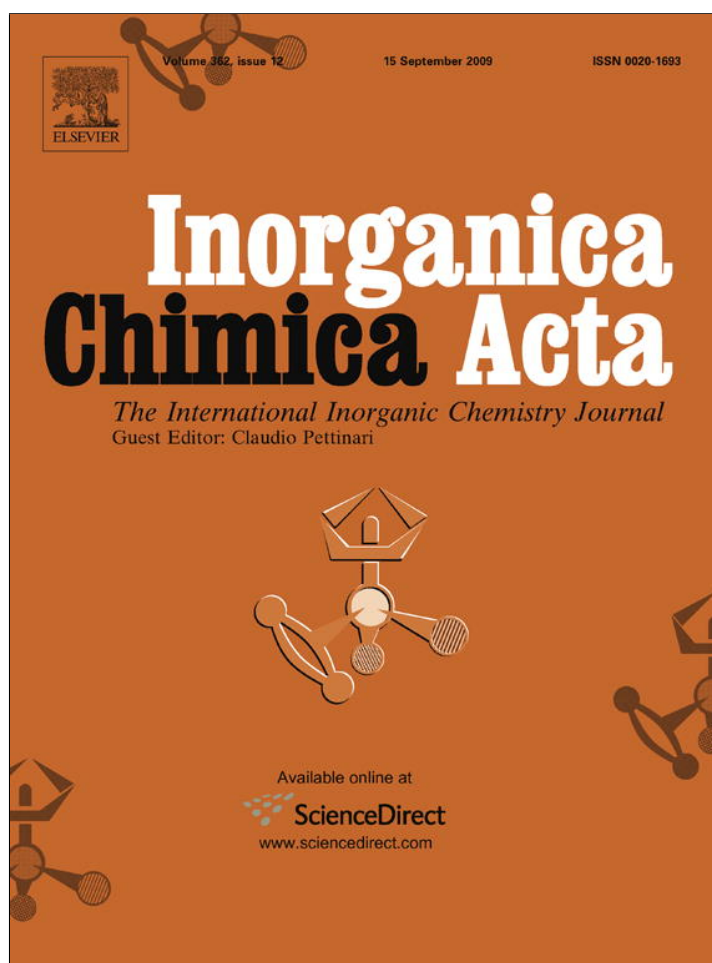343 PUBLICATIONS   5,994 CITATIONS

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Tris(pyrazol-1-yl)borate and tris(pyrazol-1-yl)methane: A DFT study of their different binding capability toward Ag(I) and Cu(I) cations

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ABSTRACT

Density functional theory has been used to study the electronic structure of [M(tp)] and [M(tpm)]⁺ conformers (M = Cu, Ag; tp = tris(pyrazol-1-yl)borate anion, tpm = tris(pyrazol-1-yl)methane) and the energetics of their interconversions. Results for the free tp ligand are similar to those of tpm [M. Casarin, D. Forrer, F. Garau, L. Pandolfo, C. Pettinari, A. Vittadini, J. Phys. Chem. A 112 (2008) 6723], indicating an intrinsic instability of the tripodal conformation (κ^3-like). This points out that, though frequently observed, the κ^3-coordinative mode is unlikely to be directly achieved through the interaction of M(I) with the κ^3-like tp/tpm conformer. Analogously to the [M(tpm)]⁺ molecular ions, the energy barrier for the κ^2-[M(tp)] → κ^3-[M(tp)] conversion is computed to be negligible. Though κ^n-[M(tp)] and κ^n-[M(tpm)]⁺ (n = 1, 2, 3) have similar metal–ligand covalent interactions, the negative charge associated to the tp ligand makes the M-tp bonding stronger.

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1. Introduction

Tris(pyrazol-1-yl)borate anion (hereafter, tp) and tris(pyrazol-1-yl)methane (hereafter, tpm) ligands play a leading role in modern coordination chemistry [1]. In fact, they are able, both in the substituted and unsubstituted forms, to supply an important steric shielding of the metal center serving, at the same time, as reliable spectator ligands. Complexes of the tp-based ligands are known for most of the metals in the periodic table and have applications in diverse and important fields ranging from catalysis to biomedicine, from metal extraction to biomimetic inorganic chemistry [1]. The common coordination geometry for both tp and tpm is the tripodal one[1] (κ^3-) where the lone pairs of the nitrogen heteroatoms [N(•)] of two pyrazolyl fragments attached to B (tp) or C (tpm) act like the pincers of a scorpion binding the metal centre, while the third pyrazolyl attached to the central atom rotates forward like a scorpion's tail to "sting" the metal. The family of ligands with this coordination

capability, whose simplest members are tp and tpm, is know as "scorpionates". However, we recently showed [3] that crystal data for both "uncoordinated" tp [2a,b] and free tpm [4] ligands suggest alternative and less evocative coordination modes. In fact, both tp and tpm are characterized by the presence of a single pyrazolyl group with N(•) in *trans* with respect to the B–H (tp)/C–H (tpm) fragments.[2]

Theoretical work so far devoted to the study of the interaction of tp and tpm ligands with metal ions is rather limited. A few years ago, De Bari and Zimmer [6] carried out a conformational study based on molecular mechanics and structural database analysis of tp and tpm behaving as κ^3-tripodal ligands. They concluded that "tripodal scorpionate ligands can accommodate a variety of metal sizes by opening up the ligand". More recently, we employed the density functional theory (DFT) to study the electronic structure of [M(tpm)]⁺ molecular ion conformers (M = Cu, Ag) as well as the energetics of their interconversion [3].

In this paper we study the κ^1-monodentate, κ^2-chelating, and κ^3-tripodal conformers of [M(tp)] (M = Cu, Ag). Our aim is to investigate the electronic properties and the energetics of the interconversion of the conformers, and to make a comparison with the results previously obtained with the analogous [M(tpm)]⁺

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[1] tp and tpm may also act as κ^2-ligands bonded to a single metal (κ^2-chelating), as κ^1–κ^2-ligands bridging two metals or, hardly ever, as κ^1-ligands likely depending on the steric congestion around the metal center and the number of donor substituents on the central atom X, which may be P and Ga other than B and C (see Refs. [1,2]). tp may also have a "κ^0" denticity as shown by the Carmona group in Rh(I) and Rh(III) complexes [2a,b].

[2] The relative position of pyrazolyl fragments in substituted and unsubstituted tp and tpm is strongly influenced by the steric hindrance of substituents possibly present on the ring carbon atoms [5].

complexes [3]. The first section of this contribution is dedicated to the assessment of the conformational properties of the free tp ligand leaving aside any problem concerning optical isomerism, while in the second part we focus on the binding energies and electronic properties of the [M(tp)] conformers, and we finally make a comparison between the [M(tpm)]⁺ and [M(tp)] bonding schemes.

2. Computational details

All the presented results are based on DFT, and have been obtained by running the Amsterdam Density Functional (ADF) package [7] and adopting the scalar relativistic zeroth-order regular approximation (ZORA) [8]. Generalized gradient corrections have been self-consistently included through the Becke–Perdew formula [9], TZP ZORA basis sets have been adopted for all the atoms [10]; inner cores of Cu (1s2s2p3s3p), Ag (1s2s2p3s3p3d), B (1s), C (1s), and N (1s) atoms were kept frozen throughout the calculations. Geometries for ground- and transition-states (GS and TS, respectively) have been optimized without imposing any symmetry. All TS's have been estimated through the following procedure: (i) a linear transit (LT) calculation has been run by varying a dihedral angle;[3] (ii) from the TS guess provided by step (i), a stationary point on the energy surface has been searched; (iii) the adequacy of the TS estimate has been then checked by computing vibrational frequencies at the corresponding geometry and verifying that one of them is imaginary; (iv) the Hessian computed in the third step is employed for the final TS optimization. Binding energies (*BE*) were analyzed in terms of fragment molecular orbitals (FMO) by applying the Ziegler's extended transition state method (ETS) [11]. According to the ETS scheme,

$$BE = \Delta E_{es} + \Delta E_{Pauli} + \Delta E_{int} + \Delta E_{prep} \qquad (1)$$

where ΔE_{es} is the pure electrostatic interaction, ΔE_{Pauli} is the destabilizing two-orbital-four-electron interaction between the occupied orbitals of the interacting fragments (($\Delta E_{es} + \Delta E_{Pauli}$) corresponds to the so called steric interaction (ΔE_{st}) contribution), ΔE_{int} derives from the stabilizing interaction between occupied and empty orbitals of the interacting fragments, and ΔE_{prep} is the energy required to relax the structure of the free fragments to the geometry they assume in the final system. *BE*s were further corrected by taking into account the basis set superposition error (*BSSE*) which was estimated by making use of reference energies calculated with "ghost" fragments [12].

One-electron levels are displayed as density of states (hereafter, DOS) by using a 0.25 eV Lorentzian broadening factor. These plots, based on Mulliken's prescription for partitioning the overlap density [13], have the advantage of providing insights into the atomic composition of MOs over a broad range of energy. Finally, information about the localization and the bonding/antibonding character of selected MOs was obtained by using crystal orbital overlap populations (COOP) [14] computed by weighting one-electron energy levels by their basis orbital percentage.

3. Results and discussion

Tp and tpm are potentially tripodal ligands characterized by the presence of three pyrazolyl moieties bonded to a central B and C atom, respectively. The MO structure of both the Hpz free molecule and the [M(Hpz)]⁺ complexes have been recently described by our group [3], We briefly resume the main findings in the following. Hpz is planar, fully conjugated, and isoelectronic with the cyclopentadienyl anion, though characterized by a high electronic
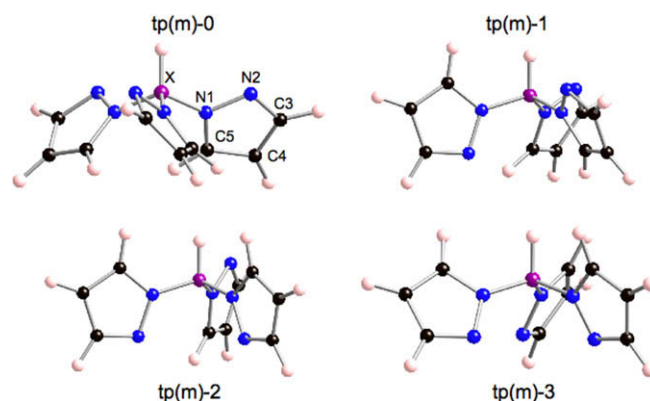

Fig. 1. Schematic representation of possible relative arrangements of the three pyrazolyl fragments in tp (X = B) and tpm (X = C).

Table 1
Relative binding energy contributions (kcal/mol) for tp and tpm free ligands.

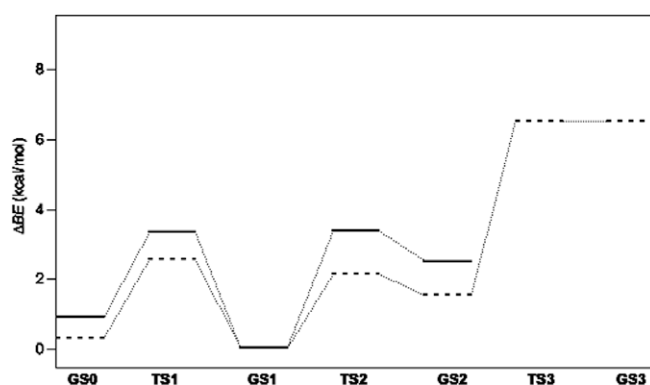|	tp-0(tpm-0)	tp-1/(tpm-1)	tp-2/(tpm-2)	tp-3/(tpm-3)
$\Delta(\Delta E_{Pauli})$	−7.86 (−17.51)	–(–)	3.29 (3.18)	6.14 (−1.17)
$\Delta(\Delta E_{el})$	−2.25 (−1.37)	–(–)	−0.87 (−0.42)	−4.99 (−3.76)
$\Delta(\Delta E_{st})$	−10.10 (−18.88)	–(–)	2.42 (2.75)	1.15 (−4.93)
$\Delta(\Delta E_{int})$	10.38 (19.76)	–(–)	−0.89 (−0.25)	5.35 (13.32)

Fig. 2. Relative *BE* values of GS0, TS1, GS1, TS2, and GS2 for tp (dashed lines) and tpm (solid lines); TS3 and GS3 are limited to tp (see text). The zero energy value corresponds to the GS1 *BE*.

charge density on N atoms both in the molecular plane and out of it. Its valence manifold includes five π-like MOs and the N(•) lone pair (hereafter, n_N). Among them, the π_1, π_2, π_3 ones and n_N are occupied, whereas the π_4 and π_5 MOs are empty. Moreover, π_3 and π_4 correspond to the Hpz HOMO and LUMO, respectively. As a consequence of these peculiarities, each tp/tpm pyrazolyl group may be involved in two competitive metal–ligand bonding mechanisms: a σ-binding implying n_N and a π-binding entailing the π states of the aromatic ring. The DFT results pertaining to σ/π [M(Hpz)]⁺ complexes revealed the importance of π contributions to the metal–ligand bond in σ-[M(Hpz)]⁺ molecular ions and the leading role played by the ΔE_{st} term of Eq. (1) in determing the final *BE* value of σ/π-[M(Hpz)]⁺ complexes.

3.1. tp conformational properties

Because of its charged nature, the free ligand cannot be characterized by X-ray diffraction. However, it is noteworthy that about 10 years ago Carmona and coworkers [2a,b] synthesized and structurally characterized what they called an isolated

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[3] A LT calculation implies a linear change of a selected LT parameter from its initial to its final value through a specified number of equidistant steps.

Table 2
Binding energy contributions in kcal/mol for the [M(tp-n)] and [M(tpm-n)]$^+$ conformers.

	[M(tp-1)] ([M(tpm-1)]$^+$)	TS(M)	[M(tp-2)] ([M(tpm-2)]$^+$)	[M(tp-3)] ([M(tpm-3)]$^+$)
$^{Cu}\Delta E_{Pauli}$	142.49 (129.59)	122.77	160.37 (143.80)	142.47 (131.68)
$^{Cu}\Delta E_{el}$	−232.29 (−130.46)	−213.24	−261.15 (−157.93)	−262.69 (−161.82)
$^{Cu}\Delta E_{st}$	−89.80 (−0.87)	−90.47	−100.78 (−14.13)	−120.22 (−30.14)
$^{Cu}E_{int}$	−103.72 (−97.18)	−95.67	−103.06 (−93.47)	−98.92 (−92.95)
$^{Cu}\Delta E_{prep}$	8.24 (6.92)		4.55 (4.67)	3.96
$^{Cu}BSSE$	2.84 (2.79)		2.42 (2.46)	2.71
^{Cu}BE	−182.44 (−88.34)		−196.87 (−100.47)	−212.47
$^{Ag}\Delta E_{Pauli}$	184.73 (152.24)	152.28	184.57 (160.19)	191.54 (160.37)
$^{Ag}\Delta E_{el}$	−191.63 (−87.48)	−172.44	−210.22 (−109.92)	−220.52 (−116.45)
$^{Ag}\Delta E_{st}$	−6.90 (64.76)	−20.16	−25.65 (50.27)	−28.98 (43.92)
$^{Ag}\Delta E_{int}$	−153.39 (−132.66)	−134.22	−144.32 (−126.87)	−154.67 (−135.32)
$^{Ag}\Delta E_{prep}$	6.01 (4.50)		4.09 (3.91)	2.14
$^{Ag}BSSE$	0.66 (0.66)		0.53 (0.52)	0.58
^{Ag}BE	−153.62 (−62.74)		−165.35 (−72.17)	−180.93

hydrotris(pyrazolyl)borate anions having a "κ^0" coordinative mode. Interestingly, the structure of this κ^0 unsubstituted tp is characterized by a single pyrazolyl group with N(•) in *trans* with respect to the hydrogen of the B–H fragment, similarly to the structural arrangement of the free tpm [5].[4] In agreement with the labeling scheme adopted in Ref. [3], this conformer has been tagged tp-1, while those corresponding to the κ^2-chelating and κ^3-tripodal coordinative modes have been labeled as tp-2 and tp-3, respectively (see Fig. 1). Obviously, the tp-0 conformer is the one with the three N(•) in *cis* with respect the B–H moiety. Optimized coordinates of tp-0, tp-1, tp-2, tp-3, TS1, TS2, TS3 are reported in Tables S0–S6 of the Supplementary material.

Analogously to tpm-0, the pyrazolyl fragments of the tp-0 optimized structure are symmetry related by a C_3 axis, and assume a propeller-like arrangement. Relative *BE*s corresponding to tp-n GS as well as to relevant saddle points are reported in Table 1 and displayed in Fig. 2 together *BE*'s of akin tpm conformers. The relative stability order of tp-n conformers (n = 0–3) is the same we found for the tpm ones [3], but the energy barriers associated to these interconversion paths (TS1, TS2, and TS3) are systematically lower than those evaluated for tpm (see Fig. 2). This is consistent with NMR data collected at room temperature by the Carmona group for the κ^0 hydrotris(pyrazolyl)borate anions [2a] which indicate a substantial free rotation around the B–N bonds.

A further point worth of note concerns the H–B vibrational frequencies (ν_{BH}) computed for the optimized tp-0, tp-1, and tp-2 structures (2517, 2513, and 2482 cm^{-1}, respectively). These values are all in reasonable agreement with the experimental κ^0 tp ν_{BH} value reported by Paneque et al. [2a] (2474 cm^{-1}). At variance to that, the calculated tp-3 ν_{BH} lies at a significantly lower frequency (2388 cm^{-1}). In this regard, it can be useful to remark that the optimized tp-1 bond lengths and bond angles agree well with structural data reported by Paneque et al. [2a], tp-0, tp-1, and tp-2 H–B bond lengths are very similar (1.201, 1.202, and 1.206 Å, respectively), while the tp-3 H–B internuclear distance (1.218 Å) is longer than that corresponding to the other tp conformers.

In general, theoretical results pertaining to tp-n reproduce those recently published for tpm-n [3]: though common, the κ^3-tripodal coordinative mode is unlikely to be achieved through a direct interaction of a metal center with the ligand having a tp-3/tpm-3 arrangement. However, at variance to the tpm case, we were able to locate the tp GS3 energy minimum. Consistently with a very flat
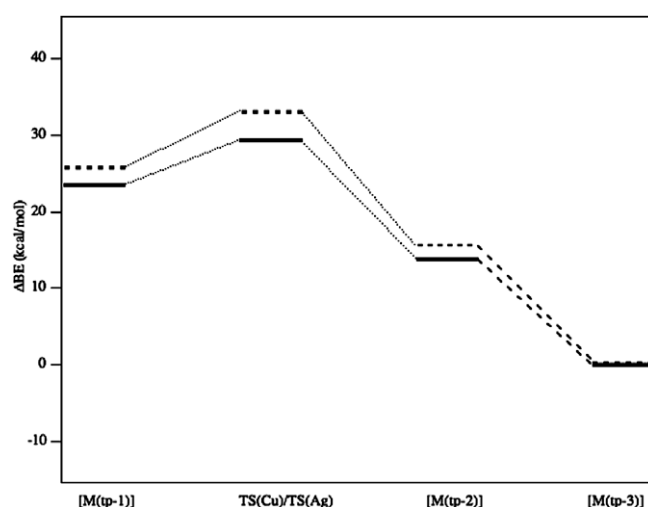

Fig. 3. Relative *BE* values of [M(tp-1)], TS(M), [M(tp-2)], and [M(tp-3)] (M = Cu (dashed lines) and Ag (solid lines)). The zero *BE* value corresponds to the [M(tp-3)] *BE*. Between [M(tp-2)] and [M(tp-3)] no TS has been found.

potential energy surface in this region, the energy difference between tp TS3 and GS3 is negligible (see Fig. 2).[5]

3.2. [Cu(tp)] and [Ag(tp)] complexes

The structural and electronic properties of tp metal complexes have been the subject of several experimental contributions [1,2,5,6,15]. From these works, it was established that N_3 tripodal ligands such as hydrotris (pyrazolyl)borate anionic ligands or tris(pyrazolyl)methane neutral ligands behave as biomimetic systems. This suggested their use as a modeling tool to investigate the catalytic activity of metal centers in biological systems. However, no study has been so far specifically dedicated to the analysis of the interplay between the metal–ligand interaction and the ligand hapticity.

The strength and the nature of the M(I)–tp bond in [M(tp-n)] (n = 1, 2, and 3) have been obtained through the ETS scheme by considering M(I) and tp as interacting fragments [11]. Optimized coordinates of [M(tp-n)] species and of TS(Cu) and TS(Ag) saddle points corresponding to the [M(tp-1)] → [M(tp-2)] conversions

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[4] Despite isolated hydrotris(pyrazolyl)borate derivatives may have different conformations, it has to be pointed out that, in these cases [5a,5e], the specific structural arrangement is ruled by steric factors.

[5] Vibrational frequencies have been evaluated for both TS3 and GS3 verifying that: (i) one of them is imaginary in the former case; and (ii) they are all positive in the latter one.

are collected in Tables S7–S14. Relative *BE*s are reported in Table 2 and displayed in Fig. 3.

As far as the relative stability of these species is concerned, a comparison between Figs. 3 and 2 reveals that, as previously found for [M(tpm-*n*)]$^+$ molecular ions [3], [M(tp-1)] is more stable than [M(tp-2)], i.e. the order is reversed with respect to the free ligand. It is also remarkable that, despite both [Cu(tp-2)] and [Ag(tp-2)] correspond to local minima, they are so shallow that we were unable to find the saddle point corresponding to the [M(tp-2)] → [M(tp-3)] conversion. This indicates that, in tune with our previous calculations on [M(tpm-*n*)]$^+$ conformers, once the κ^2-complex is formed, either from the interaction of M(I) with tp-2 or through the [M(tp-1)] → [M(tp-2)] conversion, the κ^3-tripodal species may be readily formed. However, the [M(tp-2)] → [M(tp-3)] conversion could be hampered by several reasons such as: (i) the coordinative saturation of the metal center by concurrent ligands; (ii) the coordination of the N(•) of the third pyrazolyl group to a different metal center; (iii) steric factors determined by bulky substituents on tp; (iv) electronic factors favoring specific arrangements [2,16].

Concerning the nature of the metal–ligand interaction, the ETS analysis (see Table 2) indicates that, independently of the coordi-
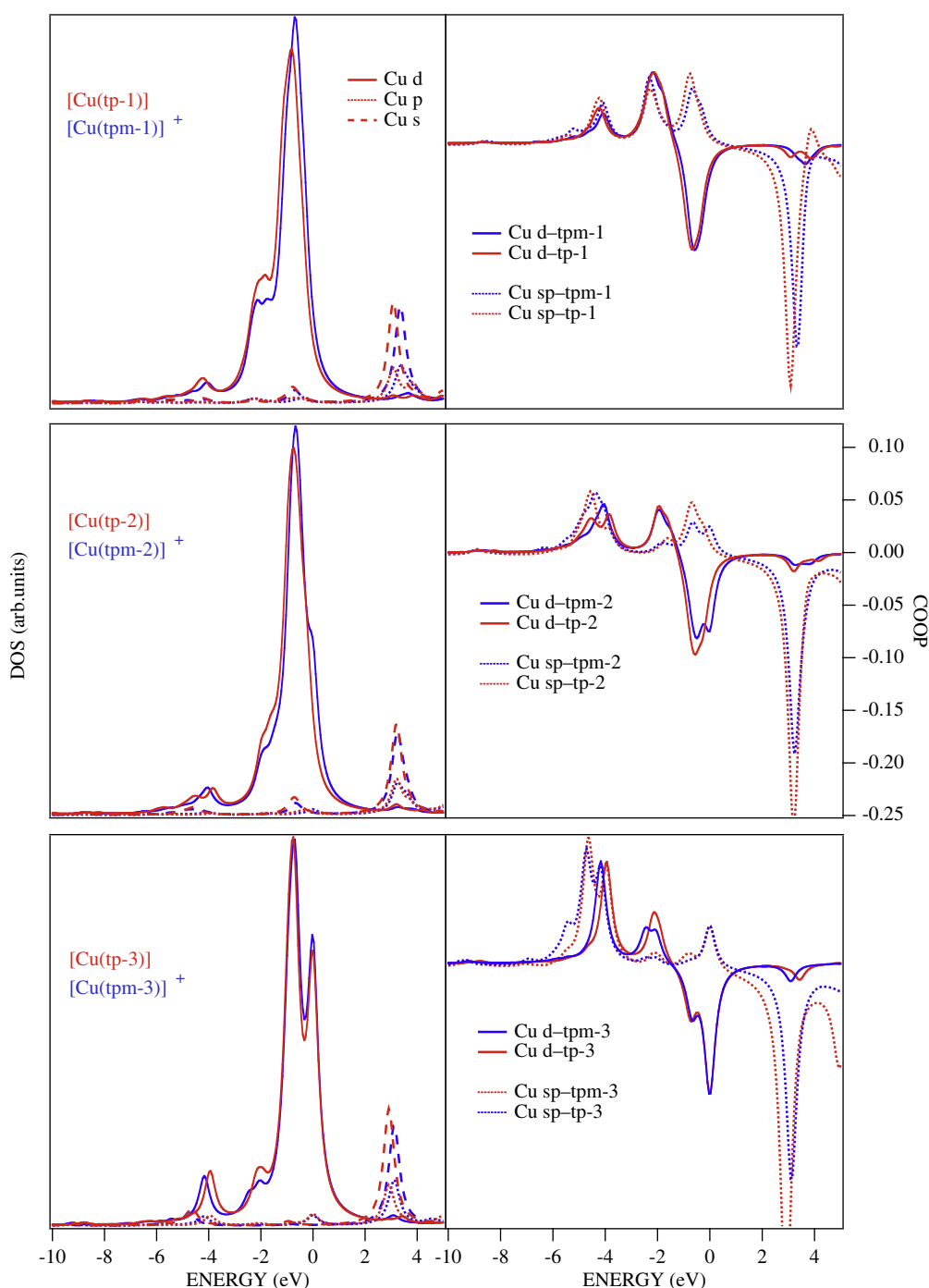

Fig. 4. (Left) d, s and p Cu PDOS of [Cu(tp-*n*)] and [Cu(tpm-*n*)]$^+$; (right) Cu–(tp-*n*) and Cu–(tpm-*n*) COOP, bonding (antibonding) states correspond to positive (negative) peaks. The zero energy matches the HOMO energy of each species.

native mode, the covalent component of the metal–ligand interaction is quite similar in [M(tp)] and [M(tpm)]$^+$, while the electrostatic interaction between M(I) and the negatively charged tp significantly strengthens the metal–ligand bond on passing from [M(tpm)]$^+$ to [M(tp)]. Further insights can be obtained from the inspection of M(I) PDOS and M(I)–ligand COOP curves (see Figs. 4 and 5) coupled to the analysis of the M(I)/ligand Hirshfeld charges [17] (Q^H) in [M(tp-n)] and [M(tpm-n)]$^+$ (Table 3). Though the overall interaction between the M(I) and tp charged fragments is definitely stronger than that between M(I) and the neutral tpm, Figs. 4, 5 and data reported in Table 3 reveal: (i) the close similarity of metal-based s, p, and d PDOS on passing from [M(tp-n)] to [M(tpm-n)]$^+$; (ii) the negligible contribution provided by the M(I) → tp/tpm backdonation to the metal–ligand interaction; (iii) the leading role played by the tp/tpm → M(I) donation in the metal–ligand bonding.

Structural and electronic differences of a series of κ^3-[Cu(tp)] and κ^3-[Cu(tpm)]$^+$ complexes have been recently investigated by Fujisawa et al. [5e] through experimental and DFT studies. One of their main conclusions was that since κ^3-tpm is a weaker donor than κ^3-tp, the Cu(I) ion in the κ^3-tpm complex is electron-poorer, and in consequence less involved in back-donation. In contrast to

Table 3
Q^H values of M, tp, and tpm fragments in [M(tp-n)] and [M(tpm-n)]$^+$ species.

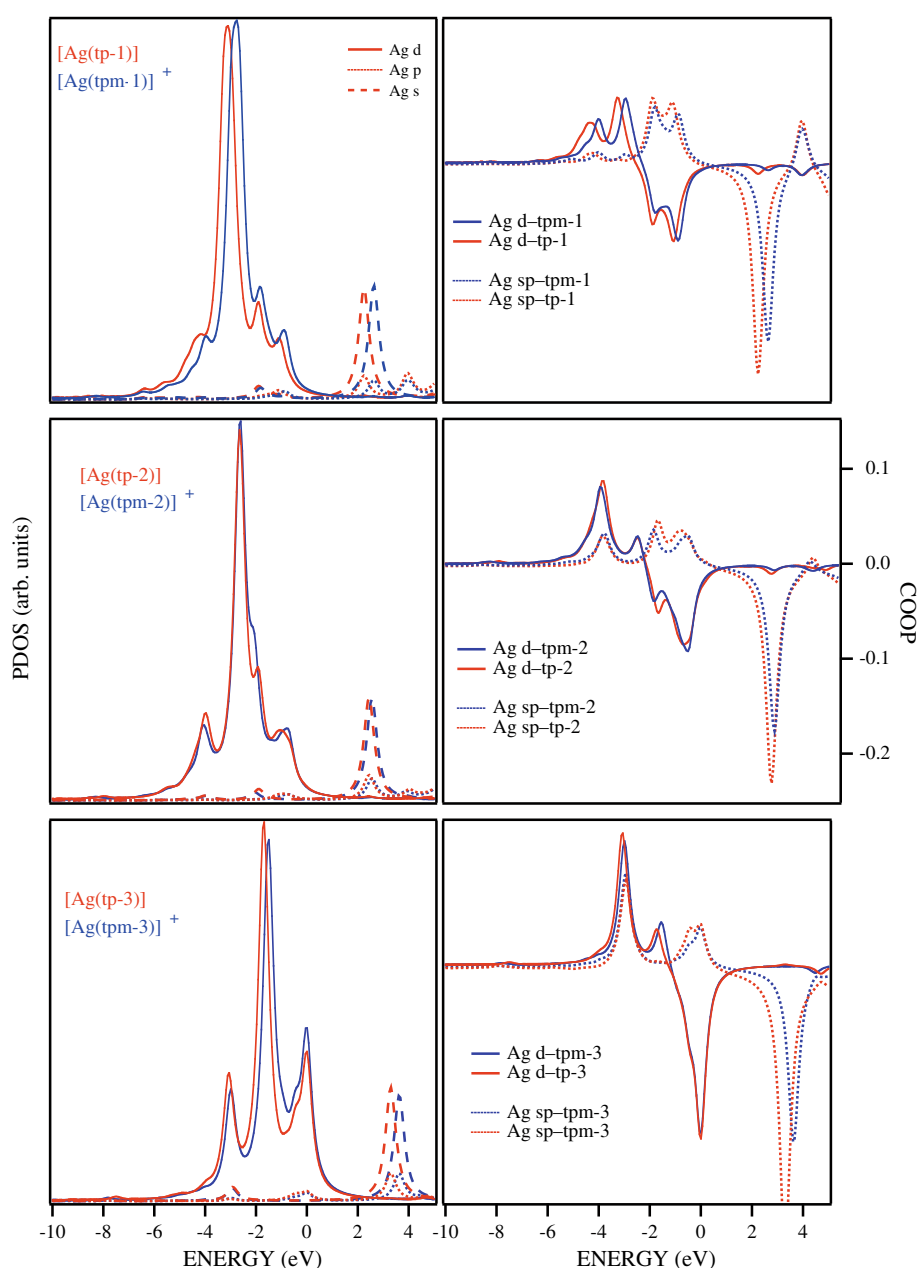|	[M(tp-1)] ([M(tpm-1)]$^+$)	[M(tp-2)] ([M(tpm-2)]$^+$)	[M(tp-3)] ([M(tpm-3)]$^+$)
Q^H_{Cu}	0.75 (0.79)	0.76 (0.78)	0.79 (0.81)
Q^H_{tp} $\left(Q^H_{tpm}\right)$	−0.75 (0.21)	−0.76 (0.22)	−0.79 (0.19)
Q^H_{Ag}	0.71 (0.75)	0.77 (0.76)	0.74 (0.77)
Q^H_{tp} $\left(Q^H_{tpm}\right)$	−0.71 (0.25)	−0.77 (0.24)	−0.74 (0.23)

Fig. 5. (Left) d, s and p Ag PDOS of [Ag(tp-n)] and [Ag(tpm-n)]$^+$; (right) Ag–(tp-n) and Ag–(tpm-n) COOP, bonding (antibonding) states correspond to positive (negative) peaks. The zero energy matches the HOMO energy of each species.

Table 4
Binding energy contributions (kcal/mol) to the interaction between M(L) and CO fragment (M = Cu,Ag; L=tp-3, tpm-3).

	M(tp-3)–CO	M(tpm-3)–CO
$^{Cu}\Delta E_{Pauli}$	127.44	109.34
$^{Cu}\Delta E_{el}$	−101.97	−92.23
$^{Cu}\Delta E_{st}$	25.46	17.11
$^{Cu}\Delta E_{int}$	−64.49	−56.14
$^{Cu}\Delta E_{prep}$	3.02	2.64
$^{Cu}BSSE$	0.81	0.96
^{Cu}BE	−35.20	−35.43
$Q^H_{M(Ligand)}$	0.15	1.10
Q^H_{CO}	−0.15	−0.10
$^{Ag}\Delta E_{Pauli}$	131.18	112.94
$^{Ag}\Delta E_{el}$	−101.53	−90.52
$^{Ag}\Delta E_{st}$	29.65	22.42
$^{Ag}\Delta E_{int}$	−58.35	−50.46
$^{Ag}\Delta E_{prep}$	0.42	0.01
$^{Ag}BSSE$	0.77	0.70
^{Ag}BE	−27.51	−27.33
$Q^H_{M(Ligand)}$	0.11	1.05
Q^H_{CO}	−0.11	−0.05

this conclusion, data reported in Table 3 indicate that the difference between the free tp and tpm charge (−1 and 0, respectively) has negligible effects on the final Q^H_M values, consistently with the rather close $^{Cu}\Delta E_{int}$(tp-3) and $^{Cu}\Delta E_{int}$(tpm-3) values. To clarify this discrepancy, we have carried out calculations also for the [M(tp-3)(CO)] and [M(tpm-3)(CO)]$^+$ model complexes. We analyzed the results on the basis of the ETS scheme, considering as interacting fragments [M(tp-3)] and [CO] in one case, and [M(tpm-3)]$^+$ and [CO] in the other one. Optimized coordinates of [Cu(tp-3)(CO)] (hereafter, ^{tp}**I**), [Cu(tpm-3)(CO)]$^+$ (^{tpm}**I**), [Ag(tp-3)(CO)] (^{tp}**II**), and [Ag(tpm-3)(CO)]$^+$ (^{tpm}**II**) are reported in Tables S15–S18, respectively, while interacting fragments Q^H and corresponding binding energies are collected in Table 4.

As far as the optimized structural parameters are concerned (see Tables S15–S18), both the Cu–CO (1.810 and 1.825 Å in ^{tp}**I** and ^{tpm}**I**, respectively) and C–O (1.153 and 1.146 Å in ^{tp}**I** and ^{tpm}**I**, respectively) bond lengths (BLs) are in reasonable agreement with experimental and theoretical data reported by Fujisawa et al. [5e]. The same holds for the ^{tp}**II** Ag–CO and C–O BLs (1.964 and 1.150 Å, respectively) which are quite similar to those experimentally determined by Dias and Jin [18] for the [Ag{HB(3,5-(CF$_3$)$_2$Pz)$_3$}(CO)] complex. No comparison with the ^{tp}**II** Ag–CO and C–O BLs (1.991 and 1.142 Å, respectively) is possible as crystallographic data pertaining to κ^3-[Ag(tpm)(CO)]$^+$-like species are unavailable.

The inspection of Table 4 results particularly useful to understand the [M(tp-3)]/[M(tpm-3)]–[CO] bonding interaction. In particular, we point out that carbon monoxide always carries a negative charge, i.e. it is a net electron acceptor; moreover, the absolute value of the charge is larger in the tp-based complexes than in the tpm-based ones. According to that, ν_{CO} (2039, 2090, 2049, 2105 cm^{-1} in ^{tp}**I**, ^{tpm}**I**, ^{tp}**II**, and ^{tpm}**II**, respectively)[6] is systematically red shifted with respect the harmonic theoretical value computed for the free CO (2113 cm^{-1}). Remarkably, the (^{tpm}**I** − ^{tp}**I**) $\Delta\nu_{CO}$ (51 cm^{-1}) exactly reproduces the experimental value reported by Fujisawa et al. [5e]. As a whole, these results confirm the conclusions reported on Ref. [5e]; however, taking advantage of the ETS analysis [11], we find that, despite the [Cu(tpm-3)]$^+$ and [Ag(tpm-3)]$^+$ positive fragments are weaker electron donor than the neutral [Cu(tp-3)] and [Ag(tp-3)] ones, the ΔBEs between [Cu(tpm-3)(CO)]$^+$ and

[Cu(tp-3)(CO)] as well as between [Ag(tpm-3)}(CO)]$^+$ and [Ag(tp-3)(CO)] are negligible. The reason is that the more negative $^M\Delta E_{int}$ term in the neutral adducts is compensated by the less positive $^M\Delta E_{st}$ contribution in the charged species.

4. Concluding remarks

In this contribution we have presented and discussed the results of a series of first-principle calculations carried out on the free tp ligand and its Cu(I) and Ag(I) complexes. The energetics of conformational transitions has been studied for the free ligand and for its complexes. Moreover, we analyzed the metal–ligand bonding showing that, independently of the coordinative mode, the covalent components are rather similar in M-tp and (M-tpm)$^+$. However, the electrostatic interaction between M(I) and the negatively charged tp significantly strengthens the metal–ligand bond on passing from (M-tpm)$^+$ to (M-tp). We have also considered the electronic and molecular properties of the adducts [Cu(tp-3)(CO)], [Cu(tpm-3)(CO)]$^+$, [Ag(tp-3)(CO)], and [Ag(tpm-3)(CO)]$^+$ showing that: (i) CO always behaves as an electron donor; (ii) the charged species [Cu(tpm-3)]$^+$ and [Ag(tpm-3)]$^+$ are weaker donor than the neutral ones; (iii) [M(tpm-3)}(CO)]$^+$ and [M(tp-3)(CO)] have, for each metal, the same binding energy.

Appendix A. Supplementary material

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.ica.2009.02.004.

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[6] Experimental ν_{CO} values reported by Fujisawa et al. [5d] for [Cu{HB(3,5-iPr$_2$pz)$_3$}(CO)] and [Cu{HC(3,5-iPr$_2$pz)$_3$}(CO)](PF$_6$) are 2056 and 2107 cm^{-1}, respectively. The blue shifted value reported by Dias and Jin [18] for [AgHB(3,5-(CF$_3$)$_2$Pz$_3$(CO)] (2162 cm^{-1}) is most probably due to the presence of CF$_3$ substituents on the pz rings.

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