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REGULAR ARTICLE

Is NICS a reliable aromaticity index for transition metal clusters?

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Abstract In the present account the nature of aromaticity/antiaromaticity of fourteen metallic complexes/clusters are reexamined. These species were classified as aromatic by means of different nucleus independent chemical shift (NICS) based approaches, previously. Visualization of the current density and magnetizability of atomic basins reveals that none of the studied systems are magnetic aromatic, i.e. sustain diamagnetic *ring* current. It is demonstrated that negative NICS values near the ring plane of the studied molecules originates from remarkably strong local paramagnetic current around their transition metal atom nuclei. This phenomenon has been observed only for Sc_3^- all-metal cluster but current study demonstrates that the influence of the local paramagnetic currents around transition metal atoms on NICS is a general phenomenon that must be carefully considered prior to classification of the metallic systems as *aromatic*. Furthermore, this study suggests that NICS is not a reliable aromaticity index for transition-metal clusters/molecules.

Keywords Aromaticity · Magnetizability · Current density · Transition metals · QTAIM · NICS

1 Introduction

Nucleus independent chemical shift or NICS is the most widely used aromaticity index; this index was first used by Bühl and van Wüllen [1] for simulation of the chemical shift of helium in the helium encapsulated fullerenes. Later Schleyer et al. used this probe extensively for investigating aromaticity of various systems [2, 3]. Utterly, after 18 years and more than 2,700 citations to reference 2, now NICS is assumed to be an undeniable tool for assessing aromaticity. However, in spite of popularity, NICS suffers from shortcomings that make it an unreliable index of aromaticity [4]. It has been shown that NICS does not correlate with ground-state indices of aromaticity [5, 6]. Furthermore, NICS is merely a local descriptor of aromaticity which cannot provide a clear picture of current density. This has been discussed in case of organic poly-aromatic hydrocarbons [7, 8], porphyrins [9], all-metal aromatics [10–13], and even hydrogen-bonded molecular clusters [14].

In the present work I briefly discuss some less pronounced reasons for failure of NICS and its derivatives for assessing the aromaticity in particular aromaticity of transition-metal clusters. Before starting the discussion, a short explanation about the terminology of aromaticity is needed.

In the present account wherever the word aromaticity is mentioned, I mean solely "magnetic aromaticity", i.e. the strength of ring currents in the ring plane of a molecule. Although, some studies about the nature of aromaticity among hydrocarbons suggest that magnetic aromaticity correlates with structural and energetic indices of aromaticity [2, 15, 16], there are strong evidences suggesting that

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these criteria of aromaticity are not necessarily correlated among metallic clusters [17–21]. Nevertheless, magnetic aromaticity is a response property that is different from energy- and structure-based aromaticity that is just related to the ground electronic state of molecular systems. To the best of author's knowledge, there is no straightforward relationship, derived from the quantum mechanics that shows ground-state properties such as energy are *linearly* correlated with magnetic response properties. Therefore, I follow a conservative philosophy and use the term *aromaticity* merely to address the strength of electronic ring currents in a molecule that is manifested in molecular magnetizability.

A less emphasized problem of NICS is its electron density dependence. In 2010 my colleagues and I showed that single point NICS calculations as well as NICS scan may not recognize fine pattern of aromaticity that is relative aromaticity between species having similar ring current strength like 6π-electron hydrocarbons [22]. One year later it was shown that NICS derivatives fail to account for relative order of aromaticity of metallic and semi-metallic clusters as well [19]. In order to solve the problem two approaches were suggested which were essentially different but interestingly came to the same order of aromaticity. The first solution was based on plotting NICS versus the electron density or the Laplacian of the electron density [22, 23]. The philosophy behind this choice is indeed very similar to the philosophy of NICS scan approach, introduced by Stanger [24] and Jiménez-Halla et al. [25]. However, instead of distance, a function of distance, the electron density or its Laplacian were selected. Later, slopes of NICS versus the electron density curves at low electron density limit were compared to assess strength of electronic current in each molecule. In fact, scanning NICS versus the electron density guarantees that NICS values of all systems are being compared at a similar condition that is the low electron density limit [26].

The other method employed for assessment of aromaticity was estimating the electronic current strength based on a double-loop ring current model [19]. This approach clearly corrects failure of NICS regarding the distance between the arbitrary point in space at which NICS is being computed and the so-called effective ring current radii [19]. Recently, Monaco and Zanasi [27] demonstrated that the double-loop model introduced by us is the most accurate non-quantum mechanical ring current model for monocyclic molecules.

It is worth noting that although these approaches are based on two different methodologies both come to the same conclusion.

To this point only the quantitative failure of NICS to reveal the fine pattern of aromaticity that is relative current density strength among different molecular systems either of the same or different families, is discussed. However, NICS may even qualitatively fail to recognize (anti) aromaticity.

In a very recent collaboration Badri et al. [18] showed that different NICS-based approaches mistakenly identify Sc_3^-, an all-metal species, as an aromatic cluster. Indeed, a closer look at the cluster based on either visualization of current density or studying the dissected magnetizability showed that the molecule is not aromatic. In fact, current density-based approaches suggest that the molecule is weakly antiaromatic, i.e. sustains paramagnetic ring current. The reason for the failure of NICS is that this probe cannot distinguish between local electron circulations around scandium atoms and the ring current of the cluster. Therefore, magnetic shielding, induced by local paramagnetic currents is misidentified as a sign of aromaticity. Very similar failure is also discussed recently by Ramírez-Tagle et al. [28] and Torres-Vega et al. [29] for various systems. But how widespread are these misidentifications? In the present work more examples from the contemporary literature are reevaluated. Before going through the examples I must emphasize that many of these systems might need to be reconsidered in future at highly correlated ab initio levels to make sure that the true nature of current density of the systems remain the same at high a level ab initio approach. Nevertheless, currently hardware/software suitable for these computations are not feasible in most computational chemistry labs. Moreover, I must stress once again that the same systems at the same theoretical levels are already reported in the literature. Here, I merely introduce problematic cases where NICS-based aromaticity is questionable. In the end, reliability of other methods for evaluation of magnetic aromaticity are also discussed briefly.

2 Computational methods

All structures are optimized at the same computational level that has been reported previously. Therefore, computational methods are mentioned for every case separately in the results and discussion section. All optimizations were performed by Gaussian rev. D02 [30] and the wave function of each system was analyzed by AIMAll suite of programs (version 14.06.21) [31] for computation of current density maps and magnetizability of system. In the current density plots diamagnetic currents are depicted clockwise and paramagnetic currents counterclockwise. A color coding from dark blue to red denotes ring current strength from strong to week. Atomic and interatomic magnetizabilities [32–34] within the context of the quantum theory of atoms in molecules [35] were computed for assessment of aromaticity as discussed elsewhere [36, 37].

3 Results and discussion

Finding examples in which NICS cannot recognize true nature aromaticity is not a trivial task. However, in general, any molecule with a NICS_{zz} scan plot like Fig. 1 is a candidate for NICS failure. In this figure NICS_{zz} values begin from highly negative, near the ring plane but change sign as the distance between NICS probe and ring plane increases. This is a sign for interference of local electronic currents in the magnitude of NICS values. Similarly, NICS scan plots which are mirror image of Fig. 1, i.e. start from positive region and end in the negative region, are probable candidates for NICS failure either as it is discussed for Cu_3^+ and Cu_4^{2-} previously [18]. In the following subsections several molecules with NICS scan plots similar to Fig. 1 are reconsidered.

3.1 $\mathrm{Ti}_3(\mathrm{CO})_3$

$\mathrm{Ti}_3(\mathrm{CO})_3$ has been synthesized in argon matrix and characterized via DFT computations by simulation of its infra-red spectrum obtained in the solid argon at BP86/6-311+G(d) level [38]. This molecule was first characterized as antiaromatic based on isotropic NICS computations but further studies based on structural, energetic and electronic criteria suggested that this molecule is both magnetic [39] and electronic [40] aromatic. The magnetic and electronic aromaticity is consistent with high symmetry (structural criterion) and the fact that the molecule is the global minimum on its potential energy surface (energetic criterion) [38, 39]. However, NICS scan of this species resembles Fig. 1 [39]. Therefore, this molecule is reconsidered to identify whether it is a magnetic aromatic molecule or not. All computations are performed at the original BP86/6-311+G(d) level of theory as noted in Methods section. Figure 2 depicts current density map of the molecule on the ring plane and 1 au above the ring plane of the system.

As it is evident in Fig. 2 electronic currents are highly localized around atoms in the molecule and no significant ring current, neither diamagnetic nor paramagnetic, is observable. Atomic and interatomic magnetizabilities, within the framework of quantum theory of atoms in molecules (QTAIM), are measures of local and interatomic electronic currents, respectively, Table 1. The out-of-plane component of interatomic magnetizability is in fact a reliable indicator of the strength of the ring current as it is a measure of current density on the ring plane that is passing through the interatomic surface of QTAIM atoms.

Table 1 demonstrates that the molecule sustains a very weak diamagnetic current, passing through interatomic surfaces. However, compared to the other studied systems the current strength is negligible [18, 36, 37]. Furthermore, comparing the magnitude of interatomic magnetizabilities with atomic magnetizability of titanium atom suggest that high negative NICS_{zz} at the ring center of the molecule (−117.89 ppm) originates from the local paramagnetic currents around the titanium atoms as it was already

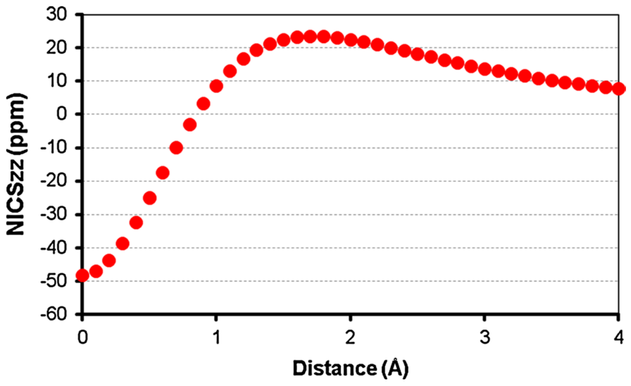

Fig. 1 Plot of NICS_{zz} versus distance for Sc_3^-; every molecule with a NICS_{zz} scan plot that moves from negative to positive region is a candidate for NICS failure

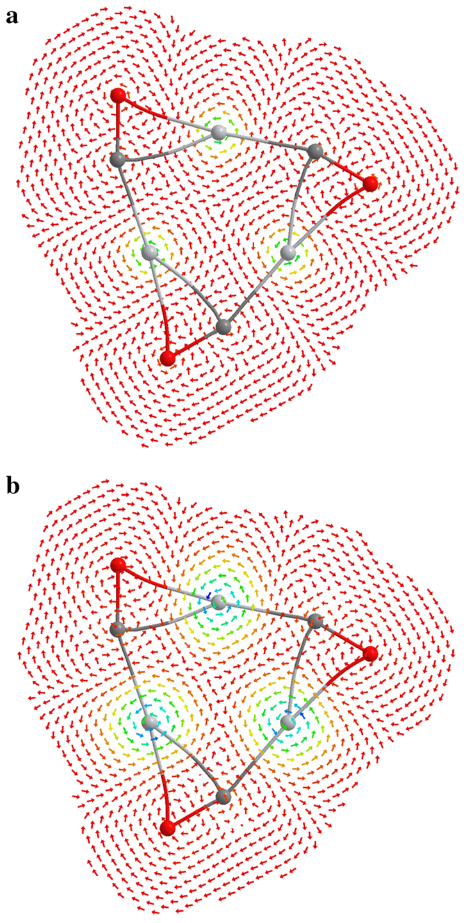

Fig. 2 Ring current plot for $\mathrm{Ti}_3(\mathrm{CO})_3$ molecule **a** on the ring plane and **b** one bohr above the ring plane of the system; *color coding* shows the strength of ring current. *Red to dark blue colors* denote weak to strong ring currents

Table 1 Out-of-plane component of atomic $\chi_{zz}(\Omega)$ and interatomic $\chi_{zz}(\Omega|\Lambda)$ magnetizability for $Ti_3(CO)_3$ system in cgs-ppm units

χ_{zz}(Ti)	χ_{zz}(C)	χ_{zz}(O)	χ_{zz}(Ti|C)[a]	χ_{zz}(Ti|O)[a]	χ_{zz}(C|O)[a]
+89.13	−1.72	−5.60	−0.75	−0.46	−1.48

[a] Sum of $\chi_{zz}(\Omega|\Lambda)$ and $\chi_{zz}(\Lambda|\Omega)$ divided by two

demonstrated in case of Sc_3^-. In a nutshell, $Ti_3(CO)_3$ should be considered a nonaromatic system and negative out-of-plane NICS in the ring center of the molecule is merely an indicator of strong local paratropic currents.

It should be emphasized that in this case magnetic response is not in line with electronic, structural and energetic properties of the system.

3.2 Y_3^-

This molecule has been suggested to be double- ($\sigma + \pi$) aromatic based on single point NICS computations by Chi and Liu [41] as well as $NICS_{zz}$ scan by Tsipis et al. [42]. Y_3^- is another all-metal cluster with a NICS scan plot similar to Fig. 1. Figure 3 depicts current density map of this species, computed at B3LYP/Def2-TZVP level [43] with non-relativistic small core pseudo-potential [44].

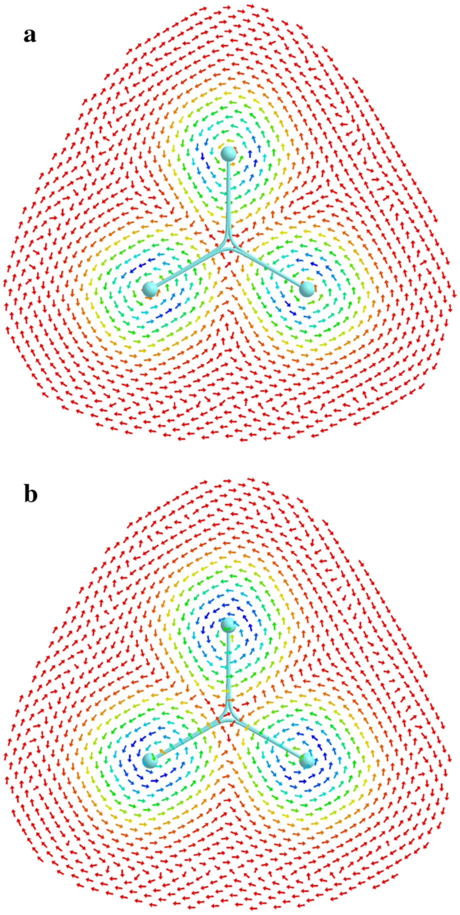

Fig. 3 Current density map of Y_3^- **a** on the ring plane and **b** 1 bohr above the ring plane of the molecule. *Red to dark blue colors* denote weak to strong ring currents

Based on the ring current plot around the yttrium atoms and close to the ring center all electronic currents are paramagnetic. Far away from the ring a weak diamagnetic ring current can be seen. In order to decipher whether the diamagnetic current is dominant or paramagnetic currents offset that, interatomic magnetizabilities were studied. Out-of-plane atomic and interatomic magnetizabilities of this species are +44.20 and +0.85 in cgs-ppm units. This suggests that weak diamagnetic ring current is completely counterbalanced by paramagnetic ring current. In this molecule just like Sc_3^- negative $NICS_{zz}$ values originate from local paratropic currents [18]. Therefore, in contrast to previous suggestions this molecule is antiaromatic in nature. One may question how antiaromatic molecules like Sc_3^- or Y_3^- with high D_{3h} symmetry can form. A possible answer to this legitimate question is that at least among transition

Table 2 Out-of-plane component of atomic $\chi_{zz}(\Omega)$ and interatomic $\chi_{zz}(\Omega|\Lambda)$ magnetizability for [cyclo-Ru3(μ_2-X)$_3$]$^{0/3+}$ systems in cgs-ppm units

[Cyclo-Ru3(μ_2-X)$_3$]$^{0/3+}$	χ_{zz}(Ru)	χ_{zz}(X)	χ_{zz}(Ru|Ru)[a]	χ_{zz}(Ru|X)[b]
1 [cyclo-Ru3(μ_2-H)$_3$]$^{3+}$	+92.61	−5.33	−4.48	−1.83
2 [cyclo-Ru3(μ_2-BH)$_3$]	+32.53	+1.82	–	−5.04
3 [cyclo-Ru3(μ_2-CH$_2$)$_3$]	+43.79	−1.58	−4.51	−3.09
4 [cyclo-Ru3(μ_2-OH)$_3$]$^{3+}$	+191.09	−9.19	–	−5.75
5 [cyclo-Ru3(μ_2-Cl)$_3$]$^{3+}$	+42.41	−27.63	–	−12.24
6 [cyclo-Ru3(μ_2-NH)$_3$]	+52.94	−3.51	–	−11.5
7 [cyclo-Ru3(μ_2-CO)$_3$]	+52.61	+0.25	−4.38	−3.42
8 [cyclo-Ru3(μ_2-O)$_3$]	+86.80	−5.11	–	−5.08
9 [cyclo-Ru3(μ_2-PH$_2$)$_3$]$^{3+}$	+45.53	−4.65	−3.98	−3.35
10 [cyclo-Ru3(μ_2-CF$_2$)$_3$]	+42.00	+1.57	−3.96	−3.19
11 [cyclo-Ru3(μ_2-CNH)$_3$]^{c}	+48.95	+0.84	−4.16	−3.35
12 [cyclo-Ru3(μ_2-N$_3$)$_3$]$^{3+}$	+125.36	−5.12	–	−5.33

[a] Wherever LCP between Ru–Ru bonds is absent interatomic magnetizability is not available

[b] Sum of $\chi_{zz}(\Omega|\Lambda)$ and $\chi_{zz}(\Lambda|\Omega)$ divided by two

[c] The average values are reported in the table since atoms are not equivalent due to symmetry

metal clusters magnetic response properties are not correlated with energetic properties of molecules. Indeed, aromaticity among hydrocarbons has a different meaning from that of transition metal clusters. Aromaticity of hydrocarbons is associated with high HOMO–LUMO gap and consequently low reactivity while the HOMO–LUMO gap of transition metals is usually very small and these species are not usually stable in condensed phase. Here I must emphasize once again that small HOMO–LUMO gap means that these species may suffer from multi-reference character and need to be studied at a highly correlated ab initio level to unveil the true nature of aromaticity. However, the fact regarding *wrong characterization of the nature of aromaticity based on the NICS at DFT level* is undeniable.

3.3 [Cyclo-$Ru_3(\mu_2\text{-}X)_3]^{0/3+}$ complexes

In a comprehensive study on the reactivity of [cyclo-$Ru_3(\mu_2\text{-}X)_3]^{0/3+}$, it was suggested that the reason for peculiar reactivity of complexes with [cyclo-$Ru_3(\mu_2\text{-}H)_3]^{3+}$ core (**1**) is antiaromaticity of this species in contrast to aromaticity of the rest of studied [cyclo-$Ru_3(\mu_2\text{-}X)_3]^{0/3+}$ species [45]. This conclusion is drawn based on the highly positive $NICS_{iso}$ values, computed along the main axis of symmetry of the molecule that is isotropic NICS scan. It is worth noting that there is no difference between $NICS_{zz}$ scan, the only component of NICS whose magnitude can be related to the strength of the ring current [4, 46], of complex **1** with $NICS_{zz}$ scan of the rest of [cyclo-$Ru_3(\mu_2\text{-}X)_3]^{0/3+}$ systems. Furthermore, $NICS_{zz}$ scan plots of these complexes, reported in the original article [45], show extremely large negative NICS values at the ring center of the complexes but the general shape of NICS scan plots resembles that of Fig. 1.

In order to recognize true nature of aromaticity among these systems structures of twelve molecules with different bridging ligands were taken from the supporting information of the original paper and magnetic response properties were studied at the same computational level (B3P86/6-31+G(d,p) and LANL2DZ for Ru atoms). For ruthenium atoms core electrons were added automatically to the wave functions for analysis according to methodology introduced by Keith and Frisch [47]. Atomic and interatomic magnetizabilities of ruthenium and bridging atoms are listed in Table 2.

Based on the magnetizability criterion the metal atoms are the source of strong local paramagnetic currents in all complexes as has been the case for $Ti_3(CO)_3$

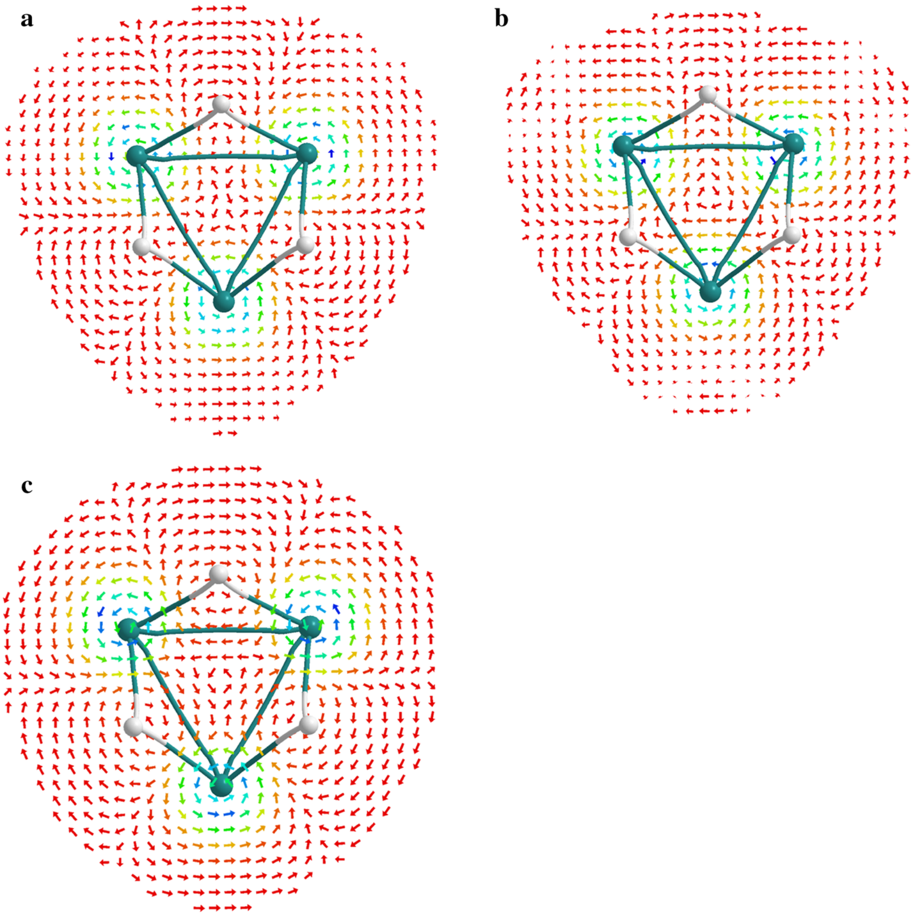

Fig. 4 Current density plots of complex 1 on the ring plane (**a**), one bohr below the ring plane (**b**) and one bohr above the ring plane (**c**); no remarkable ring current is evident in the figure. Furthermore, it seems that negative interatomic magnetizabilities originate from weak local diamagnetic currents near hydrogen atoms and near the ring center. *Red to blue colors* denote weak to strong current density. Diamagnetic currents are depicted clockwise and vice versa

and Y_3^- systems. However, in contrast to Y_3^-, all ruthenium complexes might be classified as weakly aromatic or nonaromatic molecules based on small magnitude of interatomic magnetizabilities. Nevertheless, it must be noted that compared to the well-known all-metal aromatic Al_4^{2-} with interatomic magnetizability of ~−23 in cgs-ppm units, these molecules have very small interatomic magnetizabilities that may originate from *local diamagnetic currents* either. Furthermore, according to interatomic magnetizabilities there is no meaningful difference between the electronic current pattern of complex **1** and that of the rest of complexes.

In order to make sure about the nature of electronic currents in complex **1** current density of this species was compared with that of the rest of complexes; Fig. 4 depicts current density plot of complex **1** on, above and below the Ru_3 framework. Based on the current density maps no remarkable ring current is observed in **1**, reminiscent of a

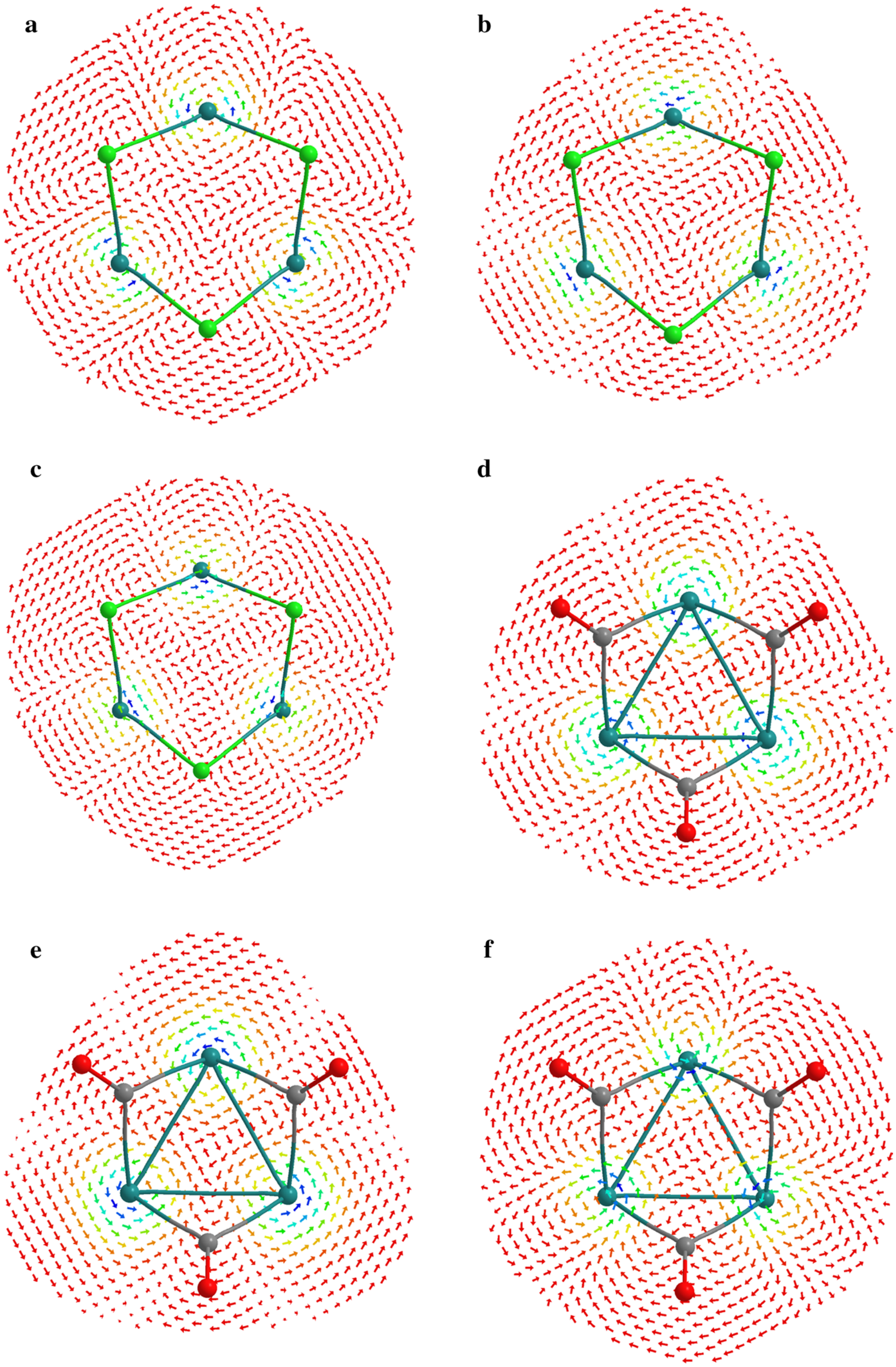

Fig. 5 Current density plots of complexes 5 (**a**–**c**) and 7 (**d**, **e**) on the ring plane (**a**, **d**), one bohr below the ring plane (**b**, **e**) and one bohr above the ring plane (**c**, **f**); no remarkable ring current is evident in the figure. Furthermore, it seems that negative interatomic magnetizabilities originate from weak local diamagnetic currents near hydrogen atoms and near the ring center. *Red to blue colors* denote weak to strong current density. Diamagnetic currents are depicted clockwise and vice versa

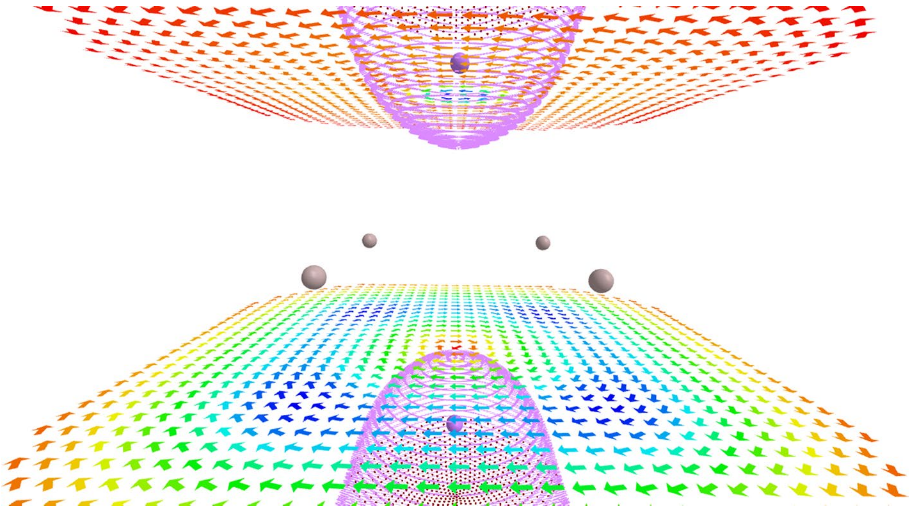

Fig. 6 Profiles of current density of Li_2Al_4 cluster; *red* to *blue colors* represent weak to strong current density. The interatomic surfaces of Li atoms are presented by *pink lines* above and below the Al_4 framework. The upper profile of current density cuts the atomic basin of Li ion and as is evident based on *color coding*, the strength of electronic current close to the Li ion is remarkable. The closer to the ion the stronger the current is. The lower current density profile is tangent to the interatomic surface between Li and Al_4 framework. Here, the current density is merely related to the Al_4 structure and is strong above the Al atoms. Any arbitrarily chosen rectangular integration plane may either penetrate the atomic basin of Li atom or excludes a part of current density that is related to the Al_4 structure

nonaromatic system. Figure 5 represents current density plots for complexes **5** and **7** (Table 2) on the ring plane as well as above and below their ring planes. Here again no significant ring current is evident suggesting that neither molecule is aromatic. Again the origin of large negative NICS is local paramagnetic currents around the ruthenium atoms and the source of negative bond magnetizability is local diamagnetic currents not a real ring current. Figure S1 represents ring current plots of all species.

Interatomic magnetizabilities and current density plots suggest that complex **1** is like the rest of studied set a non-aromatic molecule. Therefore, unusual reactivity of this molecule is not related to the magnetic antiaromaticity of the system.

3.4 Beyond NICS; shortcomings of magnetizability and ring current analysis approaches

Although interatomic magnetizability and current density analysis are superior to NICS these methods are not free of problems. If anyone wishes to work with these systems should be aware of limitations of these analyses. Unfortunately, the interatomic magnetizability is associated with interatomic surfaces and line critical points [48]. Indeed, in the absence of a line critical point, interatomic magnetizability is not measureable. In addition, interatomic magnetizability measures the effect of all local dia/paramagnetic currents, passing through the interatomic surface besides the ring current. *This is basically different from mathematical integration on the current density used by several groups* [10, 49, 50] *where all local currents mathematically cancel each other and the net strength of the ring current emerges*.

On the other hand, measuring the strength of the current density by integration of currents over an arbitrary rectangular plane between atoms in a molecule is not always straightforward. In particular, this approach may overestimate/underestimate current density in systems similar to Fig. 6. As it is shown in Fig. 6 choosing a proper integration plane that includes current density of Al_4^{2-} framework but excludes that of Li^+ ions is not a trivial task. These types of systems are in particular tricky because local currents around the Li ions do not cancel by integration over a half of the cluster. Nevertheless, combination of current density and inter/intraatomic magnetizability analyses can provide useful information regarding the strength of local and ring currents that enables one to judge about the nature of magnetic aromaticity of a molecule.

4 Conclusions

In the present account we considered fourteen metallic clusters/molecules from transition metals. Visualization of the current density and measuring the interatomic magnetizabilities clearly demonstrate that the magnitude of NICS is *not* related to the strength of current density that is the real indicator of magnetic aromaticity. Negative NICS might appear in the ring center of a molecule merely because of strong local paramagnetic currents, inducing shielding in the ring center. Accordingly, local paratropicity around the transition metal atoms is the source of misunderstanding about aromaticity of these systems. Unfortunately, neither a single point NICS nor a NICS scan curve can help to distinguish the true nature of aromaticity. In spite of negligible sources of problems in the magnetizability and current density analyses as discussed above, these approaches provide considerably clearer picture of electronic currents and consequently magnetic aromaticity. Nowadays user-friendly software packages are available for plotting current density maps. This leaves no room for black-box tools like NICS and its derivatives.

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