ChemInform Abstract: Aromaticity and Antiaromaticity in Transition-Metal Systems

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Aromaticity and antiaromaticity in transition-metal systems

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Aromaticity is an important concept in chemistry primarily for organic compounds, but it has been extended to compounds containing transition-metal atoms. Recent findings of aromaticity and antiaromaticity in all-metal clusters have stimulated further research in describing the chemical bonding, structures and stability in transition-metal clusters and compounds on the basis of aromaticity and antiaromaticity, which are reviewed here. The presence of d-orbitals endows much more diverse chemistry, structure and chemical bonding to transition-metal clusters and compounds. One interesting feature is the existence of a new type of aromaticity—δ-aromaticity, in addition to σ- and π-aromaticity which are the only possible types for main-group compounds. Another striking characteristic in the chemical bonding of transition-metal systems is the multi-fold nature of aromaticity, antiaromaticity or even conflicting aromaticity. Separate sets of counting rules have been proposed for cyclic transition-metal systems to account for the three types of σ-, π- and δ-aromaticity/antiaromaticity. The diverse transition-metal clusters and compounds reviewed here indicate that multiple aromaticity and antiaromaticity may be much more common in chemistry than one would anticipate. It is hoped that the current review will stimulate interest in further understanding the structure and bonding, on the basis of aromaticity and antiaromaticity, of other known or unknown transition-metal systems, such as the active sites of enzymes or other biomolecules which contain transition-metal atoms and clusters.

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1. Introduction

Aromaticity in compounds containing a transition-metal atom was first considered in a pioneering paper in 1979 by Thorn and Hoffmann[1] on six-membered-ring metallocyclic compounds that are derived from the prototypical aromatic benzene molecule with one C–H moiety replaced by an isolobal

Table 1 Criteria for π-aromaticity and π-antiaromaticity[33]

Property	Aromatic	Olefinic/classical	Antiaromatic
(i) Electronic nature	$(4n + 2)$ π-electron cyclic conjugation	No cyclic conjugation	$4n$ π-electron cyclic conjugation
(ii) Energy			
Cyclic conjugation	Stabilization	Standard	Destabilization
Delocalization	Enhanced	Standard	Decreased
HOMO–LUMO gap	Large	Standard	Small
(iii) Geometry			
Bond lengths	Equalization	Alternation	Alternation
(iv) Magnetic properties			
Anisotropy of diamagnetic susceptibility	Enhanced	—	Small
Susceptibility exaltation	High	—	Low
^{1}H NMR shifts	Diatropic (low-field shift)	—	Paratropic (high-field shift)
NICS (nucleus-independent chemical shift)	Large negative	Close to zero	Large positive
(v) Reactivity			
Chemical example	*e.g.*, benzene	*e.g.*, cyclohexadiene	*e.g.*, cyclooctatetraene
Retention of structure	Electrophilic substitution	Electrophilic addition	Addition
(vi) Spectroscopy			
UV spectra	High energy	Standard	Low energy
IR/Raman spectra	High symmetry	—	Low symmetry
Photoelectron spectra	High electron-detachment energies	Standard	Low electron -detachment energies

transition-metal fragment. Just three years later the first example of a stable, isolable metallobenzene—osmabenzene—was reported by Elliott *et al.*[2] A large family of metallobenzenes—the iridabenzenes—was synthesized by Bleeke and co-workers;[3–5] whereas a series of dimetallobenzenes with two metal atoms incorporated into the benzene ring was synthesized and characterized by Rothwell *et al.*[6,7] Recent advances in metallobenzenes have been reviewed by Bleeke,[8] He *et al.*,[9] Wright,[10] and Landorf and Haley.[11] A thorough chemical-bonding analysis of metallobenzene has been recently performed by Fernandez and Frenking.[12] However, aromaticity in transition-metal compounds is not restricted to metallobenzene molecules. Other molecules, in which the aromatic ring is composed of transition-metal atoms only and is not based on the prototypical benzene molecule, have also been reported recently and they are the subject of the current article.

Before discussing in detail the aromaticity in transition-metal systems, let us briefly review the concept of aromaticity, since it has been rather controversial despite the fact that it is taught routinely in general chemistry. Many books[13–21] and numerous reviews[22–29] have been published and several conferences[30–32] have been dedicated to deciphering the concept of aromaticity. We would like to adopt a view of aromaticity with which we hope most chemists can agree. Aromaticity was initially introduced into chemistry to describe the lack of reactivity of benzene and its derivatives, in spite of the apparent unsaturated nature of the carbon–carbon bonds in these molecules. Because all these molecules have an aroma, the property of chemical stability of the unsaturated bonds in the cyclic systems was called aromaticity. Nowadays most molecules which are considered to be aromatic, do not have any aroma and in order to characterize them as aromatic a variety of criteria have been proposed in the literature based on molecular orbitals or other considerations. They are summarized in Table 1 (we adopt a list of the properties proposed by Krygowski *et al.*[33] with some small modifications and additions).

These criteria have been proposed for π-aromatic and π-antiaromatic organic systems, but we will see that many of them are also applicable to σ-aromatic and σ-antiaromatic systems, as well as to δ-aromatic and δ-antiaromatic systems. We stress that one should not expect that aromaticity/antiaromaticity in transition-metal systems will manifest itself in exactly the same way as in organic chemistry. Many specific deviations are expected. Nevertheless, we believe that the overall delocalized chemical bonding and most of the molecular properties in certain transition-metal species could be understood using the aromaticity/antiaromaticity concepts.

The discovery and experimental generation of the first all-metal aromatic and antiaromatic clusters using photoelectron spectroscopy and *ab initio* calculations[34,35] have stimulated much interest in extending these ideas to other metal systems, including transition metals.[36,37] It has been understood that aromaticity/antiaromaticity in metal systems has very specific flavors if compared with organic compounds. The striking feature of chemical bonding in metal systems is the possibility of the multi-fold nature of aromaticity, antiaromaticity and conflicting aromaticity.[36–39] When only s-atomic orbitals (AOs) are involved in chemical bonding, one may expect only σ-aromaticity or σ-antiaromaticity. If p-AOs are involved, σ-tangential (σ_t-), σ-radial (σ_r-) and π-aromaticity/antiaromaticity could occur.[36] In this case, there can be multiple (σ- and π-) aromaticity, multiple (σ- and π-) antiaromaticity and conflicting aromaticity (simultaneous σ-aromaticity and π-antiaromaticity or σ-antiaromaticity and π-aromaticity). If d-AOs are involved in chemical bonding, σ-tangential (σ_t-), σ-radial (σ_r-), π-tangential (π_t-), π-radial (π_r-) and δ-aromaticity/antiaromaticity could occur. In this case, there can be multiple (σ-, π- and δ-) aromaticity, multiple (σ-, π- and δ-) antiaromaticity and conflicting aromaticity (simultaneous aromaticity and antiaromaticity involving σ, π and δ bonds).

One would expect that doubly- and triply-aromatic molecules would be significantly more stable with higher resonance energies, shortened bond lengths, enhanced ring currents, more negative NICS values, and a higher average bifurcation value of the electron-localization function (ELF) than in conventional singly-aromatic molecules. Indeed, Boldyrev and Kuznetsov,[40] and Zhan *et al.*[41] showed that the doubly

(σ- and π-) aromatic species Al_4^{2-} has a very high resonance energy of $\sim$48 kcal mol^{-1} [40] and $\sim$73 kcal mol^{-1} [41] respectively. For the prototypical singly-aromatic benzene molecule the resonance energy is only 20 kcal mol^{-1}.[13] The ring-current susceptibilities for the doubly-aromatic Al_4^{2-} dianion were also found to be 10 nA T^{-1}, which is higher than 8 nA T^{-1} in benzene.[42] Fowler *et al.* demonstrated that the contribution to the ring current from σ-delocalized electrons is significantly higher than from π-electrons.[43,44] According to Chen *et al.*,[45] Al_4^{2-} has a significant negative NICS (-30.9 ppm) compared to that in benzene (-9.7 ppm).[46] Santos *et al.*[47] showed that Al_4^{2-} has the highest average bifurcation value of ELF_σ and ELF_π among the set of various singly-aromatic systems. Establishing the overall aromaticity or antiaromaticity in molecules with conflicting aromaticity is an especially challenging task because of the simultaneous presence of aromaticity and antiaromaticity in different electronic subsystems.[35,45,48] Studies of magnetic properties of systems with conflicting aromaticity such as $Li_3Al_4^-$ and Li_4Al_4 can lead to contradictory conclusions on the overall aromaticity or antiaromaticity of the system.[35,49–51] Conflicting aromaticity also results in floppy geometries of the $Li_3Al_4^-$ and Li_4Al_4 clusters.[50] One of the most interesting features of molecules with conflicting aromaticity is the possibility of large linear and nonlinear optical properties such as linear polarizability, first hyperpolarizability and second hyperpolarizability.[52]

In the following sections we will consider in details the cases of multiple aromaticity, multiple antiaromaticity and conflicting aromaticity in recent examples of transition metal clusters and compounds, including Cu_3^+,[53] cyclo-Cu_nH_n (n = 3–6),[54] cyclo-M_nH_n (M = Ag, Au; n = 3–6),[55] cyclo-$Au_3L_nH_{3-n}$ (L = CH_3, NH_2, OH, Cl; n = 1–3),[56] cyclo-$Cu_nAg_{3-n}H_n$ (n = 1–3), cyclo-$Cu_nAg_{4-n}H_n$ (n = 1–4), and cyclo-$Cu_nAg_{5-n}H_n$ (n = 1–5),[57] Au_5Zn^+,[58] M_4Li_2 (M = Cu, Ag, Au),[59] M_4L_2 and M_4L^- (M = Cu, Ag, Au; L = Li, Na),[60] Hg_4^{6-},[61] M_3^{2-}, NaM_3^-, and Na_2M_3 (M = Zn, Cd, Hg),[62] M_3^- (M = Sc, Y, La),[63] $M_3O_9^-$ and $M_3O_9^{2-}$ (M = W, Mo),[64] $Ta_3O_3^-$,[65] and Hf_3.[66]

2. s-AO-based σ-aromaticity and σ-antiaromaticity in transition-metal systems

A. s-AO-based σ-aromaticity and σ-antiaromaticity in M_3 clusters

The prototypical system with s-AO-based σ-aromaticity is the Li_3^+ cluster, which was initially discussed by Alexandrova and Boldyrev,[67] and then by Havenith *et al.*[68] and Yong *et al.*[53] The Cu_3^+ has a similar D_{3h}, $^1A_1'$ ($1a_1'^2 1e'^4 1a_2''^2$ $2a_1'^2 1e''^4 2e'^4 2a_2''^2 3e'^4 2e''^4 3a_2''^2 3a_1'^2$) global-minimum structure.[53] As in the case of Li_3^+, the bonding in Cu_3^+ is rooted in 4s-AOs of Cu, because all the bonding and antibonding MOs ($1a_1'^2 1e'^4 1a_2''^2$ $2a_1'^2 1e''^4 2e'^4 2a_2''^2 3e'^4 2e''^4 3a_2''^2$) composed of 3d-AOs of Cu are occupied, hence the contribution to bonding from 3d-AOs of Cu is negligible. The $3a_1$-valence HOMO is a sum of the 4s-AOs of three Cu atoms (Fig. 1a). It is completely bonding and in this sense similar to the completely bonding π-MO in the prototypical π-aromatic $C_3H_3^+$ cation (Fig. 1b).

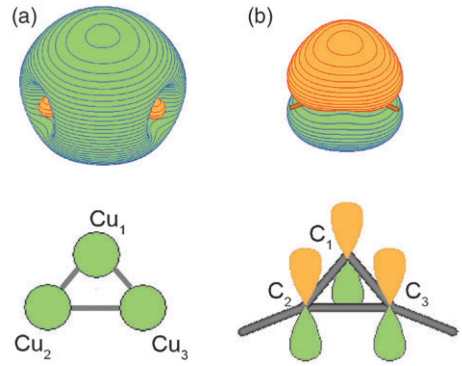

Fig. 1 (a) The $3a_1'$-HOMO of Cu_3^+ and its schematic representation as a linear combination of 4s-AOs of Cu atoms, (b) $1a_2''$-HOMO of $C_3H_3^+$ and its schematic representation as a linear combination of $2p_z$-AOs of C atoms.

The only difference is that the π-MO is a sum of $2p_z$-AOs of carbons. The delocalized π-MO in $C_3H_3^+$ renders its π-aromaticity according to the famous $4n + 2$ Hückel rule. On the basis of the analogy between the π-delocalized MO in $C_3H_3^+$ and the σ-delocalized MO in Cu_3^+ it is reasonable to call the latter σ-aromatic (the $4n + 2$ rule holds for σ-aromatic cyclic systems with valence s-AOs participating in bonding).[19] Yong *et al.*[53] considered aromaticity in the Cu_3^+ cation on the basis of nucleus-independent chemical shift (NICS) indexes.[46] Their calculations show NICS(0.0) = -28.22 ppm, NICS(0.5) = -22.59 ppm, and NICS(1.0) = -12.31 ppm at B3LYP/6-311+G*, clearly confirming the presence of σ-aromaticity in this cluster.[53] Yong *et al.*[53] also evaluated the resonance energy in the Cu_3^+ D_{3h}, $^1A_1'$ using the following equation:

$$Cu_3Cl(C_{2v}, {}^1A_1) \rightarrow Cu_2 + CuCl \qquad (1)$$

where Cu_2 and CuCl are reference classical molecules. According to their calculations, the energy of reaction (1), which is also the resonance energy for Cu_3^+, is 36.8 kcal mol^{-1} (B3LYP/6-311+G(3df)). The calculated resonance energy is certainly very high compared to the Cu_2 dissociation energy (41.7 kcal mol^{-1} at the same level of theory). Thus, the use of the σ-aromaticity for the description of the Cu_3^+ cation is justified. Apparently, the concept of σ-aromaticity based on the s-AOs should be applicable to Ag_3^+ and Au_3^+, though in the last case the s–d hybridization may play a more significant role.

For σ-antiaromatic species (with ns-AOs participating in bonding) the counting rule is $4n$ (singlet coupling). The Cu_3^- anion is a good example of σ-antiaromatic system with 4σ-electrons. The electronic configuration for the singlet state of Cu_3^- at the D_{3h} symmetry is $1a_1'^2 1e'^2$ (only bonding MOs are included), and the triangular structure with the singlet electronic state must undergo the Jahn–Teller distortion towards linear $D_{\infty h}$ structure with a $1\sigma_g^2 1\sigma_u^2$ valence electronic configuration.

Two σ-delocalized MOs can be approximately localized into two 2c–2e bonds and the linear structure of Cu_3^- can be formally considered as a classical structure. This situation is similar to the antiaromatic cyclobutadiene structure, which

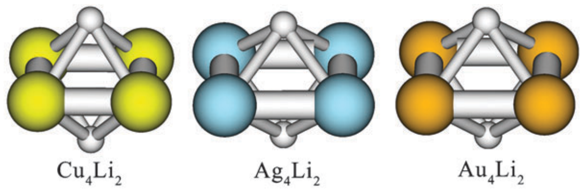

Fig. 2 Optimized structures of Cu_4Li_2, Ag_4Li_2 and Au_4Li_2.[59]

can be considered as having two double and two single carbon–carbon bonds, and thus can be described using a single Lewis structure. The antiaromaticity should manifest itself in the reduction of the stability of the molecule. Two reactions below show that the atomization energy of Cu_3^- (reaction 2, CCSD(T)/6-311 + G(2df)//CCSD(T)6-311 + G* + ZPE/CCSD(T)/6-311 + G*) is indeed substantially lower than the atomization energy of Cu_3^+ (reaction 3, CCSD(T)/6-311 + G(2df)//CCSD(T)6-311 + G* + ZPE/CCSD(T)/6-311 + G*).

$$\begin{aligned} Cu_3^-(D_{\infty h},\ {}^1\Sigma_g^+) &\rightarrow 2Cu(^2S) + Cu^-(^1S) \\ \Delta E &= +82.4\ \text{kcal mol}^{-1} \end{aligned} \tag{2}$$

$$\begin{aligned} Cu_3^+(D_{3h},\ {}^1A'_1) &\rightarrow 2Cu(^2S) + Cu^+(^1S) \\ \Delta E &= +106.3\ \text{kcal mol}^{-1}. \end{aligned} \tag{3}$$

B. s-AO-based σ-aromaticity in M_4^{2-} clusters

Initially aromaticity in the M_4^{2-} (M = Cu, Ag, Au) dianions as parts of M_4Li_2 (M = Cu, Ag, Au) neutral species was studied by Wannere *et al.*[59] They found that the Li_2M_4 species have distorted octahedral D_{4h}, $^1A_{1g}$ structures (Fig. 2) with the M_4^{2-} dianion forming a perfect square with two Li^+ cations located above and below the square on the C_4 axis. The significant charge transfer from Li to M_4 was confirmed by the natural population analysis (NPA) charges. For example, in Cu_4Li_2, the NPA charge on Li is +0.8 *e*. These authors also reported the NICS values in the centers of Cu_4Li_2 (−14.5 ppm), Ag_4Li_2 (−14.1 ppm) and Au_4Li_2 (−18.6 ppm) (all at PW91PW91/LANL2DZ) clusters which show the presence of aromaticity in the M_4^{2-} dianions. Wannere *et al.*[59] stated that the participation of p-orbitals in the bonding (and cyclic electron delocalization) in these clusters is negligible. Instead, these clusters benefit strongly from the delocalization of d-orbitals and, to some extent, s-orbitals. They also pointed out that d-orbital aromaticity of Cu_4Li_2 is indicated by its high (243.2 kcal mol^{-1}) atomization energy.

Lin *et al.*[60] reported a joint photoelectron spectroscopy and theoretical study of Cu_4Na^- and Au_4Na^- as well as theoretical results on Cu_4Li^-, Ag_4Li^-, Ag_4Na^-, Au_4Li^-, Cu_4Li_2, Ag_4Li_2, Au_4Li_2 and Cu_4^{2-}. They found that the Cu_4Li^-, Cu_4Na^-, Ag_4Li^- and Ag_4Na^- anions have a pyramidal structure consistent with the bipyramidal structure reported by Wannere *et al.*, while the Au_4Li^- and Au_4Na^- anions were found to be planar. The pyramidal structure of Cu_4Na^- with the Na^+ cation located above the square-planar Cu_4^{2-} dianion was confirmed by good agreement between theoretical and experimental vertical detachment energies (VDEs) for this system.

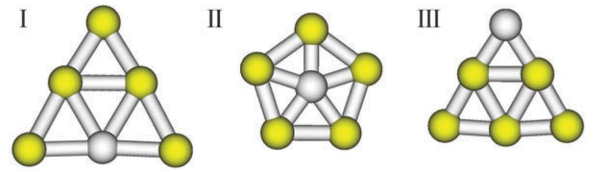

Fig. 3 Three reported isomers of Au_5Zn^+.[58]

Using the gauge-including magnetically-induced current (GIMIC) method, Lin *et al.*[60] concluded that strong ring currents are sustained mainly by the HOMO derived from the Cu 4s-AOs. Thus, the GIMIC calculations show that the Cu_4^{2-} ring is σ-aromatic due to 4s-AOs and that the d-orbitals do not play any significant role for the electron-delocalization effects. This study did not support the notion by Wannere *et al.*[59] that the square-planar Cu_4^{2-} is the first example of d-orbital aromatic molecules.

If bonding in the Cu_4^{2-} and Ag_4^{2-} rings is primarily due to σ-orbitals, than these systems are examples of systems with six valence σ-electrons and should be regarded as σ-aromatic according to the $4n + 2$ rule, similar to the Li_4^{2-}, Mg_4^{2+} and Li_2Mg_2 main-group clusters with six bonding σ-electrons considered by Alexandrova and Boldyrev.[67]

C. s-AO-based σ-aromaticity in the Au_5Zn^+ cluster and Au_6

The Au_5Zn^+ cation was found to be the most abundant cluster in the mass-spectrum of Au_nZn^+ (n = 2–44) by Tanaka *et al.*[58] The authors performed MP2/Zn/6-311 + G*/Au/5s5p4d1f calculations and identified three lowest isomers I, II and III for Au_5Zn^+ (Fig. 3). For the two lowest isomers, Tanaka *et al.*[58] presented MO pictures (Fig. 4) showing that six valence σ-electrons are delocalized over the whole cluster. The Au_5Zn^+ cluster is isoelectronic to the Au_6 cluster and its most stable structure is the same as the D_{3h} global-minimum structure of Au_6, which possesses a large HOMO–LUMO gap and a very stable electronic configuration.[69,70]

The MO pattern of Au_5Zn^+ depicted in Fig. 4 resembles those of prototypical aromatic organic molecules C_6H_6 and $C_5H_5^-$, except for their nodal properties in the molecular plane. The six delocalized electrons with the appropriate nodal pattern in Au_5Zn^+ satisfy the $4n + 2$ rule for σ-aromaticity. Tanaka *et al.*[58] also performed NICS calculations for all three structures and concluded that the negative NICS indexes are larger than in the prototypical aromatic organic molecules C_6H_6 and $C_5H_5^-$, confirming the presence of aromaticity in Au_5Zn^+. Overall, the Au_5Zn^+ cluster can be regarded as a σ-aromatic bimetallic cluster with six delocalized σ-electrons and the enhanced stability of Au_5Zn^+ may be ascribed to its aromaticity.

D. s-AO-based σ-aromaticity in the cyclo-M_nH_n (M = Cu, Ag, Au; n = 3–6), cyclo-$Au_3L_nH_{3-n}$ (L = CH_3, NH_2, OH, Cl; n = 1–3), cyclo-$Cu_nAg_{k-n}H_n$ (n = 1–k, k = 3–5) clusters

Tsipis and Tsipis[54] performed B3LYP/6-311 + G* calculations on Cu_nH_n (n = 3–6) cyclic species (Fig. 5) as models for the well-documented cyclic organocopper(I) compounds, such as the square-planar four-membered ring Cu_4R_4 (R = CH_2SiMe_3) with short Cu–Cu distances of 2.42 Å.[71] Tsipis

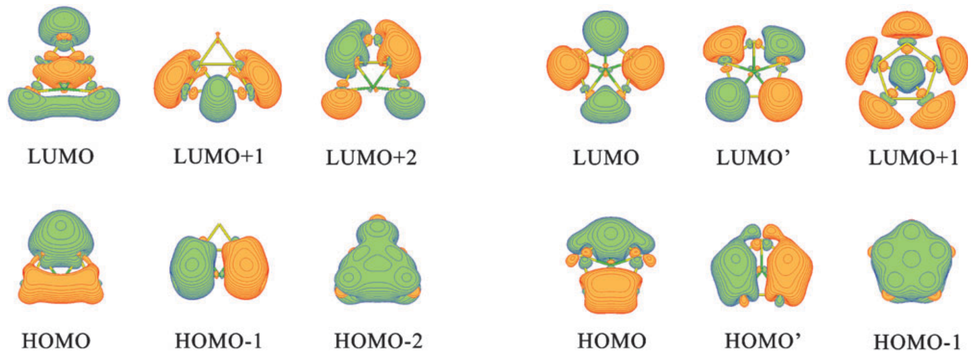

Fig. 4 Pictures of valence MOs of the Au_5Zn^+ isomers shown in Fig. 3 (I) (left) and 3 (II) (right).

and Tsipis[54] also calculated the 3D structures for Cu_nH_n (n = 4–6) and concluded that they are significantly less stable than the planar ones. In follow-up articles,[55–57] Tsipis and co-workers studied cyclo-M_nH_n (M = Ag, Au; n = 3–6), cyclo-$Au_3L_nH_{3-n}$ (L = CH_3, NH_2, OH, Cl; n = 1–3), cyclo-$Cu_nAg_{3-n}H_n$ (n = 1–3), cyclo-$Cu_nAg_{4-n}H_n$ (n = 1–4), and cyclo-$Cu_nAg_{5-n}H_n$ (n = 1–5). The Cu_nH_n (n = 3–6) cyclic species are discussed here, and the other species are similar.

All Cu_nH_n (n = 3–6) species were found to be cyclic with short Cu–Cu distances (between 2.404 Å in Cu_3H_3 to 2.556 Å in Cu_6H_6). Tsipis and Tsipis[54] stated that the equivalence of the Cu–Cu and Cu–H bonds in these species is indicative of the aromatic character of the cyclic hydrocopper(I) compounds. In addition, they reported binding energies, NICS values and the electrophilicity index ω (Table 2), which also support the aromatic nature of these species.

Clar[21] stated that all the metallocycles exhibit a composite bonding mode involving σ, π and δ components on the basis of their analysis of occupied valence MOs. However, we found a rather different picture. We performed an NBO analysis of the representative Cu_4H_4 (D_{4h}, $^1A_{1g}$) cluster at the B3LYP/6-311++G** level of theory. According to our NBO analysis the Cu atoms have $4s^{0.56}3d^{9.91}4p^{0.02}$ valence atomic occupations and a effective atomic charge of +0.50 e, while the H atoms have $1s^{1.49}$ atomic occupation and an effective atomic charge of −0.50 e. One can see that the 3d-AOs of Cu are almost completely occupied and thus do not significantly contribute to bonding. The bonding from completely delocalized δ-HOMO-11, π-HOMO-17, π-HOMO-18, σ-HOMO-19

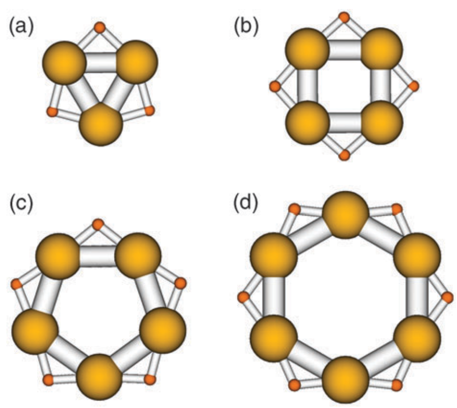

Fig. 5 Optimized planar cyclic structures of Cu_nH_n clusters.[54]

Table 2 Binding energies ΔE_1 and ΔE_2, GIAO-SCF (gauge-including atomic orbitals–self-consistent field) NICS and electrophilicity of Cu_nH_n (n = 3–6)

Cluster	$\Delta E_1{}^a$/kcal mol^{-1}	$\Delta E_2{}^b$/kcal mol^{-1}	NICS/ppm	ω/eV
Cu_3H_3, D_{3h}	81.5	260.9	−8.4	1.595
Cu_4H_4, D_{4h}	137.0	376.1	−4.2	1.743
Cu_5H_5, D_{5h}	180.1	479.0	−1.4	2.040
Cu_6H_6, D_{6h}	217.5	576.2	−0.2	2.230

^{a} $\Delta E_1 = E(\mathrm{CuH})_n - nE(\mathrm{CuH})$. ^{b} $\Delta E_1 = E(\mathrm{CuH})_n - n[E(\mathrm{Cu}) + E(\mathrm{H})]$.

and σ-HOMO-20 (Fig. 6) will be offset by the effect of antibonding orbitals (Fig. 6) composed of d-AOs of Cu atoms. Thus, the net bonding effect from MOs composed of 3d-AOs cannot be significant. Rather, the bonding in the Cu_nH_n cyclic clusters comes from an ionic contribution between $H^{-0.501}$ and $Cu^{+0.501}$ and from delocalized MOs composed out of 4s-AOs on Cu. In fact, NBO analysis of Cu_4H_4 reveals one resonance structure (the same way as NBO produces some of the Kekule resonance structure for benzene), in which there are four Cu–H 2c–2e bonds composed of 1s-AOs of H and 4s-AOs of Cu with the occupation number 1.744 e alternated over the Cu_4H_4 distorted planar octahedron. This confirms the aromatic nature of the Cu_nH_n clusters, but the aromaticity is due to delocalization of σ-bonds (composed of 1s-AOs of H and 4s-AOs of Cu) and not due to the delocalized σ-, π- and δ-MOs composed of 3d-AOs of Cu. Thus, aromaticity in the Cu_nH_n clusters is neither π nor δ but rather σ in nature. Lin *et al.*,[60] however, reported that they did not find any strong magnetically-induced ring current in Cu_4H_4. This might be a sign of the weak aromaticity in Cu_nH_n clusters. Due to relativistic effects, s–d hybridization started to play a bigger role in Ag_nH_n and Au_nH_n clusters, but additional research accounting for the relativistic effects should be performed before making any conclusions on the bonding nature of these clusters.

3. p-AO-based aromaticity and antiaromaticity in transition metal systems

Double aromaticity (simultaneous presence of σ- and π-aromaticity) was introduced in chemistry by Chandrasekhar *et al.* to explain the properties of the 3,5-dihydrophenyl cation.[72] Simultaneous presence of aromaticity and antiaromaticity was first used by Martin-Santamaria and Rzepa[73] to explain

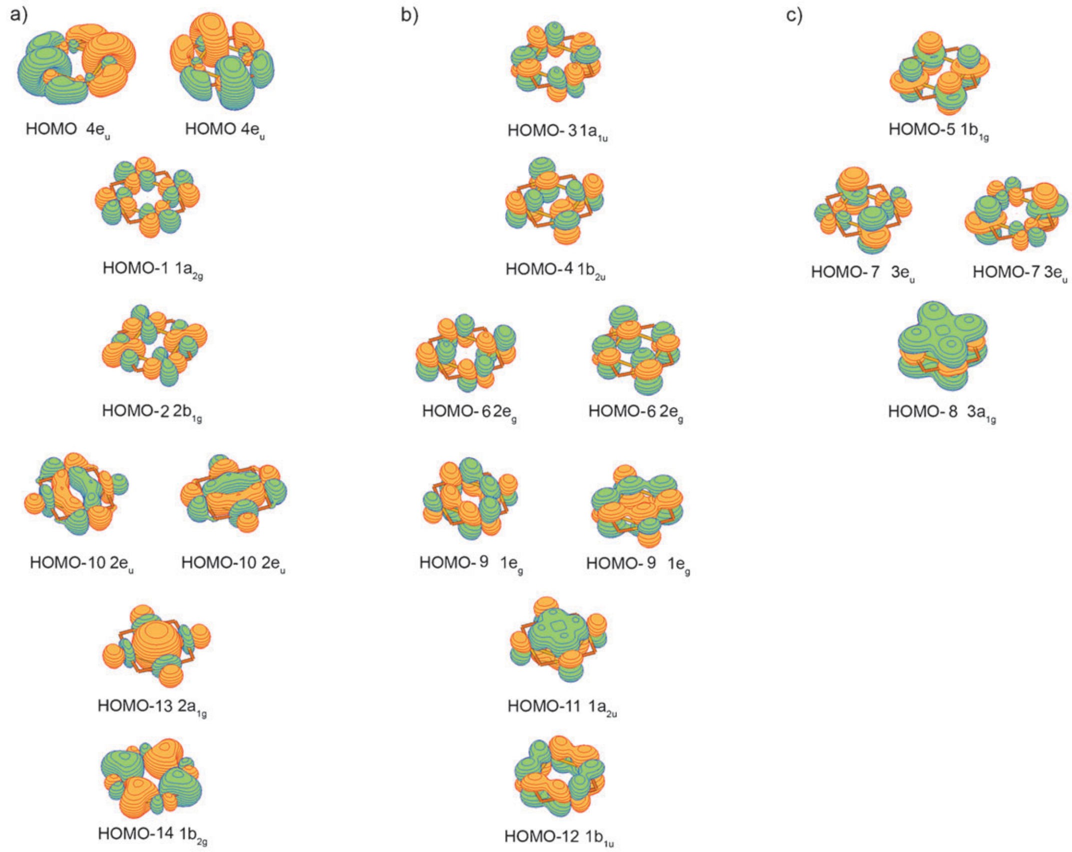

Fig. 6 (a) σ-MOs, (b) π-MOs, and (c) δ-MOs composed out of d-AOs of Cu in Cu_4H_4 (D_{4h}, $^1A_{1g}$).

chemical bonding in small carbon rings. Präsang *et al.*[74,75] have shown that small carborane molecules containing 3- and 4-membered rings also exhibit both σ- and π-aromaticity. The Hg_4^{6-} cluster was the first transition-metal system where double (σ- and π-) aromaticity due to p-AOs was discovered.[73]

A. p-AO-based multiple aromaticity in the Hg_4^{6-} cluster

Mercury has a closed-shell electron configuration ($6s^2$) and therefore a neutral Hg_4 cluster is expected to be a van der Waals complex. However, it was shown in the solid that one particular sodium–mercury amalgam Na_3Hg_2 contains Hg_4^{6-} square units as its building blocks.[61] The high stability of the Hg_4^{6-} building block was explained once we recognized that it is isoelectronic to the first all-metal aromatic cluster, Al_4^{2-}.[34] Basically, the bonding in Hg_4^{6-} is due to Hg 6p-AO-based MOs and the completely occupied Hg d-AOs do not contribute to bonding.[61] Fig. 7 displays the seven valence MOs of the square-planar Hg_4^{6-}, which are very similar to those in Al_4^{2-}.[34]

The HOMO ($1b_{2g}$), HOMO-1 ($1a_{2u}$) and HOMO-2 ($2a_{1g}$) are completely bonding orbitals formed from the Hg 6p-AOs and represent $p_{\sigma-t}$-MOs (tangential MO), p_π-MOs and $p_{\sigma-r}$-MOs (radial MO) respectively. The remaining four MOs are bonding, non-bonding and antibonding orbitals formed primarily from the filled valence 6s orbitals of Hg and can be viewed as atomic $6s^2$ lone pairs. Thus, the upper three MOs are mainly responsible for the chemical bonding in Hg_4^{6-}. If we split the σ- and π-orbitals into two separate sets, we can represent the MOs formed by the Hg 6p-AOs with the MO diagram shown in Fig. 8.

The lowest-lying π-MO and the two lowest-lying σ-MOs are completely bonding, whereas the highest-lying ones are completely antibonding. The two MOs in the π-set and the four MOs in the σ-set that are located in between the completely bonding and antibonding MOs are doubly degenerate with bonding/antibonding characters. The $2e_u$- and $3e_u$-MOs are composed of $p_{\sigma-r}$- and $p_{\sigma-t}$-AOs. This is the reason why $p_{\sigma-r}$- and $p_{\sigma-t}$-MOs are presented as one set in Fig. 8. On the basis of this mixing in the $p_{\sigma-r}$- and $p_{\sigma-t}$-AOs, the counting rule for σ-electrons for cyclic systems with even number of vertices should be $(4n + 4)/(4n + 6)$ for aromaticity/antiaromaticity

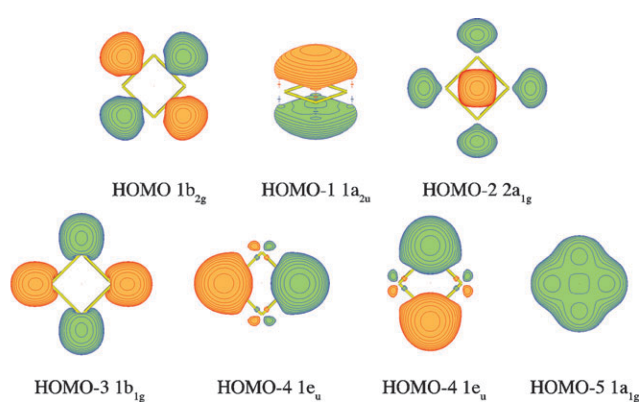

Fig. 7 Valence molecular orbitals of Hg_4^{6-}.

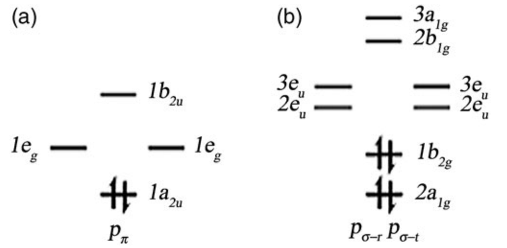

Fig. 8 Molecular orbital diagram for (a) p-MOs and (b) s-MOs for Hg_4^{6-}.

(in the simplest case of the occupation of just one $p_{\sigma-r}$- or one $p_{\sigma-t}$-MO the system is also aromatic), but they are $(4n + 2)/(4n)$ for the cyclic systems with the odd number of vertices. On the basis of two distinct types of MOs, we can introduce one types of aromaticity: π-aromaticity based on the p_π MOs, and two types of σ-aromaticity based on the $p_{\sigma-r}$ and $p_{\sigma-t}$ MOs. The occupation of all three bonding MOs in Hg_4^{6-} makes its shape a perfect square and renders its doubly (σ- and π-) aromatic nature.

The finding of the double aromaticity in Hg_4^{6-} establishes a solid bridge between our gas-phase studies of multiply-aromatic clusters and bulk materials containing such species. It is surprising that such an ancient material as amalgams can be rationalized on the basis of multiple aromaticity initially discovered in the gas-phase studies of the Al_4^{2-} all-metal aromatic cluster,[34,41,76,77] produced in the form of MAl_4^- in the gas phase, where M = Li, Na, Cu.

B. p-AO-based multiple aromaticity in the M_3^{2-}, NaM_3^-, Na_2M_3 (M = Zn, Cd, Hg) clusters

Yong and Chi[62] have recently shown using B3LYP, B3PW91 and CCSD(T) calculations that a series of M_3^{2-}, NaM_3^-, Na_2M_3 (M = Zn, Cd, Hg) clusters all have the M_3^{2-}, D_{3h}, $^1A_1'$ core, which is π-aromatic. Like in Hg_4^{6-}, neither 5d- nor 6s-AOs participate in the bonding in M_3^{2-}. Its bonding is due to the a_2''-HOMO, which is composed of the outer p-AOs of M. This is a completely bonding π-MO similar to the $1a_2''$-HOMO in the $C_3H_3^+$ cation (Fig. 1b). Thus, in all the M_3^{2-}, NaM_3^-, Na_2M_3 (M = Zn, Cd, Hg) systems, bonding in the M_3^{2-} core is due to π-aromaticity only, without the formation of a σ-framework. A similar bonding pattern was previously reported for Mg_3^{2-}, $NaMg_3^-$ and Na_2Mg_3 systems by Kuznetsov and Boldyrev.[78] Yong and Chi[62] also calculated a sizable resonance energy of 24.8 kcal mol^{-1} (Zn_3^{2-}), 12.9 kcal mol^{-1} (Cd_3^{2-}) and 12.1 kcal mol^{-1} (Hg_3^{2-}) (either at CCSD(T)/6-311+G* or CCSD(T)/LANL2DZ), as well as large negative values of NICS: −24.86 ppm (Zn_3^{2-}), −19.59 ppm (Cd_3^{2-}) and −15.40 ppm (Hg_3^{2-}), further confirming their π-aromaticity.

4. d-AO-based aromaticity and antiaromaticity in transition metal systems

Due to the more complicated nodal structure of d-AOs that can form δ-bond in addition to σ- and π-bonds, transition-metal systems can provide a more diverse array of aromaticity–antiaromaticity combinations. We may expect σ-tangential (σ_t), σ-radial (σ_r), π-tangential (π_t), π-radial (π_r) and δ-MOs. For σ- and π-MOs, the counting rules are $4n + 4$ (aromaticity) and $4n + 6$ (antiaromaticity) for cyclic structures with an even number of atoms, and $4n + 2$ (aromaticity) and $4n$ (antiaromaticity) for cyclic structures with an odd number of atoms. For δ-MOs the counting rule is $(4n + 2)/(4n)$ for aromaticity/antiaromaticity. In general, there can be multiple (σ-, π- and δ-) aromaticity, multiple (σ-, π- and δ-) antiaromaticity and conflicting aromaticity (simultaneous aromaticity and antiaromaticity among the three types of σ-, π- and δ-MOs). So far only a few transition-metal systems with d-AO-based aromaticity have been reported.[63–66]

A. d-AO-based σ-aromaticity in the $Mo_3O_9^{2-}$ and $W_3O_9^{2-}$ clusters

The first cases of d-orbital aromaticity in 4d and 5d transition-metal-oxide clusters, $Mo_3O_9^-$ and $W_3O_9^-$, were reported by Huang *et al.* by combining photoelectron spectroscopy and theoretical calculations.[64] They found that the M_3O_9, $M_3O_9^-$ and $M_3O_9^{2-}$ (M = Mo, W) clusters all have D_{3h} structures and each metal atom is bonded to two bridged O-atoms and two terminal O-atoms (Fig. 9).

The attachment of the first and second electrons to the M_3O_9 species reduces the M–M distance significantly: 0.25 Å for $Mo_3O_9^-$ and 0.29 Å for $W_3O_9^-$, and 0.20 Å for $Mo_3O_9^{2-}$ and 0.19 Å for $W_3O_9^{2-}$. The large geometry changes induced by addition of one or two electrons to the M_3O_9 species agree with the nature of the HOMO in the singly- ($M_3O_9^-$) and doubly-charged ($M_3O_9^{2-}$) anions (Fig. 10).

The completely bonding nature of the σ-HOMO in $M_3O_9^-$ and $M_3O_9^{2-}$ species renders their σ-aromaticity. Calculations of NICS at the center of $Mo_3O_9^{2-}$ (−21.5 ppm) and $W_3O_9^{2-}$ (−20.5 ppm) also support the presence of aromaticity. Huang *et al.*[64] also estimated a sizable (7.6 kcal mol^{-1}) resonance energy for $W_3O_9^-$. These results provide solid evidence that the anionic $Mo_3O_9^-$, $W_3O_9^-$, $Mo_3O_9^{2-}$ and $W_3O_9^{2-}$ species with the D_{3h} ($^2A_1'$ or $^1A_1'$) structure are the first experimentally-confirmed d-orbital aromatic (σ) species.

B. d-AO-based σ- and π- double aromaticity in X_3^- (X = Sc, Y, La) clusters

The first systems with double (σ- and π-) aromaticity have been recently reported by Chi and Liu.[63] They

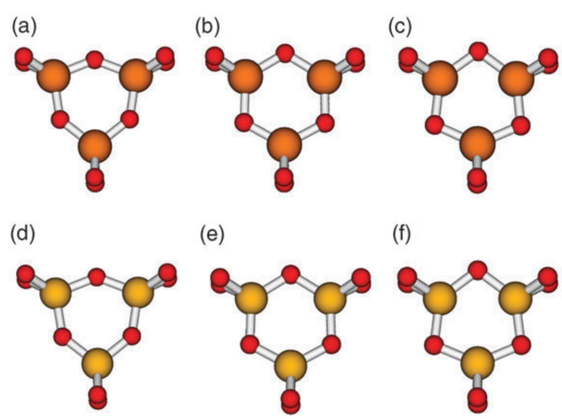

Fig. 9 Optimized structures for M_3O_9 (a, d) $M_3O_9^-$ (b, e) and $M_3O_9^{2-}$ (c, f) (M = Mo, W) clusters.[64]

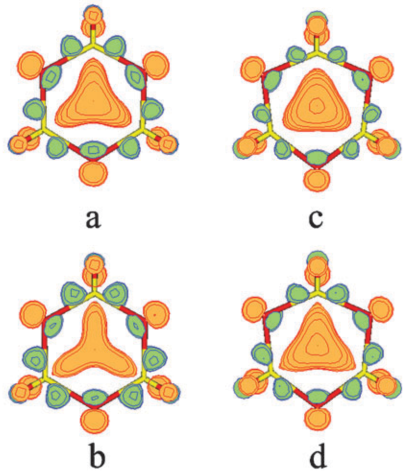

Fig. 10 HOMOs in the $M_3O_9^-$ ((a) M = W, (b) M = Mo) and $M_3O_9^{2-}$ ((c) M = W, (d) M = Mo) species.[64]

demonstrated, using B3LYP, B3PW91, MP2 and CCSD(T) levels of theory with 6-311+G* basis sets for Sc and LANL2DZ basis sets with relativistic effective core potentials for Y and La, that the D_{3h} ($^1A_1'$) structures are the global-minimum structures for X_3^- (X = Sc, Y, La). All three species have the same valence electronic configuration $1a_1'^2 1e'^4 1a_2''^2 2a_1'^2$, though the order of the MOs varies (Fig. 11). Here the $1a_1'$- and $1e'$-MOs are formed by the *ns*-AOs and do not contribute to bonding significantly, because all the bonding and antibonding MOs composed of the *ns*-AOs are occupied and the bonding effect from the $1a_1'$-MO is compensated by the antibonding effect from the $1e'$-MOs. Valence $1a_2''$- and $2a_1'$-MOs are responsible for bonding in the X_3^- anions. The $1a_2''$-MO is a completely bonding π-MO and it renders π-aromaticity. The $2a_1'$-MO is a completely bonding σ-MO and it renders σ-aromaticity in X_3^-. Thus all three anions are d-orbital doubly (σ- and π-) aromatic systems. Chi and Liu[63] also reported large negative NICS values for all three anions, thus supporting the presence of aromaticity in Sc_3^-, Y_3^- and La_3^-.

C. d-AO-based π- and δ- double aromaticity in the $Ta_3O_3^-$ cluster

It was shown by Zhai *et al.*[65] using photoelectron spectroscopy and theoretical calculations that the $Ta_3O_3^-$ cluster possesses a global minimum with a perfect D_{3h} ($^1A_1'$) planar triangular structure (Fig. 12a).

The structure and bonding in $Ta_3O_3^-$ can be understood by analyzing their molecular orbitals (Fig. 12b). Out of 34 valence electrons in $Ta_3O_3^-$, 24 belong to either pure oxygen lone pairs or those polarized towards Ta (responsible

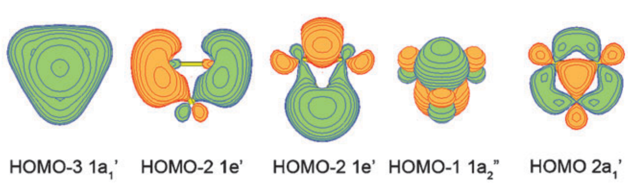

Fig. 11 Valence MOs of X_3^- (X = Sc, Y, La) anions.

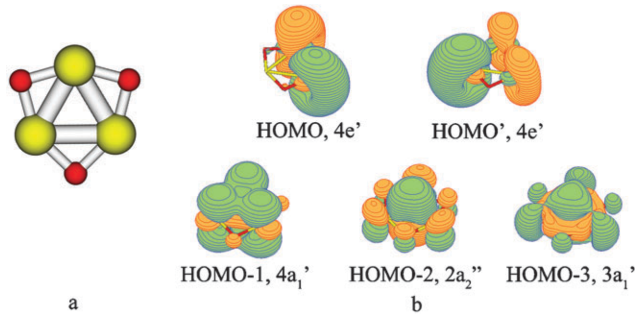

Fig. 12 Optimized structure (a) and valence MOs (b) of $Ta_3O_3^-$.[65]

for the covalent contributions to Ta–O bonding). The other ten valence electrons are responsible for the direct metal–metal bonding, as shown in Fig. 12b. Among the five upper MOs, three MOs are of σ-type: the partially bonding/antibonding doubly-degenerate $4e'$ HOMO and the completely bonding $3a_1'$ HOMO-3. The antibonding nature of the completely occupied doubly-degenerate HOMO significantly reduces the bonding contribution of completely bonding HOMO-3 to the σ-bonding in the Ta_3 framework. If the HOMO ($4e'$) and the HOMO-3 ($3a_1'$) were composed of the same s–d hybrid functions, bonding due to these MOs would be completely canceled. However, the hybridization in the $4e'$ and $3a_1'$ orbitals is somewhat different. Therefore, there should remain some σ-aromatic bonding in $Ta_3O_3^-$. In the $Ta_3O_3^-$ anion, the HOMO-2 ($2a_2''$) is a completely bonding π-orbital composed primarily of the 5d-orbitals of Ta, giving rise to π-aromatic character according to the ($4n + 2$) Hückel rule for π-aromaticity for ring molecules with odd numbers of atoms in the ring. Here, we apply the ($4n + 2$) counting rule (odd number of atoms in the metal cycle) separately for each type of aromaticity encountered in a particular planar system, *i.e.* separately for σ-, π- and δ-type molecular orbitals.

The HOMO-1 ($4a_1'$), which is a completely bonding orbital mainly coming from the overlap of the d_{z^2} orbital on each Ta atom, is in fact a δ-aromatic orbital. This orbital has the "appearance" of a π-orbital with major overlaps above and below the molecular plane, but it is not a π-type MO because it is symmetric with respect to the molecular plane. This MO possesses two nodal surfaces perpendicular to the molecular C_3 axis, and thus it is a δ-orbital (see detailed discussion in ref. 65). Therefore, the $Ta_3O_3^-$ cluster possesses an unprecedented double (δ- and π-) aromaticity, which is responsible for the metal–metal bonding and the perfect triangular Ta_3 framework. The energy ordering of σ (HOMO-3) < π (HOMO-2) < δ (HOMO-1)[65] molecular orbitals indicates that the strength of the metal–metal bonding increases from δ to π to σ, in agreement with the intuitive expectation that σ-type overlap is greater than π-type overlap, and δ-type overlap is expected to be the weakest.

D. d-AO-based σ-, π- and δ- triple aromaticity in the Hf_3 cluster

Averkiev and Boldyrev[66] theoretically predicted that the Hf_3 cluster in the D_{3h}, $^1A_1'$ ($1a_1'^2 2a_1'^2 1e'^4 1a_2''^2 3a_1'^2$) state

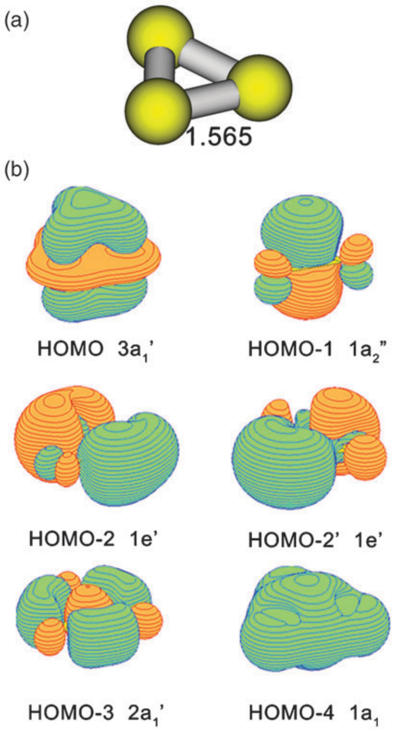

Fig. 13 Optimized structure (a) and valence MOs (b) of the Hf_3 cluster in the D_{3h}, $^1A_1'$ state.

possesses triple (σ-, π- and δ-) aromaticity. The valence $1a_1'$- and $1e'$-MOs are primarily composed out of 6s-AOs of Hf and, as in $Ta_3O_3^-$, do not contribute to bonding significantly (Fig. 13).

The six d-electrons populate the completely bonding delocalized σ-MO ($2a_1'$), π-MO ($1a_2''$) and δ-MO ($3a_1'$) (Fig. 13b). The former three MOs render σ-, π- and δ-aromaticity just like the completely bonding π-delocalized MO in $C_3H_3^+$ renders π-aromaticity in $C_3H_3^+$. Thus the Hf_3 cluster in the D_{3h}, $^1A_1'$ state represents the first example of a chemical system with the triple (σ-, π-, and δ-) aromaticity.

5. Summary and overview

The goal of this review is to demonstrate that the concepts of aromaticity and antiaromaticity, initially introduced in organic chemistry, can and should be applied to the description of chemical bonding in transition-metal systems. At present, systems containing transition-metal clusters are being actively studied both experimentally and theoretically in chemistry and biochemistry. Clearly there is a need for convenient tools that connect electronic structure with molecular properties of such systems. We have shown that aromaticity and antiaromaticity are useful tools indeed for explaining and understanding chemical bonding in transition-metal systems.

Aromaticity and antiaromaticity have been established in the gas-phase Cu_3^+ and Cu_3^- clusters. The aromaticity in Cu_3^+ helped to explain its high symmetry (D_{3h}) structure, high atomization and resonance energies, and high negative value of NICS. The antiaromaticity of Cu_3^- helped to explain its linear structure and low atomization energy.

Similarly, aromaticity in cyclo-Cu_nH_n (n = 3–6), cyclo-M_nH_n (M = Ag, Au; n = 3–6), cyclo-$Au_3L_nH_{3-n}$ (L = CH_3, NH_2, OH, Cl; n = 1–3), cyclo-$Cu_nAg_{3-n}H_n$ (n = 1–3), cyclo-$Cu_nAg_{4-n}H_n$ (n = 1–4), and cyclo-$Cu_nAg_{5-n}H_n$ (n = 1–5) helped to explain the planar cyclic structure of these species, their high binding energies and their negative NICS values. Also, aromaticity in these model systems was used to rationalize the planar cyclic organocopper(I) compounds in the condensed phase. The recognition of aromaticity in the gas-phase Au_5Zn^+ cluster helped to understand its high abundance observed in the mass spectrum. The presence of aromaticity in gas-phase clusters M_4Li_2 (M = Cu, Ag, Au), M_4L_2 and M_4L^- (M = Cu, Ag, Au; L = Li, Na) allowed us to understand the square-planar structure of Cu_4^{2-} and Ag_4^{2-} structural units. The presence of double (σ- and π-) aromaticity in the Hg_4^{6-} building block of the Na_3Hg_2 amalgam explains the square-planar structure as well as its stability in the stabilizing external field of Na^+ cations. π-Aromaticity in M_3^{2-}, NaM_3^-, Na_2M_3 (M = Zn, Cd, Hg) is responsible for their stability. Double (σ- and π-) aromaticity in gas-phase M_3^- (M = Sc, Y, La) clusters is responsible for their high symmetry (D_{3h}) structure, high atomization and resonance energies, and high negative value of NICS.

True d-orbital aromaticity was first observed in $M_3O_9^-$ and $M_3O_9^{2-}$ (M = W, Mo) metal-oxide clusters. The presence of σ-aromaticity in these anions is responsible for their high symmetry (D_{3h}) structure, appreciable resonance energies and high negative value of NICS. The high symmetry (D_{3h}) of $Ta_3O_3^-$ and high first VDE could be explained on the basis of the presence of double (π- and δ-) aromaticity. This oxide cluster is the first example of δ-aromaticity in a transition-metal system. Finally, the Hf_3 cluster in the D_{3h}, $^1A_1'$ ($1a_1'^2 2a_1'^2 1e'^4 1a_2''^2 3a_1'^2$) state is the first example of triple (σ-, π- and δ-) aromaticity.

It is clear that aromaticity and antiaromaticity could be very useful concepts in explaining structure, stability and other molecular properties of isolated and embedded clusters of transition-metal and transition-metal-oxide clusters. The chemical bonding in transition-metal clusters can come from s-AOs, p-AOs, and d-AOs, and can be expressed as a variety of multiple aromaticities and antiaromaticities as well as of conflicting aromaticities. We believe that transition-metal systems with triple antiaromaticity and all types of conflicting aromaticity outlined in the introduction should all exist and should represent a research frontier. Furthermore, atomic f-AOs in lanthanide and actinide clusters offer additional possibilities of forming ϕ-bonds and thus could lead to systems with an even richer variety of ϕ-aromaticity/antiaromaticity. Such systems have not yet been reported and may suggest new research opportunities both computationally and experimentally.

The counting rules for s-AO-based σ-aromaticity are the same as the Hückel $(4n + 2)/(4n)$ rules for aromaticity/antiaromaticity for all cyclic structures. The counting rules for p-AO-based σ-aromaticity are $4n + 4$ (aromaticity) and $4n + 6$ (antiaromaticity) for cyclic structures with an even number of atoms, and $4n + 2$ (aromaticity) and $4n$ (antiaromaticity) for cyclic structures with an odd number of atoms because there are two types of σ-orbitals: $p_{\sigma-r}$- and $p_{\sigma-t}$-MOs which should be considered together. In the simplest case of the occupation of just one $p_{\sigma-r}$- or one $p_{\sigma-t}$-MO the system is also aromatic. For p-AO-based π-aromaticity the counting rules are $(4n + 2)/(4n)$ for aromaticity/antiaromaticity for all cyclic structures. For d-AO-based σ- and π-aromaticity the counting rules are $4n + 4$ (aromaticity) and $4n + 6$ (antiaromaticity) for cyclic structures with an even number of atoms and $4n + 2$ (aromaticity) and 4n (antiaromaticity) for cyclic structures with an odd number of atoms because there two types of σ-orbitals: $d_{\sigma-r}$- and $d_{\sigma-t}$-MOs and two types of p-orbitals: $d_{\pi-r}$- and $d_{\pi-t}$-MOs. For d-AO-based δ-aromaticity the counting rule is $(4n + 2)/(4n)$ for aromaticity/antiaromaticity respectively.

It is hoped that the introduction of the aromatic and antiaromatic concepts would stimulate theoretical analysis of chemical bonding in other known or unknown inorganic compounds and metallo-biomolecules containing transition-metal atoms and clusters. Such analysis may establish simple and robust rules connecting electronic and molecular structures with stability and reactivity. It may be possible that aromaticity and antiaromaticity may become as useful concepts in deciphering the chemical bonding in transition-metal systems as they are in organic chemistry.

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