Aromaticity and antiaromaticity in transition-metal systems

Dmitry Yu. Zubarev, Boris B. Averkiev, Hua-Jin Zhai, Lai-Sheng Wang* and Alexander I. Boldyrev*

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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—d-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 multifold 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.

1. Introduction

Aromaticity in compounds containing a transition-metal atom was first considered in a pioneering paper in 1979 by Thorn and Hoffmann1 on six-membered-ring metalloccyclic compounds that are derived from the prototypical aromatic benzene molecule with one C–H moiety replaced by an isolobal...
transition-metal fragment. Just three years later the first example of a stable, isolable metallobenzene—osmabenzenene—was reported by Elliott et al. A large family of metallobenzenes—the iridabenzenes—was synthesized by Bleeke and co-workers, whereas a series of dimetallobenzenes with two metal atoms incorporated into the benzene ring was synthesized and characterized by Rothwell et al. Recent advances in metallobenzenes have been reviewed by Bleeke, Wright, and Landorf and Haley. A thorough chemical-bonding analysis of metallobenzenes has been recently performed by Fernandez and Frenking. 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 have been published and several conferences 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. 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 have stimulated much interest in extending these ideas to other metal systems, including transition metals. 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. 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∥), σ-radial (σ⊥), and π-aromaticity/antiaromaticity could occur. In this case, there can be multiple (σ and π) aromaticity, multiple (σ and δ) aromaticity, and conflicting aromaticity (simultaneous aromaticity and antiaromaticity or σ-antiaromaticity and π-aromaticity). If d-AOs are involved in chemical bonding, σ-tangential (σ∥), σ-radial (σ⊥), π-tangential (π∥), π-radial (π⊥), and δ-aromaticity/antiaromaticity could occur. In this case, there can be multiple (σ, π and δ) aromaticity, multiple (σ, π and δ) aromaticity, 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, and Zhan et al. showed that the doubly

Table 1 Criteria for π-aromaticity and π-antiaromaticity

<table>
<thead>
<tr>
<th>Property</th>
<th>Aromatic</th>
<th>Olefinic/classical</th>
<th>Antiaromatic</th>
</tr>
</thead>
<tbody>
<tr>
<td>(i) Electronic nature</td>
<td>(4n + 2) π-electron cyclic conjugation</td>
<td>No cyclic conjugation</td>
<td>4n π-electron cyclic conjugation</td>
</tr>
<tr>
<td>(ii) Energy</td>
<td>Stabilization</td>
<td>Standard</td>
<td>Destabilization</td>
</tr>
<tr>
<td>(iii) Geometry</td>
<td>Enhanced</td>
<td>Standard</td>
<td>Decreased</td>
</tr>
<tr>
<td>(iv) Magnetic properties</td>
<td>Equalization</td>
<td>Alternation</td>
<td>Alternation</td>
</tr>
<tr>
<td>(v) Reactivity</td>
<td>e.g., benzene</td>
<td>e.g., cyclohexadiene</td>
<td>e.g., cyclooctatetraene</td>
</tr>
<tr>
<td>(vi) Spectroscopy</td>
<td>High energy</td>
<td>Standard</td>
<td>Low energy</td>
</tr>
<tr>
<td></td>
<td>High symmetry</td>
<td>—</td>
<td>Low symmetry</td>
</tr>
<tr>
<td></td>
<td>High electron-detachment energies</td>
<td>Standard</td>
<td>Low electron-detachment energies</td>
</tr>
</tbody>
</table>
(σ- and π-) aromatic species $\text{Al}_4^{2-}$ has a very high resonance energy of $\sim$48 kcal mol$^{-1}$ and $\sim$73 kcal mol$^{-1}$ respectively. For the prototypical singly-aromatic benzene molecule the resonance energy is only 20 kcal mol$^{-1}$. The ring-current susceptibilities for the doubly-aromatic $\text{Al}_4^{2-}$ dianion were also found to be 10 nA T$^{-1}$, which is higher than 8 nA T$^{-1}$ in benzene.\textsuperscript{42} Fowler \textit{et al.} demonstrated that the contribution to the ring current from σ-delocalized electrons is significantly higher than from π-electrons.\textsuperscript{43, 44} According to Chen \textit{et al.},\textsuperscript{45} $\text{Al}_4^{2-}$ has a significant negative NICS (−30.9 ppm) compared to that in benzene (−9.7 ppm).\textsuperscript{46} Santos \textit{et al.}\textsuperscript{47} showed that $\text{Al}_4^{2-}$ 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.\textsuperscript{35, 45, 46} Studies of magnetic properties of systems with conflicting aromaticity such as Li$_3$Al$_4^{2-}$ and Li$_4$Al$_4$ can lead to contradictory conclusions on the overall aromaticity or antiaromaticity of the system.\textsuperscript{35, 49–51} Conflicting aromaticity also results in floppity geometries of the Li$_3$Al$_4^{2-}$ and Li$_4$Al$_4$ clusters.\textsuperscript{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.\textsuperscript{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$_3$\textsuperscript{+},\textsuperscript{53} cyclo-Cu$_3$H$_6$ ($n = 3–6$),\textsuperscript{54} cyclo-M$_3$H$_6$ ($M = \text{Ag, Au}$; $n = 3–6$),\textsuperscript{55} cyclo-Au$_n$L$_n$H$_{3n}$ ($L = \text{CH}_3$, NH$_2$, OH, Cl; $n = 1–3$),\textsuperscript{56} cyclo-Cu$_3$Ag$_3$H$_9$ ($n = 1–3$),\textsuperscript{56} cyclo-Cu$_3$Ag$_4$H$_n$ ($n = 1–4$), and cyclo-Cu$_3$Ag$_n$H$_n$ ($n = 1–5$),\textsuperscript{57} Au$_3$Zn$^+$,\textsuperscript{58} M$_4$Li$_2$ ($M = \text{Cu, Ag, Au}$),\textsuperscript{59} M$_4$L$_2$ and M$_4$L$^-$ ($M = \text{Cu, Ag, Au}$; $L = \text{Li, Na}$),\textsuperscript{60} Hg$_6$\textsuperscript{2+},\textsuperscript{61} M$_2^-$,\textsuperscript{61} Na$_2$M$_3$,\textsuperscript{62} and Na$_2$M$_3$ ($M = \text{Zn, Cd, Hg}$),\textsuperscript{62} M$_5^-$ ($M = \text{Sc, Y, La}$),\textsuperscript{63} M$_4$O$_6^-$ and M$_4$O$_6^{2-}$ ($M = \text{W, Mo}$),\textsuperscript{64} Ta$_3$O$_5^-$,\textsuperscript{65} and Hf$_2$\textsuperscript{66}.

\section{2. s-AO-based σ-aromaticity and σ-antiaromaticity in transition-metal systems}

\subsection{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,\textsuperscript{67} and then by Havenith \textit{et al.}\textsuperscript{68} and Yong \textit{et al.}\textsuperscript{53} The Cu$_3^+$ anion has a similar $D_{3h}$, 1$A_1^+$ (1$a_1^+1e^-1a_2^+ 2a_1^+1e^-2e^-4 2a_2^+3e^-2e^-3 3a_2^+3a_2^-$) global-minimum structure.\textsuperscript{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 (1$a_1^+1e^-1a_2^+ 2a_1^+1e^-2e^-4 2a_2^+3e^-2e^-3 3a_2^+3a_2^-$) 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 CH$_3$H$_3^+$ cation (Fig. 1b).

\begin{figure}[h]

\centering
\includegraphics[width=\textwidth]{fig1.png}
\caption{(a) The 3$a_1^-$HOMO of Cu$_3^+$ and its schematic representation as a linear combination of 4s-AOs of Cu atoms, (b) 1$a_2^+$HOMO of Cu$_3^+$ and its schematic representation as a linear combination of 2p$_z$-AOs of C atoms.}
\end{figure}

The only difference is that the π-MO is a sum of 2p$_z$-AOs of carbons. The delocalized π-MO in CH$_3$H$_3^+$ renders its π-aromaticity according to the famous 4$n$ + 2 Hückel rule. On the basis of the analogy between the σ-delocalized MO in C$_2$H$_2^+$ and the σ-delocalized MO in Cu$_3^+$ it is reasonable to call the latter σ-aromatic (the 4$n$ + 2 rule holds for σ-aromatic cyclic systems with valence s-AOs participating in bonding).\textsuperscript{10} Yong \textit{et al.}\textsuperscript{53} considered aromaticity in the Cu$_3^+$ cation on the basis of nucleus-independent chemical shift (NICS) indexes.\textsuperscript{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.\textsuperscript{53} Yong \textit{et al.}\textsuperscript{53} also evaluated the resonance energy in the Cu$_3^+$ $D_{3h}$, 1$A_1^+$ using the following equation:

$$\text{Cu}_3\text{Cl}(2v_1, 1A_1^+) \rightarrow \text{Cu}_2 + \text{CuCl}$$

(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 m-AOs participating in bonding) the counting rule is 4$n$ (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 1$a_2^+1e^-$ (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$σ_g^+1σ_u^-$ 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
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$_4$ (reaction 3, CCSD(T)/6-311 + G(2df)/CCSD(T)/6-311 + G* + ZPE/CCSD(T)/6-311 + G*).

\[
\begin{align*}
\text{Cu}_4^+ (D_{ab}, \ 1^1\Sigma^+_{g}) & \rightarrow 2\text{Cu}^2(S) + \text{Cu}^- (1^1S) \\
\Delta E & = +82.4 \text{ kcal mol}^{-1} \\
\text{Cu}_4^+ (D_{ab}, \ 1^1\A^1g) & \rightarrow 2\text{Cu}^2(S) + \text{Cu}^+ (1^1S) \\
\Delta E & = +106.3 \text{ kcal mol}^{-1}.
\end{align*}
\]

### 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$_4$Li$_2$ (M = Cu, Ag, Au) neutral species was studied by Wannere et al.\textsuperscript{59} They found that the Li$_4$M$_4$ species have distorted octahedral $D_{ab}$, $1^1\Sigma^+_g$ 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$_4$Li$_2$, the NPA charge on Li is $+0.8$ e. These authors also reported the NICS values in the centers of Cu$_4$Li$_2$ (14.5 ppm), Ag$_4$Li$_2$ (14.1 ppm) and Au$_4$Li$_2$ (18.6 ppm) (all at PW91/PW91/LANL2DZ) clusters which show the presence of aromaticity in the M$_4^{2-}$ dianions. Wannere et al.\textsuperscript{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$_4$Li$_2$ is indicated by its high (243.2 kcal mol$^{-1}$) atomization energy.

Lin et al.\textsuperscript{60} reported a joint photoelectron spectroscopy and theoretical study of Cu$_4$Na$^-$ and Au$_4$Na$^-$ as well as theoretical results on Cu$_4$Li$^-$, Ag$_4$Li$^-$, Ag$_4$Na$^-$, Au$_4$Li$^-$, Cu$_4$Li$_2$, Ag$_4$Li$_2$, Au$_4$Li$_2$ and Cu$_4$Li$_2$. They found that the Cu$_4$Li$^-$, Cu$_4$Na$^-$, Ag$_4$Li$^-$ and Ag$_4$Na$^-$ anions have a pyramidal structure consistent with the bipyramidal structure reported by Wannere et al., while the Au$_4$Li$^-$ and Au$_4$Na$^-$ anions were found to be planar. The pyramidal structure of Cu$_4$Na$^-$ 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.

Using the gauge-including magnetically-induced current (GIMIC) method, Lin et al.\textsuperscript{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.\textsuperscript{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, then 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$_2$Mg$_2$ main-group clusters with six bonding σ-electrons considered by Alexandrova and Boldyrev.\textsuperscript{67}

### C. s-AO-based σ-aromaticity in the Au$_5$Zn$^+$ cluster and Au$_6$

The Au$_5$Zn$^+$ cation was found to be the most abundant cluster in the mass-spectrum of Au$_5$Zn$^+$ (n = 2–44) by Tanaka et al.\textsuperscript{58} The authors performed MP2/Zn/6-311 + G*/Au/5s5p4d ff calculations and identified three lowest isomers I, II and III for Au$_5$Zn$^+$ (Fig. 3). For the two lowest isomers, Tanaka et al.\textsuperscript{58} presented MO pictures (Fig. 4) showing that six valence σ-electrons are delocalized over the whole cluster. The Au$_5$Zn$^+$ 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.\textsuperscript{69,70}

The MO pattern of Au$_5$Zn$^+$ depicted in Fig. 4 resembles those of prototypical aromatic organic molecules C$_6$H$_6$ and C$_5$H$_5$-$\pi$, except for their nodal properties in the molecular plane. The six delocalized electrons with the appropriate nodal pattern in Au$_5$Zn$^+$ satisfy the 4n + 2 rule for σ-aromaticity. Tanaka et al.\textsuperscript{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$_6$H$_6$ and C$_5$H$_5$, confirming the presence of aromaticity in Au$_5$Zn$^+$. Overall, the Au$_5$Zn$^+$ cluster can be regarded as a σ-aromatic bimetallic cluster with six delocalized σ-electrons and the enhanced stability of Au$_5$Zn$^+$ may be ascribed to its aromaticity.

### D. s-AO-based σ-aromaticity in the cyclo-M$_n$H$_n$ (M = Cu, Ag, Au; n = 3–6), cyclo-Au$_n$Li$_{3-n}$ (L = CH$_3$, NH$_2$, OH, Cl; n = 1–3), cyclo-Cu$_n$Ag$_{8-k}$-$s$-H$_n$ (n = 1–k, k = 3–5) clusters

Tsipis and Tsipis\textsuperscript{54} performed B3LYP/6-311 + G* calculations on Cu$_n$H$_n$ (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$_4$R$_4$ (R = CH$_3$SiMe$_3$) with short Cu–Cu distances of 2.42 Å.\textsuperscript{71} Tsipis
and Tsipis also calculated the 3D structures for Cu₆H₆ (n = 4–6) and concluded that they are significantly less stable than the planar ones. In follow-up articles, Tsipis and co-workers studied cyclo-M₃H₃ (M = Ag, Au; n = 3–6), cyclo-Au₃L₃H₃−ₙ (L = CH₃, NH₂, OH, Cl; n = 1–3), cyclo-Cu₃Ag₁−ₙH₆ (n = 1–3), cyclo-Cu₄Ag₄−ₙH₆ (n = 1–4), and cyclo-Cu₆Ag₅−ₙH₆ (n = 1–5). The Cu₆H₆ (n = 3–6) cyclic species are discussed here, and the other species are similar.

All CuₖHₖ (n = 3–6) species were found to be cyclic with short Cu–Cu distances (between 2.404 Å in Cu₃H₃ to 2.556 Å in Cu₆H₆). Tsipis and Tsipis 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(II) 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 stated that all the metallacycles 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 Cu₄H₄ (D₁₉h, 1A₁g) cluster at the B3LYP/6-311++G** level of theory. According to our NBO analysis the Cu atoms have 4s⁰.⁵⁶3d⁰.⁹¹4p⁰.⁰₂ valence atomic occupations and a effective atomic charge of +0.50 e, while the H atoms have 1s¹.⁴⁹ 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 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 CuₖHₖ cyclic clusters comes from an ionic contribution between H⁻⁰.⁵⁰¹ and Cu⁺¹.⁰⁵¹ and from delocalized MOs composed out of 4s-AOs on Cu. In fact, NBO analysis of Cu₄H₄ reveals one resonance structure (the same way as NBO produces some of the Kekule structures), 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 Cu₄H₄ distorted planar octahedron. This confirms the aromatic nature of the Cu₄H₄ 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 Cu₄H₄ clusters is neither π nor δ but rather σ in nature. Lin et al., however, reported that they did not find any strong magnetically-induced ring current in Cu₄H₄. This might be a sign of the weak aromaticity in Cu₄H₄ clusters. Due to relativistic effects, s–d hybridization started to play a bigger role in Ag₃H₃ and Au₅H₅ 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. Simultaneous presence of aromaticity and antiaromaticity was first used by Martin-Santamaria and Rzepa to explain...
chemical bonding in small carbon rings. Prasang et al. have shown that small carborane molecules containing 3- and 4-membered rings also exhibit both σ- and π-aromaticity. The Hg₄⁶⁻ 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 Hg₄⁶⁻ cluster

Mercury has a closed-shell electron configuration (6s²) and therefore a neutral Hg₄ cluster is expected to be a van der Waals complex. However, it was shown in the solid that one particular sodium–mercury amalgam Na₃Hg₂ contains Hg₄⁶⁻ square units as its building blocks.61 The high stability of the Hg₄⁶⁻ building block was explained once we recognized that it is isoelectronic to the first all-metal aromatic cluster, Al₄³⁻.34

Basically, the bonding in Hg₄⁶⁻ is due to Hg 6p-AOs and the completely occupied Hg d-AOs do not contribute to bonding.61 Fig. 7 displays the seven valence MOs of the square-planar Hg₄⁶⁻, which are very similar to those in Al₄³⁻.34

The HOMO (1b₂g), HOMO-1 (1a₂u) and HOMO-2 (2a₁g) are completely bonding orbitals formed from the Hg 6p-AOs and represent pσ⁻⁻MOs (tangential MO), pσ-MOs and pπ⁻⁻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 6s² lone pairs. Thus, the upper three MOs are mainly responsible for the chemical bonding in Hg₄⁶⁻. 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 pσ⁻⁻ and pπ⁻⁻-AOs. This is the reason why pσ⁻⁻ and pπ⁻⁻-MOs are presented as one set in Fig. 8. On the basis of this mixing in the pσ⁻⁻ and pπ⁻⁻-AOs, the counting rule for σ-electrons for cyclic systems with even number of vertices should be \((4n + 4)/(4n + 6)\) for aromaticity/antiaromaticity.

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Fig. 6 (a) σ-MOs, (b) π-MOs, and (c) δ-MOs composed out of d-AOs of Cu in Cu₄H₄ (D₄h, 1A₁g).

Fig. 7 Valence molecular orbitals of Hg₄⁶⁻.
The occupation of all three bonding MOs in Hg$_3$ makes its shape a perfect square and renders its doubly ($\sigma$- and $\pi$-) aromatic nature. The finding of the double aromaticity in Hg$_4$ is surprising that such an ancient material as amalgams can be a solid bridge between our gas-phase studies of multiply-aromatic clusters and bulk materials containing such species. It is due to the more complicated nodal structure of d-AOs that their $\pi$-aromaticity only, without the formation of $\delta$-MOs, transition metal systems can provide a more diverse array of aromaticity–antiaromaticity combinations. We may expect $\sigma$-tangential ($\sigma_t$), $\sigma$-radial ($\sigma_r$), $\pi$-tangential ($\pi_t$), $\pi$-radial ($\pi_r$) and $\delta$-MOs. For $\sigma$- and $\pi$-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 $\delta$-MOs the counting rule is $(4n + 2)/(4n)$ for aromaticity/antiaromaticity. In general, there can be multiple ($\sigma$-, $\pi$- and $\delta$-) aromaticity, multiple ($\sigma$-, $\pi$- and $\delta$-) antiaromaticity and conflicting aromaticity (simultaneous aromaticity and antiaromaticity among the three types of $\sigma$-, $\pi$- and $\delta$-MOs). So far only a few transition-metal systems with d-AO-based aromaticity have been reported.$^{61-66}$

A. d-AO-based $\sigma$-aromaticity in the Mo$_3$O$_9^{2-}$ and W$_3$O$_9^{2-}$ clusters

The first cases of d-orbital aromaticity in 4d and 5d transition-metal-oxide clusters, Mo$_3$O$_9^{2-}$ and W$_3$O$_9^{2-}$, were reported by Huang et al. by combining photoelectron spectroscopy and theoretical calculations.$^{64}$ They found that the Mo$_3$O$_9^{2-}$ and Mo$_3$O$_9^{2-}$ ($M = Mo, W$) clusters all have $D_{3d}$ 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 Mo$_3$O$_9$ species reduces the M–M distance significantly: 0.25 Å for Mo$_3$O$_9^{2-}$ and 0.29 Å for W$_3$O$_9^{2-}$, and 0.20 Å for Mo$_3$O$_9^{2-}$ and 0.19 Å for W$_3$O$_9^{2-}$. The large geometry changes induced by addition of one or two electrons to the Mo$_3$O$_9$ 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 $\sigma$-HOMO in Mo$_3$O$_9$ and Mo$_3$O$_9^{2-}$ species renders their $\sigma$-aromaticity. Calculations of NICS at the center of Mo$_3$O$_9^{2-}$ ($-20.5$ ppm) and W$_3$O$_9^{2-}$ ($-20.5$ ppm) also support the presence of aromaticity. Huang et al.$^{64}$ also estimated a sizable ($7.6$ kcal mol$^{-1}$) resonance energy for W$_3$O$_9^{2-}$. These results provide solid evidence that the anionic Mo$_3$O$_9^{2-}$, W$_3$O$_9^{2-}$, Mo$_3$O$_9^{2-}$ and W$_3$O$_9^{2-}$ species with the $D_{3d}$ ($\tilde{A}'_1$ or $\tilde{A}'_1$) structure are the first experimentally-confirmed d-orbital aromatic ($\sigma$) species.

B. d-AO-based $\sigma$- and $\pi$- double aromaticity in X$_3^{2-}$ ($X = Sc, Y, La$) clusters

The first systems with double ($\sigma$- and $\pi$-) aromaticity have been recently reported by Chi and Liu.$^{63}$ They

![Fig. 8 Molecular orbital diagram for (a) p-MOs and (b) s-MOs for Hg$_4$.](image)

![Fig. 9 Optimized structures for M$_3$O$_9$ (a, d) M$_3$O$_9^{2-}$ (b, e) and M$_3$O$_9^{2-}$ (c, f) ($M = Mo, W$) clusters.](image)
determined, 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 $D_{3h}$ ($^3A_1'$) structures are the global-minimum structures for $X_3$ (X = Sc, Y, La). All three species have the same valence electronic configuration $1a_1^21e^42a_2^22a_1^2$, though the order of the MOs varies (Fig. 11). Here the $1a_1$, $1e$, and $2e$-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 $2a_2$ and $2a_1$-MOs are responsible for bonding in the $X_3$ anions. The $1a_2$-MO is a completely bonding $\pi$-MO and it renders aromativity. The $2a_1$-MO is a completely bonding $\sigma$-MO and it renders $\sigma$-aromaticity in $X_3$. Thus all three anions are $\sigma$-orbital doubly (\(\sigma\) and $\pi$-) 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 $\pi$- and $\delta$- double aromaticity in the $Ta_3O_3^-$ cluster**

It was shown by Zhai\textit{et al.}\(^{65}\) using photoelectron spectroscopy and theoretical calculations that the $Ta_3O_3^-$ cluster possesses a global minimum with a perfect $D_{3h}$ ($^3A_1'$) 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 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 $\sigma$-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 $\sigma$-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 $\sigma$-aromatic bonding in $Ta_3O_3^-$. In the $Ta_3O_3^-$ anion, the HOMO-2 ($2a_2''$) is a completely bonding $\pi$-orbital composed primarily of the $5d$-orbitals of Ta, giving rise to $\pi$-aromatic character according to the $(4n + 2)$ Hückel rule for $\pi$-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 $\sigma$-, $\pi$-, and $\delta$-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 $\delta$-aromatic orbital. This orbital has the “appearance” of a $\pi$-orbital with major overlaps above and below the molecular plane, but it is not a $\pi$-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 $\delta$-orbital (see detailed discussion in ref. 65). Therefore, the $Ta_3O_3^-$ cluster possesses an unprecedented double ($\delta$- and $\pi$-) aromaticity, which is responsible for the metal–metal bonding and the perfect triangular $Ta_3$ framework. The energy ordering of $\sigma$ (HOMO-3) $< \pi$ (HOMO-2) $< \delta$ (HOMO-1)\(^{65}\) molecular orbitals indicates that the strength of the metal–metal bonding increases from $\delta$ to $\pi$ to $\sigma$, in agreement with the intuitive expectation that $\sigma$-type overlap is greater than $\pi$-type overlap, and $\delta$-type overlap is expected to be the weakest.

**D. d-AO-based $\sigma$-, $\pi$- and $\delta$- triple aromaticity in the $Hf_3$ cluster**

Averkiev and Boldyre\textit{v}\(^{66}\) theoretically predicted that the $Hf_3$ cluster in the $D_{3h}$, $^1A_1'$ ($1a_1^22a_1^21e^42a_2^22a_1^2$) state

**Fig. 10** HOMOs in the $M_3O_9^-$ ((a) $M = W$, (b) $M = Mo$) and $M_3O_{12}^-$ ((c) $M = W$, (d) $M = Mo$) species.\(^{64}\)

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

**Fig. 12** Optimized structure (a) and valence MOs (b) of $Ta_3O_3^-$.\(^{65}\)
Aromaticity and antiaromaticity have been established in cyclo-
C_{0}H_{n} (n = 3–6), cyclo-
M_{0}H_{n} (M = Ag, Au; n = 3–6), cyclo-Au_{2}L_{0}H_{3–n} (L =
CH_{3}, NH_{2}, OH, Cl; n = 1–3), cyclo-Cu_{2}Ag_{3–n}H_{n} (n = 1–3),
cyclo-Cu_{2}Ag_{3–n}H_{n} (n = 1–4), and cyclo-Cu_{2}Ag_{3–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_{2}Zn^{+} cluster helped to understand its high
abundance observed in the mass spectrum. The presence of
aromaticity in gas-phase clusters M_{4}L_{2} (M = Cu, Ag, Au),
M_{4}L_{2} and M_{4}L^{−} (M = Cu, Ag, Au; L = Li, Na) allowed us to
understand the square-planar structure of Cu_{2}^{2−} and Ag_{2}^{2−}
structural units. The presence of double (σ- and π-) aromaticity
in the Hg_{4}^{2−} building block of the Na_{3}Hg_{2} amalgam
explains the square-planar structure as well as its stability in
the stabilizing external field of Na^{+} cations. π-Aromaticity in
M_{2}^{2−}, NaM_{3}^{−}, Na_{2}M_{3} (M = Zn, Cd, Hg) is responsible for
their stability. Double (σ- and π-) aromaticity in gas-phase
M_{4}^{−} (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_{4}O_{9}^{−}
and M_{4}O_{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_{3}O_{6}^{−} and first VDE could be explained on the basis
of the presence of double (σ- 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′}
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 possi-
bilities 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 (anti-
aromaticity) for cyclic structures with an odd number of atoms
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5. Summary and overview

The goal of this review is to demonstrate that the concepts of
aromaticity and antiaromaticity, initially introduced in organ-
ic 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_{n}H_{n} (n = 3–6), cyclo-
M_{n}H_{n} (M = Ag, Au; n = 3–6), cyclo-Au_{2}L_{n}H_{3–n} (L =
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the occupation of just one pσMO or one pπMO 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 are two types of σ-orbitals: dσσ- and dσπ- t-MOs. For d-AO-based σ-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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