The method used by Matsumoto *et al.* to synthesize their semiconductor also deserves attention. The authors used a new breed of material preparation called combinatorial synthesis, which is becoming increasingly important for screening the vast range of possible compositions and conditions available to inorganic materials (*8*). In Matsumoto *et al.*'s experiments, intense ultraviolet laser light hits selected targets, giving rise to ablation of the material (see the figure on page 840). The ablated material is deposited on a separate substrate in an oxygen atmosphere, resulting in doped oxide formation. The use of masks leads to a series of thin films with different compositions on a single substrate while keeping other growth conditions virtually constant.

Combinatorial synthesis is critically important for performing efficient searches for materials with specific properties. Promising alternatives such as material design based on first-principle calculations are being developed and have been applied to transition metal–doped zinc oxides (*9*), but the extent to which the method can be applied remains to be seen.

What gives rise to room-temperature ferromagnetism in the new material is not clear yet. The mean field model for carrier-induced ferromagnetism in III-V and II-VI magnetic semiconductors (*10*) does not seem capable of explaining the observations. More investigation is necessary to elucidate the underlying mechanism.

Matsumoto *et al.*'s discovery of a transparent semiconductor with room-temperature ferromagnetism adds a new dimension to the already widespread use of permanent magnets in our everyday life, from refrigerator magnets to mass storage in information technology. Through this transparent material, we get a glimpse of the spintronic devices of the future.

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PERSPECTIVES: CHEMISTRY

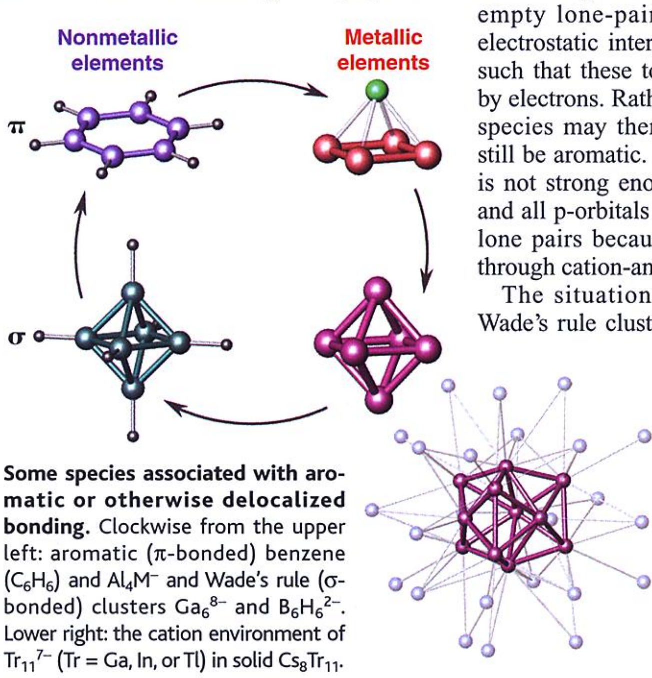
Aromatic Metal Clusters

Dong-Kyun Seo and John D. Corbett

Why certain molecules are more stable than others is not always easy to understand, not least because nature's diversity does not permit a unified answer for all classes of compounds. Among the useful concepts is aromaticity, the simplest and yet most successful description of the particular stability of unsaturated cyclic hydrocarbons with 2, 6, 10, ... ($4n + 2$) electrons delocalized in π-orbitals perpendicular to the ring plane. A similar concept, Wade's rules for closed shell deltahedra (*1*), describes delocalized σ-bonding among gas-phase and solid-state cluster compounds, including those of the electron-poor elements Ga, In, and Tl (*2*, *3*). But stability based on aromaticity has not been confirmed unambiguously for any molecular moiety other than the hydrocarbons and related compounds (*4*).

On page 859 of this issue, Li *et al.* (*5*) report the most convincing evidence to date for aromaticity in an all-metal system. The authors have created through laser vaporization a series of bimetallic clusters consisting of a square planar Al_4^{2-} anion face-capped by an M^+ cation (M = Li, Na, Cu) (see the figure). Photoelectron spectroscopic measurements and ab initio calculations show that the anions have two electrons in the π-bonding highest occupied molecular orbital (HOMO) on Al_4^{2-}. The results have important implications for related polyanions in the solid state.

In considering the electronic structures of clusters without externally bound atoms, it is customary to fill lone-pair molecular orbitals (MOs—orbitals delocalized over three or more atoms), which are regarded as nonbonding, with two electrons. This is also consistent with the electronic structure schemes for hydrogen-terminated carbon or boron clusters. It is therefore tempting to assume that an aromatic Al_4 cluster should have six negative charges and should be isoelectronic with the analogous $C_4H_4^{2+}$. In contrast, Li *et al.*'s novel aluminum tetramer has only two negative charges and yet exhibits one filled π-HOMO because two of the four lone-pair–like MOs lie higher in energy and are empty, whether an M^+ ion is attached or not. The expected instability of Al_4^{2-} toward the loss of an electron ($Al_4^{2-} \rightarrow Al_4^- + e^-$) is eliminated by the substantial coulombic (and covalent) energy, around 200 kcal/mol, that is gained upon capping the square with M^+ to form Al_4M^+ (*6*). This is reminiscent of the importance of cation-aromatic ring interactions in organic and biological systems (*7*).



Some species associated with aromatic or otherwise delocalized bonding. Clockwise from the upper left: aromatic (π-bonded) benzene (C_6H_6) and Al_4M^- and Wade's rule (σ-bonded) clusters Ga_6^{8-} and $B_6H_6^{2-}$. Lower right: the cation environment of Tr_{11}^{7-} (Tr = Ga, In, or Tl) in solid Cs_8Tr_{11}.

Will this π-bonding be preserved in an equivalent Al_4^{2-} unit when the tetramer is surrounded by cations in a solid? Probably not, for the following reasons. First, the surrounding cations will probably stabilize empty lone-pair–like orbitals through electrostatic interactions and polarization, such that these too will need to be filled by electrons. Rather than M_2Al_4, the stable species may then be M_6Al_4, which may still be aromatic. Second, if the π-bonding is not strong enough, it may break down and all p-orbitals may be filled to become lone pairs because of the energy gained through cation-anion interactions.

The situation is rather different for Wade's rule clusters. Their polyhedral geometries (see the figure) allow the formation of only skeletal σ-orbitals, in addition to lower lying lone pairs (or B–H bonds in the case of the boranes) that are always filled. There is no evidence that stabilization of lone pairs by cations drastically alters the electronic

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structures of the many Wade's rule clusters of the heavier group 13 to 15 elements.

Over the past decade, we and others have shown that the remarkable stability of alkali metal salts of Ga, In, and Tl clusters must in part originate from the large coulombic energy attained through intimate packing of the surrounding cations with cluster anions (*8*). Some of these polyanions follow Wade's rule (such as the octahedral Ga_6^{8-} and the tetrahedral In_4^{8-}), whereas many others are hypoelectronic by this criterion (for example, In_{11}^{8-} and Tl_{13}^{11-}) and form new deltahedral configurations (*2*). No aluminum analogs have been found, however; in fact, Al forms alkali-metal compounds only with Li.

The above results suggest indirectly that potential M_2Al_4 or $M'Al_4M$ salts will not be stable in the solid state. First, the clusters of the heavier group 13 elements appear to be stable as simple salts only when many alkali metal cations surround each cluster, thus preventing additional bond formation between the polyanions; the lowest ratio of cations per cluster known is for In_{11}^{7-} and its analogs (see the figure), although examples with still lower ratios may be found in network structures (*3*). Second, further reaction and condensation of MAl_4^- clusters are expected because of the availability of low-energy, vacant "frontier orbitals," which play an important role in many reactions in condensed systems (*9*). [In contrast, isosteric clusters of later, electron-richer main-group metals, such as the square planar analog Bi_4^{2-} with all skeletal bonding and lone-pair orbitals filled, are even stable to amines (*3*).] Phosphine ligands R_3P are commonly used to stabilize polygold clusters against further condensation (*10*), and something similar may be possible here. But even if these attempts are unsuccessful, the hypothetical aromatic M_6Al_4 species already noted may be better candidates for synthesis and may turn out to be stable in the solid state. Chemistry is exciting when novel ways are found to get around such perceived problems, which are always too heavily predicated on just what is known.

Li *et al.*'s surprising aluminide clusters not only extend aromaticity into metallic elements but also bring to our attention to other factors that govern structural patterns and the stability of solids. These are especially clear here because the aromatic clusters are gaseous, allowing the origin of their stability to be singled out in terms of their electronic structures. Similarly interesting gas-phase species can be anticipated for heavier elements such as Ga, In, and Tl, for which the strength of π-bonding has been controversial and the lone-pair states are increasingly core-like (*2*, *11*).

References and Notes

1. All the faces of a deltahedron are triangles. The simplest regular deltahedron is the tetrahedron, and the most complex is the icosahedron.

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4. Recent studies have shown that aromatic polysilicon anions exist in solids (*12*), but aromaticity is by no means the only important factor determining their stability (*13*).

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NOTA BENE: ANIMAL BEHAVIOR

Texas Elephants Stomp to Victory

The old saying "putting an ear to the ground" may turn out to be literally true for elephants, according to a recent report by O'Connell-Rodwell and her colleagues (*1*). When elephants generate their low-frequency vocalizations (rumbles), acoustic sound waves traveling through the air are accompanied by seismic waves that travel through the ground. Given that a variety of creatures, from insects to rodents and even the enormous elephant seal, use the generation and detection of terrestrial vibrations to communicate, O'Connell-Rodwell and her team wondered if elephants, too, have this seismic signaling capability.

Eschewing the grasslands of Africa for a residential facility in Texas, the scientists analyzed acoustic and seismic signals generated by two captive Asian elephants. Whenever the elephants "rumbled" or stomped their feet during mock charges, seismic data were collected with geophones—sensitive microphones placed 10 m and 30 m from the elephants' pen that transformed terrestrial vibrations into electrical signals. Simultaneously, acoustic data were collected with audio equipment.

The seismic and acoustic waves generated by rumbles and foot stomps had similar frequencies (20 to 24 Hz) that fell within the ideal range for the long-distance transmission of low-frequency sounds. Intriguingly, the two sets of waves had different velocities (248 to 264 m/s in the ground, and 309 m/s in the air), so that they were no longer in phase as they traveled further away from their source. This hints that elephants may make their rumbles and foot stomps loud enough to produce separate acoustic and seismic waves.

Through mathematical modeling, the investigators estimated that the seismic waves created by their stomping elephants traveled at least 36 km. Conceivably, these long-distance seismic signals may enable elephants to communicate with other herds. The location of a distant herd could be pinpointed by assessing the time delay between the arrival of seismic and acoustic signals.

Elephants are known to move toward thunderstorms that are more than 25 km away, too far for them to hear the sound of thunder. It is possible that they can detect the terrestrial vibrations associated with distant storms, presumably a major advantage in their search for new water sources.

Generating seismic signals is easy, but what about detecting them? The elephant's trunk has mechanoreceptors that respond to mechanical pressure. There may also be similar receptors in the elephant's well-innervated foot pads. These mechanoreceptors may explain foot-lifting behavior during which elephants lean forward and lift up one foot, possibly to improve their sensitivity to ground vibrations.

Establishing that elephants use seismic signaling for long-distance communication is no easy task. Undaunted, O'Connell-Rodwell and her team plan to train their elephants to respond to seismic waves by pulling a lever with their trunk or pressing a button with their feet—with, of course, the provision of a reward for the correct response.

—**ORLA SMITH**

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