copper ion with interconversion between square pyramidal and trigonal bipyramidal forms, yielding a water exchange rate of $(5.7 \pm 0.2) \times 10^9\ \mathrm{s^{-1}}$, slightly enhanced with respect to the value obtained previously assuming sixfold coordination [$(4.4 \pm 0.1) \times 10^9\ \mathrm{s^{-1}}$] (*15*).

The frequency of occurrence of both five- and sixfold-coordinated Cu(II) ions in crystalline compounds (*24*) suggests that these coordinations are competitive. This work shows that, at variance with the sixfold coordination of cations of similar charge and size such as Ni(II) and Mg(II) (*26*), the Cu(II) aqua ion adopts a fivefold coordination. This is a direct consequence of the $3d^9$ electronic structure of its atomic shell, which causes a departure from octahedral coordination because of the Jahn-Teller effect.

References and Notes

1. E. Ochiai, *Bioinorganic Chemistry, An Introduction* (Allyn & Bacon, Boston, 1977).
2. H. Ohtaki, M. Maeda, *Bull. Chem. Soc. Jpn.* **47**, 2197 (1974).
3. M. Magini, *Inorg. Chem.* **21**, 1535 (1982).
4. G. Licheri *et al.*, *J. Chem. Phys.* **80**, 5308 (1984).
5. T. K. Sham, J. B. Hastings, M. L. Perlman, *Chem. Phys. Lett.* **83**, 391 (1981).
6. Y. Tajiri, H. Wakita, *Bull. Chem. Soc. Jpn.* **59**, 2285 (1986).
7. M. Nomura, T. Yamaguchi, *J. Chem. Phys.* **92**, 6157 (1988).
8. J. Garcia *et al.*, *Chem. Phys.* **132**, 295 (1989).
9. B. Beagley *et al.*, *J. Phys. Condens. Matter* **1**, 2395 (1989).
10. P. S. Salmon, G. W. Neilson, J. E. Enderby, *J. Phys. C Solid State Phys.* **21**, 1335 (1988).
11. P. S. Salmon, G. W. Neilson, *J. Phys. Condens. Matter* **1**, 5291 (1989).
12. S. E. Okan, P. S. Salmon, *Mol. Phys.* **85**, 981 (1995).
13. P. S. Salmon, W. S. Howells, R. Mills, *J. Phys. C Solid State Phys.* **20**, 5727 (1987).
14. R. Poupko, Z. Luz, *J. Chem. Phys.* **57**, 3311 (1972).
15. D. H. Powell, L. Helm, A. E. Merbach, *J. Chem. Phys.* **95**, 9258 (1991).
16. D. H. Powell, G. W. Neilson, J. E. Enderby, *J. Phys. Condens. Matter* **1**, 8721 (1989).
17. ———, *J. Phys. Condens. Matter* **5**, 5723 (1993).
18. R. Car, M. Parrinello, *Phys. Rev. Lett.* **55**, 2471 (1985).
19. A. Pasquarello, K. Laasonen, R. Car, C. Lee, D. Vanderbilt, *Phys. Rev. Lett.* **69**, 1982 (1992).
20. K. Laasonen, A. Pasquarello, R. Car, C. Lee, D. Vanderbilt, *Phys. Rev. B* **47**, 10142 (1993).
21. These solutions were acidified to suppress hydrolysis.
22. J. C. Gallucci, R. E. Gerkin, *Acta Crystallogr.* **C45**, 1279 (1989).
23. The neutron diffraction measurements were carried out at ambient temperature (26°C) using the D4B diffractometer at the Institut Laue-Langevin in Grenoble. The wavelength of the incident neutrons was 0.6991 Å, and the momentum transfer range measured by the diffractometer extended to a maximum value of $Q_{\mathrm{max}} \approx 16$ Å^{-1}. In the data reduction, we took the total cross sections for H_2O and D_2O at the incident wavelength from (*32*) and all the other neutron scattering lengths and cross sections from (*33*).
24. B. J. Hathaway, in *Comprehensive Coordination Chemistry*, G. Wilkinson, Ed. (Pergamon, Oxford, 1987), vol. 5, pp. 533–774.
25. Charge neutrality was ensured by adding a uniform background of negative charge. We used a cubic supercell at the experimental density of water. Valence electronic wave functions were expanded on a plane-wave basis set, and core-valence interactions were accounted for by ultrasoft pseudopotentials (*20*). The exchange and correlation energy was described by a generalized gradient approximation (*28, 29*), which has been shown to give an accurate description for liquid water (*27, 34*). We used a spin-polarized functional to cope with the open-shell electronic structure in this system.
26. D. T. Richens, *The Chemistry of Aqua Ions* (Wiley, Chichester, UK, 1997).
27. P. L. Silvestrelli, M. Parrinello, *J. Chem. Phys.* **111**, 3572 (1999).
28. A. D. Becke, *Phys. Rev. A* **38**, 3098 (1988).
29. C. Lee, W. Yang, R. G. Parr, *Phys. Rev. B* **37**, 785 (1988).
30. J. Burgess, *Ions in Solution: Basic Principles of Chemical Interactions* (Ellis Horwood, Chichester, UK, 1988), p. 34.
31. S. F. Lincoln, A. E. Merbach, *Adv. Inorg. Chem.* **42**, 1 (1995).
32. D. I. Garber, R. R. Kinsey, *Brookhaven Natl. Lab.* **BNL 325**, 3rd Ed., Vol. II (1976).
33. V. F. Sears, *Neutron News* **3**, 26 (1992).
34. M. Sprik, J. Hutter, M. Parrinello, *J. Chem. Phys.* **105**, 1142 (1996).
35. We thank A. Dal Corso, A. Stirling, and J. C. Wasse for useful interactions. A.P. and D.H.P. acknowledge support from the Swiss National Science Foundation under the program PROFIL. I.P. thanks the University of East Anglia for financial support. Partial support from the Fonds UNIL-EPFL 1997 is acknowledged by the groups at ICMA and IRRMA. The calculations were performed on the NEC-SX4 of the Swiss Center for Scientific Computing.

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Observation of All-Metal Aromatic Molecules

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Aromaticity is a concept invented to account for the unusual stability of an important class of organic molecules: the aromatic compounds. Here we report experimental and theoretical evidence of aromaticity in all-metal systems. A series of bimetallic clusters with chemical composition $\mathrm{MAl_4^-}$ (M = Li, Na, or Cu), was created and studied with photoelectron spectroscopy and ab initio calculations. All the $\mathrm{MAl_4^-}$ species possess a pyramidal structure containing an $\mathrm{M^+}$ cation interacting with a square $\mathrm{Al_4^{2-}}$ unit. Ab initio studies indicate that $\mathrm{Al_4^{2-}}$ exhibits characteristics of aromaticity with two delocalized π electrons (thus following the $4n + 2$ electron counting rule) and a square planar structure and maintains its structural and electronic features in all the $\mathrm{MAl_4^-}$ complexes. These findings expand the aromaticity concept into the arena of all-metal species.

The name "aromatic compound" was initially bestowed on benzene, its derivatives, and related compounds because of their aroma. Today, the terms "aromatic" and "aromaticity" are used to describe cyclic, planar, and conjugated molecules possessing $(4n + 2)\ \pi$ electrons and having specific chemical and structural stability. Despite the undeniable usefulness of the aromaticity concept, it remains controversial and its physical origin is still being debated (*1–3*). Thus, recent years have seen a resurgence in the development of various criteria of aromaticity and in theoretical investigations aimed at gaining a deeper insight into the origin of this phenomenon (*4–8*). In this report, we present experimental and theoretical evidence of aromaticity in an all-metal system: the $\mathrm{Al_4^{2-}}$ dianion in a series of bimetallic ionic systems with chemical composition $\mathrm{MAl_4^-}$ (M = Li, Na, or Cu). The $\mathrm{Al_4^{2-}}$ unit was found to be square planar and to possess two delocalized π electrons, thus conforming to the $(4n + 2)$ electron counting rule for aromaticity.

Using a laser vaporization source and negative ion photoelectron spectroscopy (*9, 10*), we produced and investigated a series of $\mathrm{MAl_4^-}$ clusters (*11*). The negative ion technique affords convenient size selectivity, and photoelectron spectroscopy is quite suitable for providing unique electronic structure information pertaining to the neutral species. We have found that combining photoelectron spectroscopy and ab initio calculations offers a particularly powerful approach to investigating the structure and bonding of novel molecular and cluster species (*12*). Photoelectron spectra of the three $\mathrm{MAl_4^-}$ species were measured at two different photon energies. The spectra of the three species are similar (Fig. 1), each with an intense threshold peak (*X* and *A*) followed by two weaker features (*B* and *C*). The *X* and *A* features overlapped heavily and were only resolved in the 355-nm spectrum of $\mathrm{NaAl_4^-}$. The vertical electron detachment energies of these features were measured from the peak maxima (Table 1) and compared to the results of the

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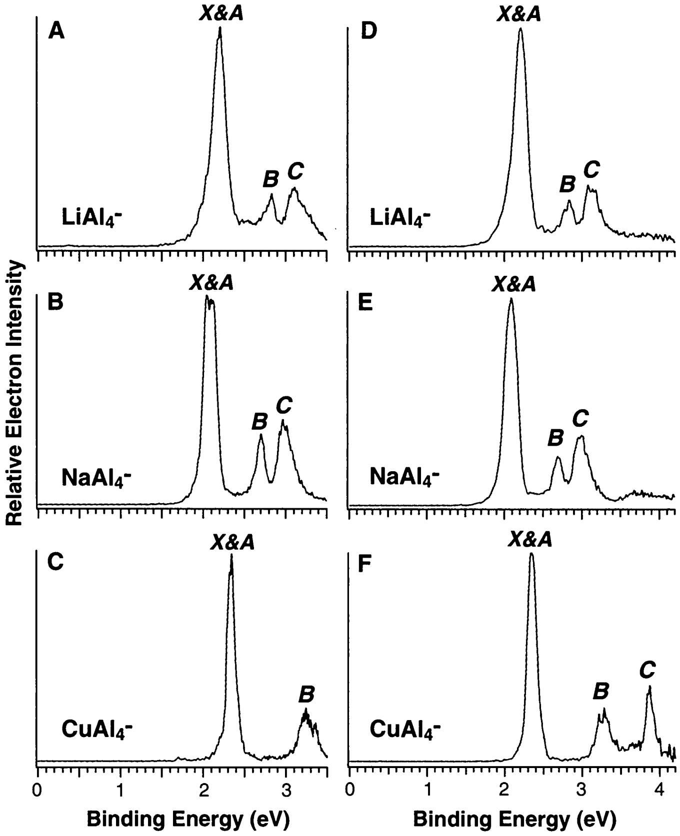
Fig. 1. Photoelectron spectra at 355 nm (3.496 eV) for (**A**) $LiAl_4^-$, (**B**) $NaAl_4^-$, and (**C**) $CuAl_4^-$ and at 266 nm (4.661 eV) for (**D**) $LiAl_4^-$, (**E**) $NaAl_4^-$, and (**F**) $CuAl_4^-$. The four detachment features are labeled *X*, *A*, *B*, and *C* (see Table 1).



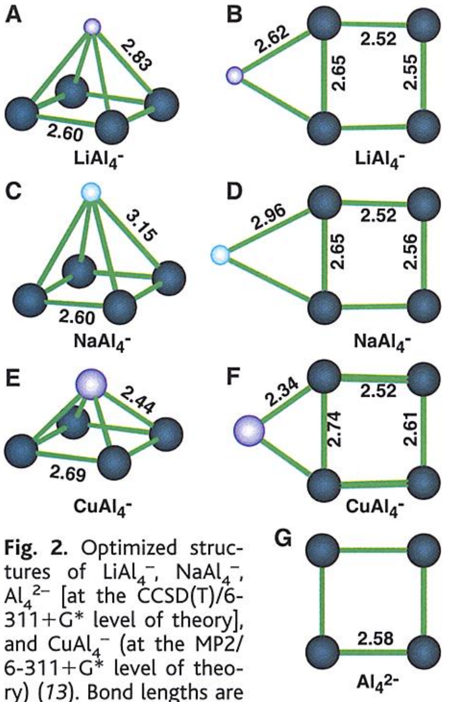


Fig. 2. Optimized structures of $LiAl_4^-$, $NaAl_4^-$, Al_4^{2-} [at the CCSD(T)/6-311+G* level of theory], and $CuAl_4^-$ (at the MP2/6-311+G* level of theory) (*13*). Bond lengths are given in Å. (**A**) Square pyramidal $LiAl_4^-$ (C_{4v}, $^1A_1$). (**B**) Fully planar $LiAl_4^-$ (C_{2v}, $^1A_1$). (**C**) Square pyramidal $NaAl_4^-$ (C_{4v}, $^1A_1$). (**D**) Fully planar $NaAl_4^-$ (C_{2v}, $^1A_1$). (**E**) Square pyramidal $CuAl_4^-$ (C_{4v}, $^1A_1$). (**F**) Fully planar $CuAl_4^-$ (C_{2v}, $^1A_1$). (**G**) Square planar Al_4^{2-} (D_{4h}, $^1A_1$).

ab initio calculations discussed below.

We performed ab initio calculations on a wide variety of structures in a search for the global minimum, using three different theoretical methods (*13*, *14*). We found that the most stable structure for all three MAl_4^- species is a square pyramid (Fig. 2) consisting of an M^+ cation coordinated to a square planar Al_4^{2-} unit. All the MAl_4^- species were also found to possess a fully planar low-lying isomer, with the M^+ cation coordinated to the edge of a square planar Al_4^{2-} unit. The optimized geometries, vibrational frequencies, and relative energies agreed well at the three levels of theory used in this work for all three MAl_4^- species. At our highest level of theory, the pyramidal structures were found to be more stable than the planar structures by 5.6, 7.6, and 7.6 kcal/mol for $LiAl_4^-$, $NaAl_4^-$, and $CuAl_4^-$, respectively. Other isomers were also located, but all had higher energies than the pyramidal and planar structures. Therefore, we conclude that the pyramidal structures detailed in Fig. 2 are the global minimum for the MAl_4^- species.

We also determined theoretical predictions for the four lowest lying, vertical, one-electron detachment processes for the pyramidal and planar species (Table 1). Excellent agreement was obtained for all three anions between the theoretical vertical detachment energies (VDEs) of the pyramidal structures and the experimental spectra. The predicted VDEs for the low-lying planar isomers do not agree well with the experimental data, suggesting that this isomer was not significantly populated in the experiment. We have found previously that the Green's Function method used here is capable of predicting photoelectron spectral features fairly accurately (*12*). Therefore, the excellent agreement between the calculated spectra for the pyramidal structures and the experimental spectra lends considerable support to the idea that the pyramidal structures are the global minimum for the MAl_4^- species.

The local structure of the Al_4^{2-} unit appears to be similar or nearly identical in both the pyramidal global minima and the low-lying planar isomer of all three MAl_4^- species (Fig. 2). To gain more insight into the structural and bonding properties of the MAl_4^- systems, we performed a detailed theoretical investigation of the isolated Al_4^{2-} species. Even though this dianion was not expected to be thermodynamically stable toward autodetachment of an electron, we anticipated that metastable local minima could be located. Indeed, we found a perfect planar structure for the isolated Al_4^{2-} (Fig. 2G). The isolated square planar Al_4^{2-} seems to undergo very little structural change in forming the MAl_4^- molecules. To understand the planarity and structural integrity of the Al_4^{2-} unit, we analyzed its valence molecular orbitals (Fig. 3). The highest occupied molecular orbital (HOMO), which is doubly occupied, is a delocalized π orbital; the rest of the molecular orbitals are either bonding σ-type or lone pairs. The observation of the delocalized π HOMO is surprising. We found that a similar delocalized π orbital is also present in the MAl_4^- species in both its pyramidal and planar isomers. This π orbital holds the key to understanding the structure and bonding of the MAl_4^- species.

Examination of its structure and bonding revealed that Al_4^{2-} exhibits characteristics of aromaticity. First, it possesses two completely delocalized π electrons (Fig. 3), which satisfy the $(4n + 2)$ electron counting rule for aromatic compounds. Second, Al_4^{2-} has a perfect square structure, due to the delocalization of the π electrons, exactly as expected for an aromatic system. Analogy can be made with the prototypical aromatic system, benzene, in which aromaticity is responsible for its perfect hexagonal structure with all equal C-C bonds, rather than the classical alternating single and double bonds. Finally, like benzene in $M(C_6H_6)_2$ sandwich complexes, the Al_4^{2-} dianion preserves its structural integrity in forming the MAl_4^- complexes (Fig. 2). Furthermore, we found that the vibrational frequencies of the isolated Al_4^{2-} dianion are very similar to those in the pyramidal and planar structures of the three MAl_4^- species. We also investigated theoretically the structures of neutral M_2Al_4 species and found

Table 1. Experimental (exp.) and theoretical (theo.) vertical electron detachment energies in eV for $LiAl_4^-$, $NaAl_4^-$, and $CuAl_4^-$. MO, molecular orbital.

Observed features	VDE (exp.)	Square pyramid		Fully planar	
		MO	VDE (theo.)*	MO	VDE (theo.)*
			$LiAl_4^-$		
X	2.15 ± 0.06	$3a_1$	2.09 (0.86)	$4a_1$	1.96 (0.86)
A	2.20 ± 0.06	$1b_1$	2.17 (0.85)	$1b_1$	1.98 (0.86)
B	2.82 ± 0.08	$2a_1$	2.69 (0.85)	$3a_1$	2.52 (0.85)
C	3.09 ± 0.04	$1b_2$	2.97 (0.85)	$2b_2$	3.01 (0.85)
			$NaAl_4^-$		
X	2.04 ± 0.05	$3a_1$	1.92 (0.86)	$1b_1$	1.83 (0.85)
A	2.09 ± 0.05	$1b_1$	2.05 (0.85)	$4a_1$	1.86 (0.86)
B	2.70 ± 0.05	$2a_1$	2.52 (0.86)	$3a_1$	2.31 (0.85)
C	2.96 ± 0.05	$1b_2$	2.86 (0.84)	$2b_2$	2.83 (0.84)
			$CuAl_4^-$		
X	2.32 ± 0.06	$2b_1$	2.32 (0.86)	$2b_1$	2.18 (0.86)
A	2.35 ± 0.06	$4a_1$	2.39 (0.87)	$6a_1$	2.21 (0.86)
B	3.24 ± 0.09	$2b_2$	3.35 (0.85)	$5a_1$	3.24 (0.85)
C	3.84 ± 0.06	$3a_1$	3.65 (0.86)	$3b_2$	3.33 (0.86)

*The VDEs were calculated at the OVGF/6-311+G(2df) level of theory. The numbers in parentheses indicate the pole strength, which characterizes the validity of the one-electron detachment picture.

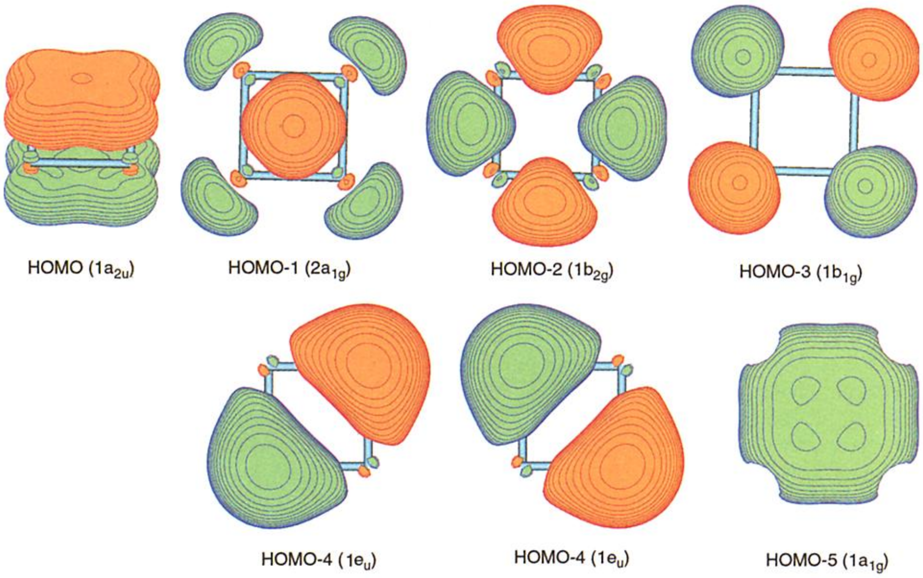


Fig. 3. Molecular orbital pictures (*17*) of square planar Al_4^{2-}, showing the HOMO ($1a_{2u}$) down to the fifth valence molecular orbital from the HOMO (HOMO-5, $1a_{1g}$). HOMO-4 consists of a degenerate pair ($1e_u$).

again that the most stable structures contain the intact Al_4^{2-} dianion.

Polyanions of the main group elements (known as Zintl anions) are building blocks of an interesting class of ionic solids (*15*, *16*). Zintl phases with the stoichiometry Na_2In, $Na_2K_{21}Tl_{19}$, La_3In_5, and many others [see a recent review (*15*)] have been synthesized, in which catenation (element-element bonding) leads to the formation of In_4^{8-}, Tl_5^{7-}, and In_5^{9-} multiply charged cluster anions. However, despite the fact that a large number of Ga, In, and Tl Zintl anions have been synthesized, their Al analogs are still elusive (*15*). The current Al_4^{2-} dianion is fundamentally different from the previously discovered heavy group-13 X_4-type polyanions, which are all tetrahedral. We believe that aromatic square planar X_4^{2-} clusters, like Al_4^{2-}, may in fact exist for the heavier group-13 elements (Ga, In, and Tl). Therefore, the current finding may not only expand the aromaticity concept into an all-metal system but may also indicate whole classes of new inorganic aromatic species.

References and Notes

1. E. D. Bergman, B. Pullman, Eds., *Aromaticity, Pseudoaromaticity, Antiaromaticity* (Israel Academy of Science and Humanities, Jerusalem, Israel, 1971).
2. P. J. Garratt, *Aromaticity* (Wiley, New York, 1986).
3. V. I. Minkin, M. N. Glukhovtsev, B. Ya. Simkin, *Aromaticity and Antiaromaticity* (Wiley, New York, 1994).
4. W. J. Hehre, L. Radom, P. v. R. Schleyer, J. A. Pople, *Ab Initio Molecular Orbital Theory* (Wiley, New York, 1986).
5. Y. Xie, H. F. Schaefer III, J. S. Thrasher, *J. Mol. Struct. Theochem.* **234**, 247 (1991).
6. S. Shaik, A. Shurki, D. Danovich, P. C. Hiberty, *J. Mol. Struct. Theochem.* **155**, 398 (1997).
7. P. v. R. Schleyer, H. Jiao, *Pure Appl. Chem.* **38**, 209 (1996).
8. P. v. R. Schleyer, H. Jiao, N. J. R. v. E. Hommes, V. G. Malkin, O. L. Malkina, *J. Am. Chem. Soc.* **119**, 12669 (1997).
9. L. S. Wang, H. S. Cheng, J. Fan, *J. Chem. Phys.* **102**, 9480 (1995).
10. L. S. Wang, H. Wu, in *Advances in Metal and Semiconductor Clusters. IV. Cluster Materials*, M. A. Duncan, Ed. (JAI Press, Greenwich, CT, 1998), pp. 299–343.
11. The MAl_4^- species were produced with a laser vaporization supersonic cluster source. A Cu/Al alloy target was used to produce the $CuAl_4^-$ anions, whereas an Al/Li_2CO_3 (Na_2CO_3) composite target was used to produce $LiAl_4^-$ ($NaAl_4^-$). The anionic species produced were analyzed with a time-of-flight mass spectrometer. The MAl_4^- anions of interest were selected for photodetachment in each experiment. Photoelectron spectra were taken at two detachment laser wavelengths, 355 and 266 nm, and were calibrated using the known spectra of Cu^-. The photoelectron energy resolution was about 25 meV for 1-eV electrons.
12. L. S. Wang, A. I. Boldyrev, X. Li, J. Simons, *J. Am. Chem. Soc.* **122**, 7681 (2000).
13. We initially optimized geometries and calculated frequencies of $Cu^+[Al_4^{2-}]$, $Na^+[Al_4^{2-}]$, $Li^+[Al_4^{2-}]$, and $[Al_4^{2-}]$ using analytical gradients with polarized split-valence basis sets (6-311+G*) and a hybrid method known in the literature as B3LYP. Then we refined geometries and calculated frequencies at the second-order Møller-Plesset perturbation theory (MP2) level. $Na^+[Al_4^{2-}]$, $Li^+[Al_4^{2-}]$, and $[Al_4^{2-}]$ were further studied using the coupled-cluster method [CCSD(T)] with the 6-311+G* basis sets. The energies of the most stable structures were refined using the CCSD(T) method and the more extended 6-311+G(2df) basis sets. The vertical electron detachment energies were calculated using the outer valence Green Function method [OVGF/6-311+G(2df)] and the MP2/6-311+G* geometries for $Cu^+[Al_4^{2-}]$ and the CCSD(T)/6-311+G* geometries for $Li^+[Al_4^{2-}]$ and $Na^+[Al_4^{2-}]$. Core electrons were kept frozen in treating the electron correlations at the MP2, CCSD(T), and OVGF levels of theory. All calculations were performed using the Gaussian 98 program.
14. The Gaussian 98 program (revision A.7) is by M. J. Frisch *et al.* (Gaussian, Inc., Pittsburgh, PA, 1998).
15. J. D. Corbett, *Angew. Chem. Int. Ed.* **39**, 670 (2000).
16. S. M. Kauzlarich, *Chemistry, Structure and Bonding of Zintl Phases and Ions* (VCH, New York, 1996).
17. Molecular orbital pictures were made using the MOLDEN3.4 program (G. Schaftenaar, MOLDEN3.4, Computer Assisted Organic Synthesis/Computer Assisted Molecular Modeling Center, the Netherlands (1998).

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