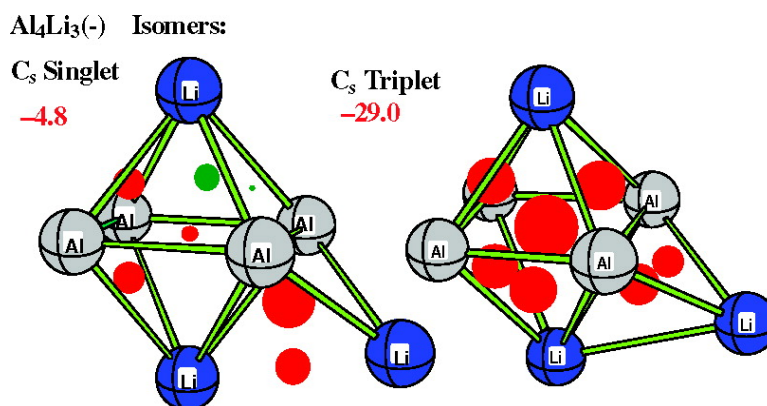


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Do All-Metal Antiaromatic Clusters Exist?

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Notable recent gas-phase observations extend the aromaticity concept¹ to all-metal clusters, NaAl_4^- ,² with aromatic, and Al_4Li_3^- ,³ with claimed “antiaromatic” character. Extensive theoretical analyses⁴ support the Boldyrev–Wang description of the central aluminum ring in NaAl_4^- : “the Al_4^{2-} dianion can be considered as π -aromatic and doubly σ -aromatic”³ due to the delocalized π and σ orbitals. However, the “antiaromaticity” claim for the lowest energy Al_4Li_3^- isomer located computationally, as well as other Al_4^{4-} -derived species,⁵ was based solely on the existence of four electrons in two π molecular orbitals and the consequent distortion (also as in cyclobutadiene)⁶ of the central Al_4 rings from square to rectangular geometries. Potentially important contributions from the delocalized σ electrons, like that in the Al_4^{2-} dianion,^{2,4} were mentioned but not evaluated. We now show that the π antiaromaticity in several Al_4^{4-} -based clusters is overwhelmed by their σ aromaticity. We find the Al_4^{4-} clusters to be net aromatic rather than antiaromatic! However, true antiaromatic all-metal clusters, such as Sn_6^{2-} ,⁷ have long existed experimentally but have escaped recognition.

We base our conclusions on new refinements of nucleus-independent chemical shift (NICS)^{8,9} analysis. These characterize the magnetic character of each canonical MO (CMO) individually in two different implementations. CMO–NICS analyses are performed by using the NBO 5.0 program¹⁰ and by computing the individual Kohn–Sham CMO contributions.¹¹ Both methods give consistent results. Using Gaussian 98,¹² geometry optimizations, frequency analyses, GIAO,¹³ and NBO CMO–NICS¹⁰ computations employed the B3LYP/6-311+G* level (except for LanL2DZp¹² with Sn_6^{2-}). CMO–NICS computations at the PW91/IGLOIII level also employed the GIAO method, but as implemented in the MAG-ReSpect program.¹⁴ NICS(0) points were computed at the centers of the four-membered rings or of the cages.

CMO–NICS(0) analysis of the two- π -electron Al_4^{2-} (D_{4h}) (Figure 1) confirms that not only the diatropic π (–17.8) but also the σ MOs (sum –11.1) contribute importantly to the considerable aromaticity^{2,4} (the total NICS(0) value of –30.9 ppm includes small core effects).

The importance of σ delocalization in the Al_4^{4-} -based clusters is documented by implementation of CMO–NICS analysis of the reported singlet Al_4Li_3^- (C_s) global minimum.³ The CMO–NICS(0) results, shown in Figure 2, are representative of both methods.

Consider first the individual π orbital contributions, diamagnetic (–12.9, as in Al_4Li_3^- , Figure 2) for the lower-lying but paramagnetic (+27.5) for the higher-lying π MO. The much stronger

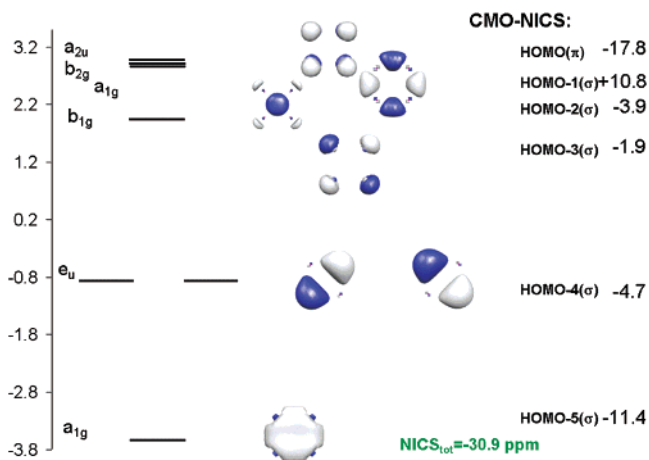


Figure 1. CMO–NICS(0) analysis at the ring center of Al_4^{2-} (D_{4h}).

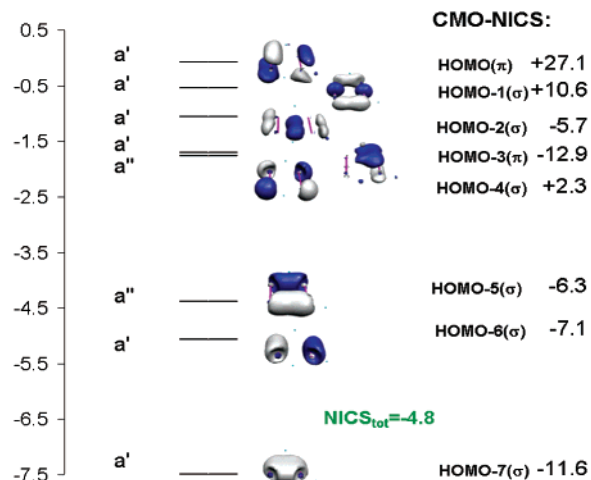


Figure 2. NBO CMO–NICS analysis at the aluminum ring center of Al_4Li_3^- (C_s).

paramagnetic effect dominates; hence, the 4e π system (NICS(0) $_{\pi}$ 14.2 ppm) of Al_4Li_3^- is antiaromatic, conforming to the Hückel rule and the Boldyrev–Wang expectations.³

However, this π antiaromaticity is overcome by the diamagnetic contributions of all the σ orbitals together (NICS(0) $_{\sigma}$ –16.8). The total NICS(0) of –4.8 ppm at GIAO–B3LYP/6-311+G* characterizes the overall aromatic character of Al_4Li_3^- (C_s) and contradicts the Boldyrev–Wang conclusions.³ If Al_4Li_3^- (C_s) were antiaromatic and destabilized, as claimed, it would adopt a different structure, since the reorganization barriers of such clusters are very low and many alternative geometries are possible.³

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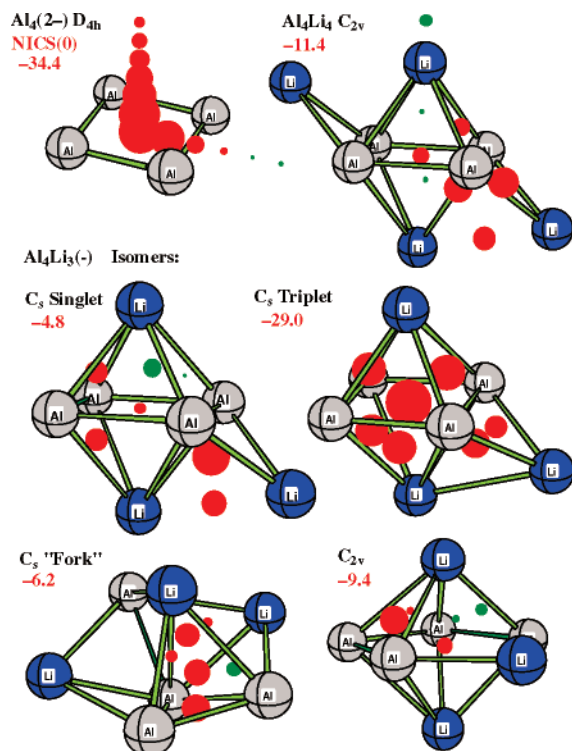


Figure 3. NICS points (red, diatropic; green, paratropic) for Al_4^{2-} and various Al_4^{4-} -related species at the GIAO/B3LYP/6-311+G* level. Magnitudes are given by the sizes of the dots. The NICS(0) values, in red, are at the Al_4 ring or cage centers.

The detailed CMO–NICS analyses of Al_4Li_4 (C_{2h}) (see Supporting Information) is like that of Al_4Li_3^- (C_3). The aromatic character of Al_4^{4-} species also is confirmed by the NICS plots in Figure 3. Besides NICS(0), these plots show additional NICS points in the centers of the unique faces of these species, as well as various Al_4Li_3^- isomers. Due to the predominant σ aromaticity discussed above, the Al_4^{4-} cores and most, but not all, of the faces are aromatic in these clusters. The substantial aromaticity of the nearly isoenergetic³ triplet is noteworthy.¹⁵

Al_4^{2-} , the Al_4^{4-} core,⁵ and cyclobutadiene (CBD), C_4H_4 (D_{2h}), afford instructive comparisons. The 14 valence electrons of Al_4^{2-} can be assigned (see Figure 1) to four lone-pair MOs (with a composite -22.7 NICS(0) contribution), two diatropic MOs, and one σ (-3.9) and one π (-17.8) as well as a paratropic σ MO ($+10.8$). The contributions to the 16-valence-electron Al_4^{4-} -based species⁵ are very similar (see Figure 2), except that the additional two electrons occupy a second, highly paratropic π MO. The 20 valence electrons of CBD occupy two additional σ MOs, both of which are highly paratropic.⁶ The effects of the first (diatropic) and second (paratropic) π orbitals oppose each other, leaving only a weakly net paratropic π contribution to NICS(0) for CBD, but larger ones for the Al_4^{4-} -based species.⁵ In contrast to the overwhelming σ aromaticity of Al_4^{2-} and the Al_4^{4-} core, CBD, like other four-membered rings,¹⁶ has a strong σ antiaromatic four-membered ring, which is primarily responsible for its large paratropic total NICS(0) ($+20.8$ at GIAO/B3LYP/6-311+G*⁶).

Truly antiaromatic all-metal clusters do exist, but this has not been appreciated. The octahedral Zintl ion, Sn_6^{2-} , prepared in the solid phase in 1993,⁷ is an example. The paratropic NICS(0) value at the cage center, $+18.8$ ppm at GIAO–B3LYP/LanL2DZp//B3LYP–LanL2DZp ($+26.8$ at GIAO–MP2/LanL2DZp//MP2/LanL2DZp), documents its strongly antiaromatic character. The

antiaromaticity of Sn_6^{2-} is related to its high octahedral symmetry, as has been discussed for the analogous Si_6^{2-} (O_h) and Si_{12}^{2-} (I_h) deltahedra.¹⁷ The symmetry of the highly degenerate O_h Sn_6^{2-} MOs precludes mixing of the external lone pair orbitals of the vertex atoms with the tangential surface skeletal orbitals. This enhances the paratropic at the expense of the diatropic contributions to the total NICS(0).

In summary, we find the very recently reported gas-phase Al_4Li_3^- species to be aromatic rather than antiaromatic, due to the predominating effects of σ aromaticity over π antiaromaticity. However, true antiaromatic all-metal clusters, such as Sn_6^{2-} ,⁷ do exist. The latter provides another example of unrecognized but novel properties of well-known compounds, akin to the aromatic Hg_4^{6-} (used since ancient times)¹⁸ and the superconducting $[\text{MgB}_2]^{19}$ (available from supply houses).

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Supporting Information Available: Figure 1S, a CMO–NICS plot of C_{2h} Al_4Li_4 (PDF). This material is available free of charge via the Internet at <http://pubs.acs.org>.

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