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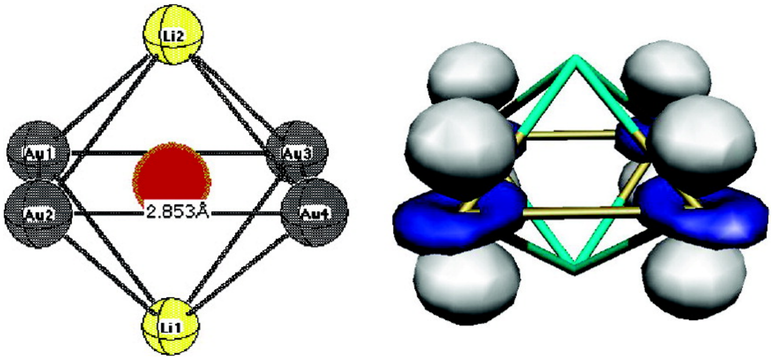

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# Evidence for d Orbital Aromaticity in Square Planar Coinage Metal Clusters

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***Abstract:*** Quantitative evidence for the existence of aromaticity involving the d orbitals of transition metals is provided for the first time. The doubly bridged square planar ($D_{4h}$) coinage metal clusters ($M_4Li_2$, M = Cu (**1**), Ag (**2**), and Au (**3**)) are characterized as aromatic by their substantial nucleus independent chemical shifts (NICS) values in the centers (−14.5, −14.1, and −18.6, respectively). Nevertheless, the participation of p orbitals in the bonding (and cyclic electron delocalization) of **1**−**3** is negligible. Instead, these clusters benefit strongly from the delocalization of d and to some extent s orbitals. The same conclusion applies to Tsipis and Tsipis' H-bridged $D_{4h}$ $Cu_4H_4$ ring (**4**). Canonical MO−NICS analysis of structures **1**−**3** shows the total diatropic d orbital contributions to the total NICS to be substantial, although the individual contributions of the five sets of filled d orbitals vary. The d orbital aromaticity of $Cu_4Li_2$ also is indicated by its atomization energy, 243.2 kcal/mol, which is larger than Boldyrev's doubly ($\sigma$ and $\pi$) aromatic $Al_4Li_2$ (215.9 kcal/mol).

## Introduction

Cyclically delocalized transition metal rings using d instead of the usual p orbitals would constitute a new type of aromaticity. How can such "$\delta$-aromaticity" be achieved? The Hückel ($4n + 2$) $\pi$-electron rule has proven to be very robust: the concept of aromaticity is no longer limited to fully conjugated organic rings or even to nonmetals. The aromaticity of planar clusters comprising main group metal atoms was first recognized clearly by Shaik, Hiberty, and their co-workers, who discussed the cyclic delocalization of the $\sigma$-electrons of $Li_6$ in the benzene context.[1] Robinson synthesized a $\pi$-delocalized $(GaR)_3^{2-}$ derivative, isoelectronic with the cyclopropenium ion.[2] The deservedly well-publicized collaborative theoretical and experimental research of Boldyrev and Wang[3] has focused attention on the double aromaticity,[4] in-plane as well as $\pi$, of main group metal rings and related clusters.[5,6] For instance, the isolated $Al_4^{2-}$ ion is characterized as aromatic on the basis of contributions from both $\sigma$- and $\pi$-orbitals.[3,5d,g] The aromaticity of post-lanthanide element rings involving mercury also has been recognized.[7]

The electron distributions in the incompletely filled subshells of coinage metal elements (e.g., Cu $3d^{10}4s^1$) and of aluminum ($3s^23p^1$) are isolobal. This analogy between the filled $d^{10}$ shell in the coinage metals and the $s^2$ electron pair in aluminum prompted us to explore the aromaticity in novel ring systems constructed from Cu, Ag, and Au (**1**−**3**, Figure 1).

Tsipis and Tsipis described a new class of aromatic hydrocopper rings, $Cu_nH_n$ (where $n$ = 3 to 6), recently.[8,9] These clusters involve hydrogen bridging around the $Cu_4$ ring akin to the bridging alkyl and aryl groups in cyclic $Cu_nR_n$ ($n$ = 4 and 5) analogues.[10] However, based on nucleus independent chemical shift (NICS)[11] values in the ring centers, the aromaticity of $D_{4h}$ $Cu_4H_4$ **4** (NICS −4.2 ppm) was only marginal, and $Cu_5H_5$ (NICS −1.2 ppm) as well as $Cu_6H_6$ (NICS −0.2 ppm) were not aromatic.[8] Even the NICS value of $D_{3h}$ $Cu_3H_3$ (−8.4 ppm)

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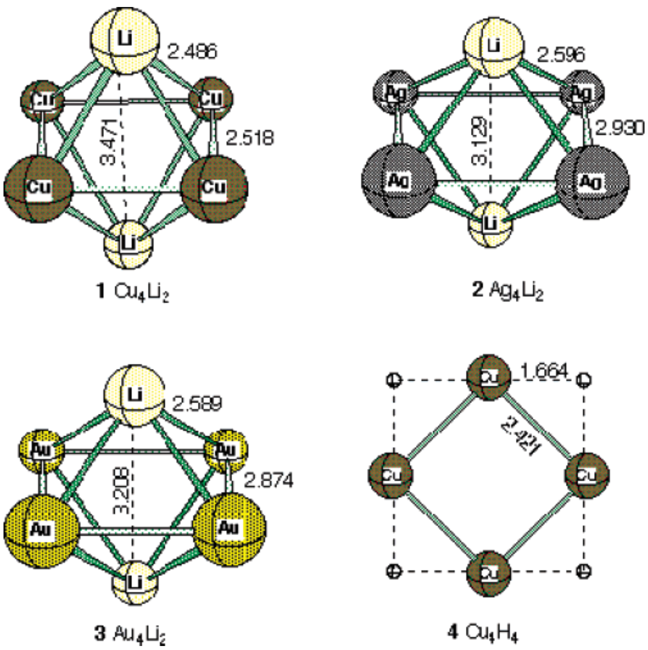

1 $Cu_4Li_2$ 2 $Ag_4Li_2$

3 $Au_4Li_2$ 4 $Cu_4H_4$

***Figure 1.*** PW91PW91/LANL2DZ optimized geometries of $Cu_4Li_2$, $Ag_4Li_2$, $Au_4Li_2$, and $Cu_4H_4$. All structures are minima and have $D_{4h}$ symmetry. Distances are in angstroms.

was much smaller than that of cyclopropane (−42.8 ppm)[11d] and the cyclopropenyl cation (−23.4 ppm).[11d] The MOs of $Cu_4H_4$ indicated d orbital involvement in the bonding, but the individual contributions of various orbitals to the total NICS were not investigated. Hence, no quantitative evidence for d orbital participation in cyclic electron delocalization was given. The Tsipis work,[8,9a] published during the course of our studies, further stimulated our study.

Although copper has only a single electron in its valence s shell and a +1 oxidation state, it does not mimic the alkali metals in its chemical behavior. The involvement of Cu d shell electrons in various metal−metal interactions is well accepted in the antiferromagnetic[12] Cu(II) carboxylates and the cyclic alkyls and alkoxides $Cu_4R_4$ with R = $CH_2SiMe_3$ and OBu.[13] The correlation of d shell electrons is important for simple systems such as $Cu_2$.[14] Furthermore, Cu···Cu interactions are responsible for the unusual electrical properties of the high-temperature cuprate superconductors.[15,16]

Silver and gold, the higher congeners of copper, have the same electronic structures and similar ionization potentials. Furthermore, both Ag and Au are known to utilize d electrons in metal−metal bonding.[9a,17] The present article employs NICS analysis of the individual molecular contributions (NBO−CMO−NICS)[18] to demonstrate the involvement of d electrons in the aromaticity of the lithium-bridged coinage metal rings.

## Computational Methods

The optimized cluster geometries were rather insensitive to the DFT levels employed. Hence, symmetry-constrained structures ($D_{4h}$) were optimized with the PW91PW91 functional and the LANL2DZ ECP basis with the Gaussian03 program.[19] All of the computed harmonic vibrational frequencies were real. NICS values (in ppm) were computed at the cluster centers. The CMO−NICS analysis employed the NBO 5.0 program[18a] at the same PW91PW91/LAN2DZ level.

## Results and Discussion

**$Cu_4Li_2$ (1) and $Cu_4H_4$ (4).** The small Tsipis NICS value (−4.2)[8a] indicated the aromatic character of the $D_{4h}$ $Cu_4H_4$ hydrocopper(I) ring (**4**) to be marginal, despite the “highly delocalized $\sigma$-, $\pi$-, and $\delta$-type [referring to the symmetry] MO’s.”[8,9a] The electronic structure of our square planar $Cu_4Li_2$ complex differs significantly from the Tsipis $Cu_4H_4$ structure (**4**).[8] At PW91PW91/LANL2DZ (Figure 1), the Cu−Cu separation (2.421 Å) in $Cu_4H_4$ (**4**) is somewhat smaller than that (2.518 Å) in $Cu_4Li_2$ (**1**). The H bridges in **4** along the ring perimeter have moderate covalent character, whereas the $Li^+$ cations above and below the $Cu_4^{2-}$ square of **1** help bind the $Cu_4Li_2$ complex electrostatically (the NPA[18a] Li charge is +0.8 versus −0.4 on H in **4**).[8a] Moreover, canonical MO analyses show that the atomic orbitals of the two capping lithiums do not contribute to the valence MOs of $Cu_4^{2-}$ and to the total NICS in $Cu_4Li_2$.

The contribution of d orbital delocalization to NICS of $Cu_4H_4$ (**4**)[8] (and of $Ag_4H_4$ and $Au_4H_4$)[9a] was not delineated quantita-

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(11) Diamagnetic and paramagnetic ring current effects associated with aromaticity and antiaromaticity, respectively, are measured simply and effectively by NICS. NICS is based on the absolute magnetic shieldings computed at ab initio, DFT, and semiempirical (MNDO) levels; the signs are reversed to conform with the NMR chemical shift convention. Significantly negative NICS values in interior positions of ring or cages indicate aromaticity, whereas positive values denote antiaromaticity. See: (a) Schleyer, P. v. R.; Maerker, C.; Dransfeld, A.; Jiao, H.; Hommes, N. J. R. v. E. *J. Am. Chem. Soc.* **1996**, *118*, 6317. (b) Schleyer, P. v. R.; Jiao, H.; Hommes, N. J. R. v. E.; Malkin, V. G.; Malkina, O. L. *J. Am. Chem. Soc.* **1997**, *119*, 12669. (c) Schleyer, P. v. R.; Manoharan, M.; Wang, Z. X.; Kiran, B.; Jiao, H.; Puchta, R.; Hommes, N. J. R. v. E. *Org. Lett.* **2001**, *3*, 2465. (d) Wannere, C. S.; Corminboeuf, C.; Allen, W. D.; Schaefer, H. F., III; Schleyer, P. v. R. *Org. Lett.*, published online March 17, 2005 http://dx.doi.org/10.1021/ol050118q.

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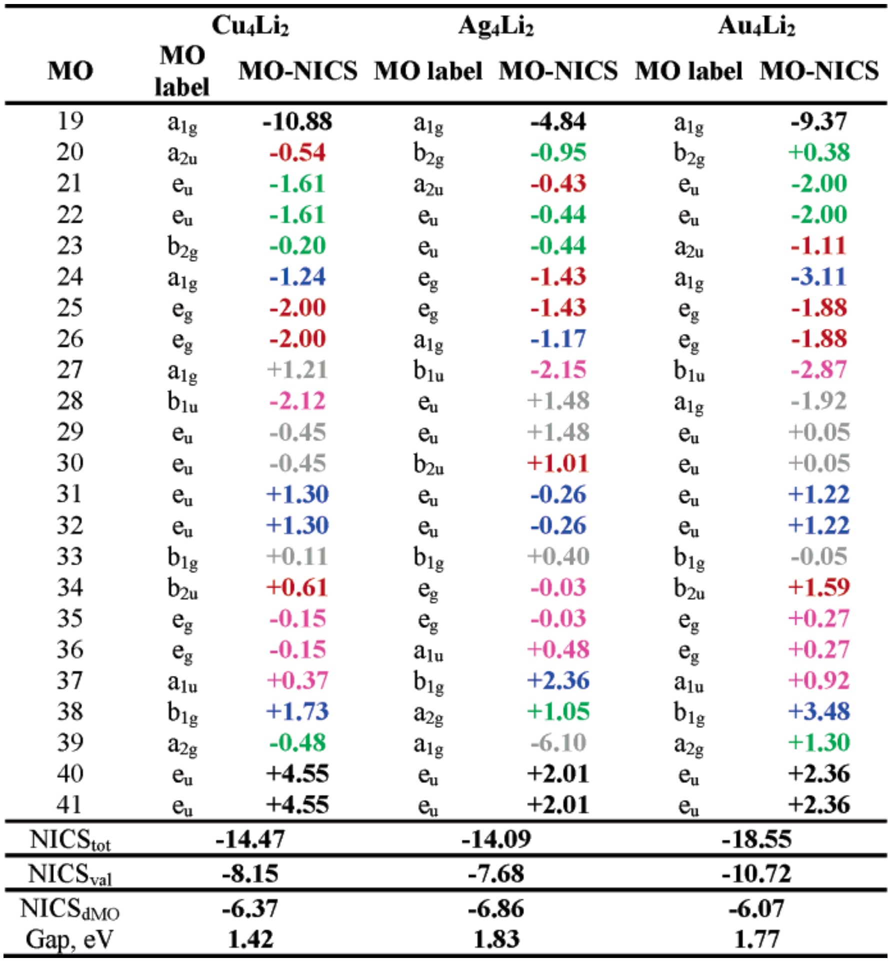
***Table 1.*** Total NICS, Valence MO Contributions to NICS, Their Total ($NICS_{val}$), and Energy Gaps for $M_4Li_2$ (M = Cu, Ag, Au) at the PW91PW91/LANL2DZ Level[a]



| MO | $Cu_4Li_2$ MO label | $Cu_4Li_2$ MO-NICS | $Ag_4Li_2$ MO label | $Ag_4Li_2$ MO-NICS | $Au_4Li_2$ MO label | $Au_4Li_2$ MO-NICS |
|---|---|---|---|---|---|---|
| 19 | $a_{1g}$ | -10.88 | $a_{1g}$ | -4.84 | $a_{1g}$ | -9.37 |
| 20 | $a_{2u}$ | -0.54 | $b_{2g}$ | -0.95 | $b_{2g}$ | +0.38 |
| 21 | $e_u$ | -1.61 | $a_{2u}$ | -0.43 | $e_u$ | -2.00 |
| 22 | $e_u$ | -1.61 | $e_u$ | -0.44 | $e_u$ | -2.00 |
| 23 | $b_{2g}$ | -0.20 | $e_u$ | -0.44 | $a_{2u}$ | -1.11 |
| 24 | $a_{1g}$ | -1.24 | $e_g$ | -1.43 | $a_{1g}$ | -3.11 |
| 25 | $e_g$ | -2.00 | $e_g$ | -1.43 | $e_g$ | -1.88 |
| 26 | $e_g$ | -2.00 | $a_{1g}$ | -1.17 | $e_g$ | -1.88 |
| 27 | $a_{1g}$ | +1.21 | $b_{1u}$ | -2.15 | $b_{1u}$ | -2.87 |
| 28 | $b_{1u}$ | -2.12 | $e_u$ | +1.48 | $a_{1g}$ | -1.92 |
| 29 | $e_u$ | -0.45 | $e_u$ | +1.48 | $e_u$ | +0.05 |
| 30 | $e_u$ | -0.45 | $b_{2u}$ | +1.01 | $e_u$ | +0.05 |
| 31 | $e_u$ | +1.30 | $e_u$ | -0.26 | $e_u$ | +1.22 |
| 32 | $e_u$ | +1.30 | $e_u$ | -0.26 | $e_u$ | +1.22 |
| 33 | $b_{1g}$ | +0.11 | $b_{1g}$ | +0.40 | $b_{1g}$ | -0.05 |
| 34 | $b_{2u}$ | +0.61 | $e_g$ | -0.03 | $b_{2u}$ | +1.59 |
| 35 | $e_g$ | -0.15 | $e_g$ | -0.03 | $e_g$ | +0.27 |
| 36 | $e_g$ | -0.15 | $a_{1u}$ | +0.48 | $e_g$ | +0.27 |
| 37 | $a_{1u}$ | +0.37 | $b_{1g}$ | +2.36 | $a_{1u}$ | +0.92 |
| 38 | $b_{1g}$ | +1.73 | $a_{2g}$ | +1.05 | $b_{1g}$ | +3.48 |
| 39 | $a_{2g}$ | -0.48 | $a_{1g}$ | -6.10 | $a_{2g}$ | +1.30 |
| 40 | $e_u$ | +4.55 | $e_u$ | +2.01 | $e_u$ | +2.36 |
| 41 | $e_u$ | +4.55 | $e_u$ | +2.01 | $e_u$ | +2.36 |
| $NICS_{tot}$ | -14.47 | | -14.09 | | -18.55 | |
| $NICS_{val}$ | -8.15 | | -7.68 | | -10.72 | |
| $NICS_{dMO}$ | -6.37 | | -6.86 | | -6.07 | |
| Gap, eV | 1.42 | | 1.83 | | 1.77 | |

[a] The same color scheme as that in Figure 2 represents each set of d orbitals. The sum of NICS for all these d orbital sets is $NICS_{dMO}$. The core MO contributions to NICS are not given by the LANL2DZ basis set.

tively by Tsipis *et al*. There are problems in doing so, since the total d orbital contribution to NICS ($NICS_{val}$) is complicated by significant mixing between the 1s hydrogen and the in-plane 3d Cu orbitals. This occurs in seven of the 24 valence orbitals of $Cu_4H_4$ (see blue labeled MOs in Table S2). However, these sd hybrid MOs contribute paratropically to the total NICS and are not responsible for the diatropically based d orbital aromaticity.[20]

The major diatropic contributions of the d orbitals of $Cu_4H_4$ (**4**) arise from the three valence MOs singled out by Tsipis (HOMO-19, HOMO-17, HOMO-11 in ref 8), which do not have s orbital involvement. Specifically, the NICS contribution of the in-plane radial d orbital (MO41 in Table S2 or HOMO-19 in ref 8) is −5.8, only 1 ppm smaller than the total NICS (−6.8 at B3LYP/6-311+G(2d,2p); Tsipis reported −4.8). The NICS of HOMO-11 (or MO49), involving a $d_{z^2}-d_{z^2}$ overlap, is −3.6, and of HOMO-17 (or MO42), characterized by $\pi$-type overlap of $d_{xz}$ AOs, is −2.6. At the same level of theory, the total NICS of $Cu_4Li_2$ (**1**) is more than two times larger (−14.2) than that of **4**, while the NICS of the valence MOs is nearly three times larger (−9.28).

The atomization energies of clusters, compared with analogous complexes, can serve as rough energetic indicators of aromaticity. The PW91PW91/LANL2DZ computed atomization energy (AE) of $Cu_4Li_2$, 243.2 kcal/mol, is larger than the AE (215.9 kcal/mol) of the comparable doubly ($\sigma$ and $\pi$) aromatic $Al_4Li_2$. However, both of these AEs are much smaller than the AE for $Cu_4H_4$ (419.2 kcal/mol; Tsipis reported 376.1 kcal/mol at B3LYP/6-311+G**) owing to a larger number of atoms and the stronger and more covalent Cu−H bonding in the hydrocopper ring.

Like $D_{4h}$ $Al_4^{2-}$ (NICS −30.8) and $C_4H_4Li_2$ (−19.3) but unlike $D_{4h}$ $Al_4Li_2$ (which is not a minimum and only has NICS −5.5) and $Cu_4H_4$ (**4**) (NICS −4.2), $Cu_4Li_2$ ($D_{4h}$ **1**), a square planar copper dianion capped by two lithium cations, exhibits pronounced diatropic character (NICS −14.5, see Table 1). The energy ordering of the valence MOs of the $Cu_4^{2-}$ dianion (depicted in Figure 2)[21] shows that the contributions of the higher energy MOs to NICS are relatively small or even paratropic (see Table 1). The largest single diatropic contribution (CMO−NICS = −10.9) is given by the lowest-lying totally symmetric valence MO ($a_{1g}$); this MO is dominated by the 4s AO components (see later discussion). However, the total +9.2 contribution from the highest energy $e_u$ set, also having considerable 4s character, largely cancels the $a_{1g}$ effect.

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(20) NICS values of the analogous $Cu_4Li_4$ ($D_{4h}$) are not presented here since it has five imaginary vibrational frequencies and an unstable wave function.

(21) This orbital ordering may depend on the theoretical level. Thus, at the PW91PW91/LANL2DZ level, the lowest $b_{2g}$ bonding orbital has nearly the same energy (<0.005 eV) as the lowest valence $e_u$ orbital set.

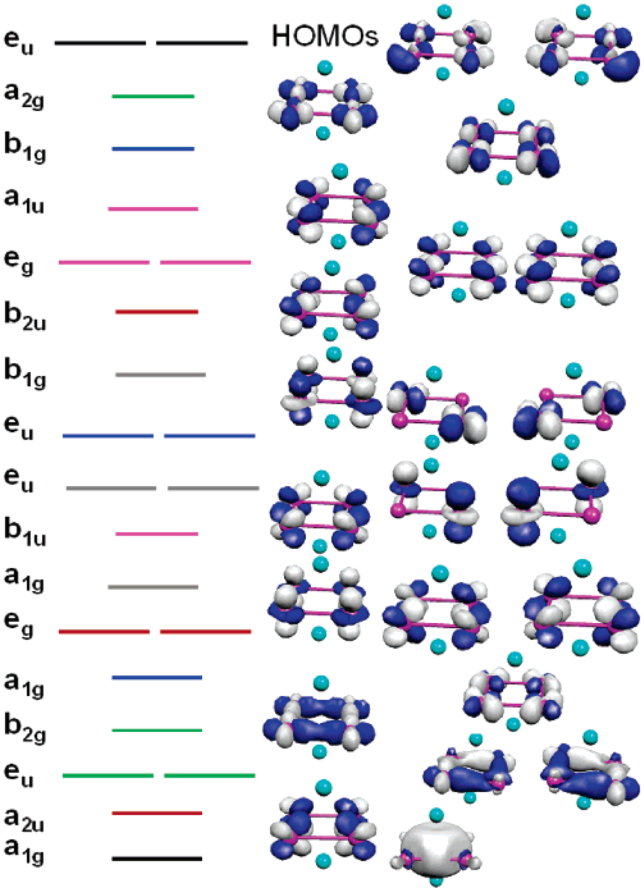

***Figure 2.*** Valence molecular orbital patterns and symmetry labels of $Cu_4Li_2$. The molecular orbitals dominated by the $d_{xy}$ atomic orbital contributions are displayed in blue, by $d_{z^2}$ in gray, and by $d_{x^2-y^2}$ in green. The linear combination of the tangential $d_{xz}$ and $d_{yz}$ orbitals are displayed in red and pink. The lowest and highest energy valence $a_{1g}$ MOs with substantial s character are shown in black.

The 40 d electrons characterizing square planar $Cu_4^{2-}$ are distributed over five sets of d orbitals ($d_{z^2}$, $d_{x^2-y^2}$, $d_{xy}$, $d_{xz}$, and $d_{yz}$) in an environment, which, obviously, is not spherically symmetrical. Hence, the shape and orientation of these filled d orbitals are important in determining the magnetic properties of the transition metal cluster. In general, each set of four filled d orbitals in $Cu_4^{2-}$ of **1** (identified by color in Figure 2) has the same energy pattern:[21] first, a bonding MO, then a doubly degenerate set of nonbonding MOs, and finally an antibonding MO. As expected, the NICS sum of each of these five different d orbital sets contributes differently to the total NICS value; e.g., the blue set (Figure 2 and Table 1, resulting from the combination of the $d_{xy}$ AOs) contributes paratropically (+3.1), whereas that of the gray MO set (from the $d_{z^2}$ combinations) is close to zero (+0.42). The three other sets of d MOs are diatropic (−3.9 green, −3.9 red, and −2.1 pink, Table 1). Taken individually, the diatropic contribution of each d orbital to NICS is obviously much smaller than a typical $\pi$ MO contribution in a p-block compound.[11,16b,22] However, there are many more diatropic filled d orbitals in **1**−**3** than filled p$\pi$ orbitals in, for example, benzene. The total of all the diatropic d MO contributions ($NICS_{dMO}$ = −6.4, Table 1) results in significant overall d orbital aromaticity in $Cu_4Li_2$.

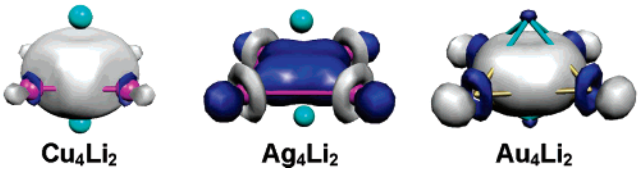

***Figure 3.*** Depictions of the strongly diatropic lowest $a_{1g}$ MOs in $M_4Li_2$ (M = Cu, Ag, Au).

**$Ag_4Li_2$ (2).** Although the transition metal−metal distance in $Ag_4Li_2$ (2.930 Å at the PW91PW91/LANL2DZ level, Figure 1) is 0.4 Å longer than that in $Cu_4Li_2$, the total NICS values of the silver (−14.1) and copper (−14.5) complexes are almost the same (Table 1) and are larger than that of Tsipis's $D_{4h}$ $Ag_4H_4$ (−4.9) and $Cu_4H_4$ (−4.8) NICS.[9a] The overall d MO contributions to NICS are −6.9 for **2** versus −6.4 for **1**. However, the detailed CMO−NICS analyses (Figure 2, Table 1) of the silver (**2**) and copper (**1**) species differ significantly in two particular aspects. First, the diatropicity of the lowest energy valence orbital ($a_{1g}$) NICS contribution is reduced substantially from −10.9 in **1** to −4.8 in **2** (see Figure 3). The −4.8 value is largely counterbalanced by the paratropic $e_u$ HOMO contributions (+4.2). Second, most of the d orbital aromatic character of $Ag_4Li_2$ (total −6.9) arises from the anomalously diatropic highest $a_{1g}$ MO (−6.1); the contributions of all the other d MOs in Table 1 largely balance.

The molecular orbital patterns of **2** are qualitatively similar to those of $Cu_4Li_2$ (Figure 1) except for the two $a_{1g}$ MOs discussed above. Figure 3 compares the lowest $a_{1g}$ MOs of **1**, **2**, and **3**. Variations in the atomic coefficients contributing to the $a_{1g}$ molecular orbitals are responsible for the differences. The lowest-lying $a_{1g}$ MO of the copper complex (**1**) is dominated by s basis functions (0.240 versus −0.082 for the second and third set of s valence basis functions, respectively). However, the contributions of the second (−0.102) and third sets (0.107) of s basis functions to the lowest $a_{1g}$ valence molecular orbital of the silver compound (**2**) are equal in magnitude but opposite in sign. This partial cancellation results in a flatter shape for the lowest $a_{1g}$ MO of **2** compared to the copper analogue (**1**) (see Figure 3). Consequently, the s orbital delocalization becomes weaker (lower MO−NICS) in $Ag_4Li_2$ than in $Cu_4Li_2$. In addition, 4d (second row) transition metals form metal−metal bonds more readily than 3d transition metals. Consequently, the contribution of the d atomic orbitals to the lowest $a_{1g}$ MO is much larger in the silver compound (see Figure 3 and Table 1).

The difference between the highest-lying $a_{1g}$ MOs of **1** and **2** can be analyzed similarly (see Supporting Information). While the same d basis functions contribute to the highest $a_{1g}$ MOs of both compounds, their coefficients differ significantly in magnitude. This results in greater d delocalization in the 4d metal silver complex (**2**) than the 3d copper complex (**1**). For example, the 7D 0 AO coefficient is 0.4128 for copper but is much smaller, 0.1307, for silver (SI, Table).

**$Au_4Li_2$ (3).** The gold complex (**3**) exhibits the largest diatropic character (greatest NICS −18.6) among the three coinage metal complexes (**1**−**3**) (Table 1). The same is true of Tsipis *et al.*'s $Au_4H_4$ $D_{4h}$ (−9.0) versus $Cu_4H_4$ (−4.8) and $Ag_4H_4$ (−4.9). The valence CMO total of **3** ($NICS_{val}$ = −10.7) also is larger than that of **1** (−8.1) or **2** (−7.7), but not as much. In fact, if only the contribution sum of the d MO sets (colored in Table 1) are

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[22] Corminboeuf, C.; King, R. B.; Schleyer, P. v. R. *J. Am. Chem. Soc.*, submitted for publication.

considered, the “d-aromaticity” of $Au_4Li_2$ (**3**) is slightly smaller ($NICS_{dMO} = -6.1$ versus $-6.4$ for **1** and $-6.9$ for **2**, Table 1).

The diatropic NICS contribution of the lowest energy MO ($a_{1g}$) NICS of **3** ($-9.4$, Figure 2) is almost as large as that of $Cu_4Li_2$ ($-10.9$, Table 1). Figure 3 shows that the lowest valence $a_{1g}$ MO of $Au_4Li_2$ (**3**) is intermediate in appearance between that of **1** and **2**. As in $Ag_4Li_2$ (**2**), this $a_{1g}$ MO of **3** is dominated by the s and d basis functions, similar to the situation except that the coefficients associated with the s basis functions are not opposed in sign in the gold compound. As in $Ag_4Li_2$ (**2**), this $a_{1g}$ MO of **3** is dominated by the s and d basis functions, but their coefficients have the same sign (unlike the Ag compound).

The major difference in the valence CMO−NICS values between the copper and the gold complexes arises from the reduced paratropic character ($+2.4$ versus $+4.6$) of the doubly degenerate HOMO (which depends on the energy gap),[22] as well as the larger diatropic contributions of the two highest $a_{1g}$ MOs ($-3.1$ and $-1.9$ for **3** versus $-1.2$ and $+1.2$ for **1**). In short, the electronic structure of the gold complex benefits from both the more pronounced d orbital delocalization characterizing 4d and 5d metals as well as the strong s orbital delocalization of the lowest MO.

Not surprisingly, $Au_4Li_2$ (**3**) behaves somewhat differently than **1** and **2**. Relativistic effects are more important in 5d transition metal clusters and result in bond shortening (Figure 1) owing to more contracted s and p subshells (the so-called relativistic stabilization).[23,24] In addition, the d (and f) subshell becomes more diffuse. The Au−Au distances (2.874 Å) in $Au_4Li_2$ (**3**) are intermediate between the Cu−Cu (**1**) and Ag−Ag (**2**) distances (Figure 1). The larger diatropic character of $Au_4Li_2$ (total NICS) compared to that of $Cu_4Li_2$ and $Ag_4Li_2$ is consistent with the discovery of many more stable gold cluster compounds[25,26] than their lighter coinage metal counterparts.

## Conclusions

Our DFT study of the coinage transition metal clusters, $(M_4^{2-})(2Li^+)$, where M = Cu (**1**), Ag (**2**), and Au (**3**), discloses distinct differences from other square $X_4^{2-}$ systems (which have p orbital involvement, as in X = CH and Al). The $M_4^{2-}\cdot 2Li^+$ set is aromatic owing to the participation of the transition metal d orbitals. Moreover, we find that the related $Cu_4H_4$ hydrocopper cluster[8] also benefits from diatropic d orbital contributions (in particular from the in-plane radial d MO) as well as from orbitals with some s character. The large negative NICS values in $Cu_4Li_2$, $Ag_4Li_2$, and $Au_4Li_2$ mainly arise from d orbital (and some s) contributions (p orbital involvement is negligible). This provides the first quantitative evidence for the existence of “d orbital aromaticity” in transition metal rings. Furthermore, the NICS values indicate that the diatropic character of $Au_4Li_2$ is largest (possibly a relativistic effect), while those of $Cu_4Li_2$ and $Ag_4Li_2$ are nearly the same.

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**Supporting Information Available:** MO coefficients for the highest-lying $a_{1g}$ MO in $M_4Li_2$ at the PW91/LANL2DZ level; total NICS, valence MO contributions to NICS, their total ($NICS_{val}$) for $Cu_4H_4$ at the B3LYP/6-311+G(2d,2p)//PW91PW91/LANL2DZ level; and PW91PW91/LANL2DZ optimized geometries of $Cu_4Li_2$, $Ag_4Li_2$, $Au_4Li_2$, and $Cu_4H_4$. This material is available free of charge via the Internet at http://pubs.acs.org.

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