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Peculiar Transformation of a Nonaromatic $Al_4Cl_4(NH_3)_4$ into an Aromatic $Na_2Al_4Cl_4(NH_3)_4$

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We analyzed the molecular orbitals for a $Al_4Cl_4(NH_3)_4$ compound, which is a model of the $(AlBr{\cdot}NEt_3)_4$ crystal structure recently reported by Schnöckel and co-workers. We found that even though $Al_4Cl_4(NH_3)_4$ contains a planar square Al_4 cluster it is not an aromatic compound. However, the addition of two sodium atoms to $Al_4Cl_4(NH_3)_4$ yields a new $Na_2Al_4Cl_4(NH_3)_4$ compound which is a π-aromatic molecule. We hope that prediction of this new compound will facilitate a synthesis of aluminum aromatic solids.

In 1994, Schnöckel and co-workers[1] reported the synthesis and the characterization of the first compound $(AlBr{\cdot}NEt_3)_4$ containing a planar square Al_4 cluster. Such an unusual structure caught our attention because we recently explained the planar square structure in a few gas-phase species containing the Al_4^{2-} dianion on the basis of the presence of aromaticity.[2] While we are not aware of the synthesis of any solid-state compound containing the Al_4^{2-} dianion, the organogallium compound, $K_2[Ga_4(C_6H_3\text{-}2,6\text{-}Trip_2)_2]$ (Trip = C_6H_2-2,4,6-iPr$_3$), with the Ga_4^{2-} cluster, has been synthesized by Twamley and Power.[3] Twamley and Power initially interpreted bonding in their gallium cluster without involving aromaticity. We reinterpreted the chemical bonding in the Ga_4^{2-} cluster based on ab initio calculations and an experimental photoelectron study of the $NaGa_4^-$ cluster and ab initio calculations of the model $K_2Ga_4(C_6H_5)_2$ molecule.[4] We have shown that the planar square structure of Ga_4^{2-} is in fact due to its aromaticity. In the current communication, we explore a possibility of aromaticity in Schnöckel's $(AlBr{\cdot}NEt_3)_4$ compound.

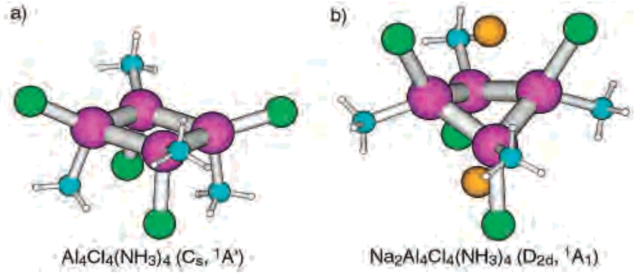

Figure 1. Optimized structures at the B3LYP/3-21+G* level of theory: (a) $Al_4Cl_4(NH_3)_4$ (D_{2d}, $^1A_1$) and (b) $Na_2Al_4Cl_4(NH_3)_4$(D_{2d}, $^1A_1$).

We optimized the geometry and calculated harmonic frequencies at the B3LYP/3-21+G* and MP2/3-21+G* levels of theory for a model $Al_4Cl_4(NH_3)_4$ compound and found that it has a minimum of C_s symmetry, which is slightly lower in energy then the high-symmetry D_{2d} structure (Figure 1a). The minimum structure contains a planar square Al_4 cluster similar to what Schnöckel and co-workers reported for their $(AlBr{\cdot}NEt_3)_4$ compound. Molecular orbitals of the $Al_4Cl_4(NH_3)_4$ compound related to the Al_4 cluster are shown in Figure 2 (the D_{2d} structure was used in order to simplify the interpretation of the MOs). These molecular orbitals can be interpreted in terms of the classical two-electron two-center bonds. The HOMO-14, HOMO-13 (HOMO-13′), and HOMO-12 can be interpreted as the symmetry adapted linear combinations of four Al−N dative bonds, and the HOMO-11, HOMO-1 (HOMO-1′), and HOMO can be interpreted as the symmetry adapted linear combinations of four two-center two-electron Al−Al bonds. This is a qualitative interpretation of delocalized MOs. To get a more quantitative analysis of bonding, we localized the molecular orbitals using natural bonding analysis (NBO)[7] at the RHF/6-311++G** level of theory. After the localiza-

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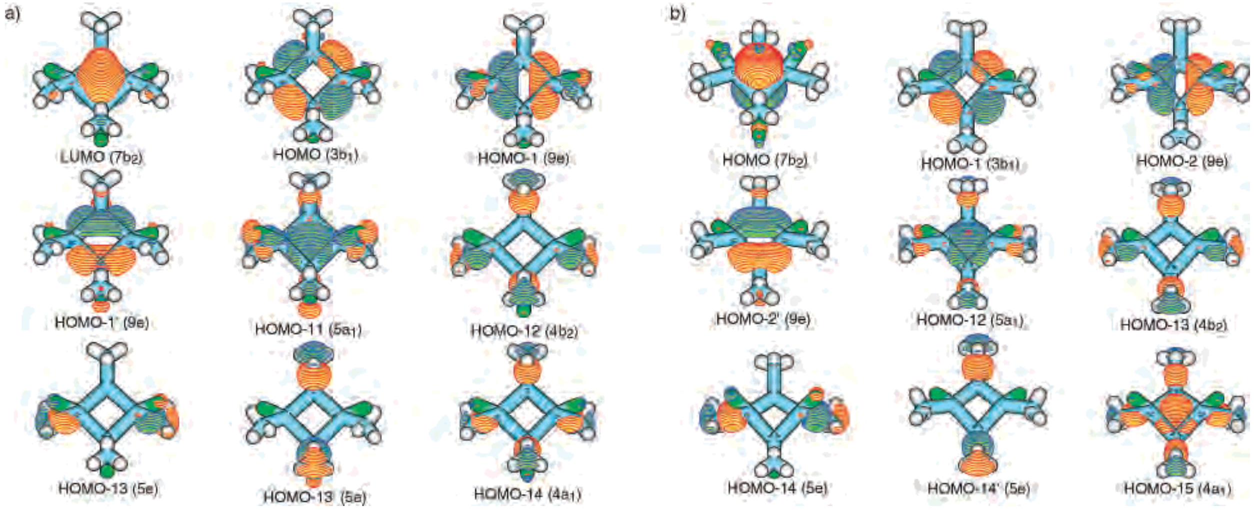

Figure 2. Molecular orbital pictures[6] of $Al_4Cl_4(NH_3)_4$ (a) and $Na_2Al_4Cl_4(NH_3)_4$ (b). LUMO shown for $Al_4Cl_4(NH_3)_4$ was calculated as HOMO for doubly charged anion $Al_4Cl_4(NH_3)_4{}^{2-}$.

tion, we indeed found four two-electron two-center Al−Al bonds (96% localization), four highly polar Al−N bonds (8% of Al and 92% of N; 99% localization), four highly polar Al−Cl bonds (15% of Al and 85% of Cl; 99% localization), twelve N−H bonds (71% of N and 29% of H; 99% localization), and twelve lone pairs of Cl (99% localization). Thus Schnöckel's compound is not a π-aromatic system like the $Al_4{}^{2-}$ and the $Ga_4{}^{2-}$ clusters in Na_2Al_4 and in $K_2[Ga_4(C_6H_4\text{-}2,6\text{-}Trip_2)_2]$, respectively. Chemical bonding in the $(AlBr{\cdot}NEt_3)_4$ compound can be simply interpreted on the basis of the classical two-center two-electron bonds. While we were disappointed that such a beautiful compound as $(AlBr{\cdot}NEt_3)_4$ is not aromatic even though it has a planar square Al_4 cluster, we noticed that our model compound has a low-lying unoccupied molecular orbital which is a four-center π-bond. We optimized the geometry for the $Na_2Al_4Cl_4(NH_3)_4$ molecule at the same level of theory (Cartesian coordinates, harmonic frequencies, and total energies of all species studied here are available from the authors upon request) with a hope that two sodium atoms might donate a pair of electrons to the π-MO which will make this new molecule aromatic. The optimized structure is shown in Figure 1b, and molecular orbitals for the $Na_2Al_4Cl_4(NH_3)_4$ structure are presented in Figure 2b. One can see that an aromatic MO ($7b_2$-HOMO) is indeed present in $Na_2Al_4Cl_4(NH_3)_4$. Our conclusion on the aromaticity of $Na_2Al_4Cl_4(NH_3)_4$ is based solely on the molecular orbital analysis. We previously made a similar conclusion about aromaticity in $Al_4{}^{2-}$ and $MAl_4{}^{-}$ (M = Li, Na, Cu) on the basis of the presence of the delocalized π-MO.[2] The authors of two follow up theoretical works[8,9] arrived at the same conclusions based on the ring current in $Al_4{}^{2-}$ and $MAl_4{}^{-}$ (M = Li, Na, Cu) induced by a perpendicular magnetic field. Therefore, we are confident that our conclusion on the aromatic nature of $Na_2Al_4Cl_4(NH_3)_4$ is sound. We roughly evaluated the energy of reaction 1.

$$Al_4Cl_4(NH_3)_4 + Na_2 \rightarrow Na_2Al_4Cl_4(NH_3)_4 \qquad (1)$$

(ΔE = −30 kcal/mol at the B3LYP/6-311++G**//B3LYP/3-21+G* and ΔE = −45.5 kcal/mol at the MP2/6-311++G**//MP2/3-21+G* levels of theory.) Calculated exothermicity was found to be very high which makes this reaction plausible. In this work, on the basis of the molecular orbital analysis and ab initio calculations, we predict that the nonaromatic $Al_4Cl_4(NH_3)_4$ compound can be transformed into the aromatic $Na_2Al_4Cl_4(NH_3)_4$ compound upon addition of two sodium atoms. This transformation occurs when a planar nonaromatic Al_4 cluster becomes an aromatic butterfly structure. At first glance, the transition from a planar to a butterfly structure in the Al_4 cluster contradicts our claim that $Al_4Cl_4(NH_3)_4$ is nonaromatic and $Na_2Al_4Cl_4(NH_3)_4$ is aromatic. However, this contradiction can be resolved. We believe that the butterfly distortion is due to the strong interactions between Cl^- anions and Na^+ cations in the $Na_2Al_4Cl_4(NH_3)_4$ compound (Figure 1b) and not due to the lack of aromaticity in the last structure. To test the influence of the interactions between Cl^- anions and Na^+ cations in the $Na_2Al_4Cl_4(NH_3)_4$ compound, we performed additional calculations of the $Al_4Cl_4(NH_3)_4{}^{2-}$ dianion. We found that the dianion indeed has an almost planar structure for the central Al_4 cluster. If the salt $Na_2(AlBr{\cdot}NEt_3)_4$ will be made, its aromatic nature can be tested through shortening Al−Al bonds in the aluminum cluster. According to our calculations, the Al−Al bonds are shorter in $Na_2Al_4Cl_4(NH_3)_4$ than in $Al_4Cl_4(NH_3)_4$ by about 0.10 Å at both levels of theory. That is close to the similar differences (0.14 Å) in carbon−carbon bonds in benzene and cyclohexene.[10] Chemical bonding

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[6] The MO pictures were made using the MOLDEN3.4 program: Schaftenaar, G. *MOLDEN3.4*; CAOS/CAMM Center: The Netherlands 1998.

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between sodium and $Al_4Cl_4(NH_3)_4$ in $Na_2Al_4Cl_4(NH_3)_4$ is rather ionic. Calculated effective atomic charges on sodium atoms are very high, +0.85 e (natural population analysis at the MP2/6-311++G** level of theory), and they clearly show that two electrons are primarily localized on π-MO of the aluminum cluster.

We stress that the aromatic Al_4 cluster in $Na_2Al_4Cl_4(NH_3)_4$ is very different from the aromatic Al_4 and Ga_4 clusters in Na_2Al_4 and in $K_2[Ga_4(C_6H_4\text{-}2,6\text{-}Trip_2)_2]$, respectively. In the last two species, Al_4 and Ga_4 clusters are actually doubly σ- and π-aromatic, while the former Al_4 cluster in $Na_2Al_4Cl_4(NH_3)_4$ is only π-aromatic. We hope that the predicted aromatic compound will facilitate the synthesis of new solid-state compounds containing aromatic Al_4 clusters and thus further extend aromaticity concepts into inorganic and organometallic chemistry.

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