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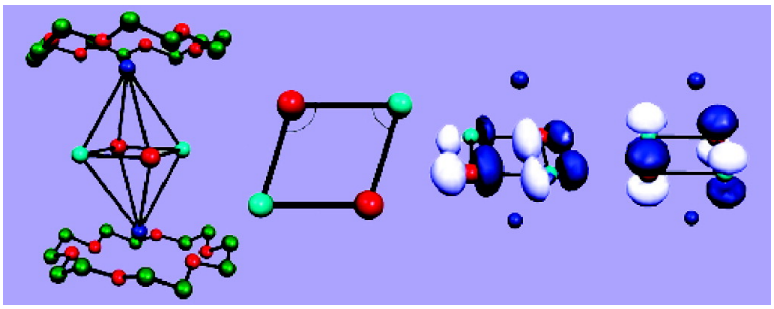

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$[Te_2As_2]^{2-}$: A Planar Motif with "Conflicting" Aromaticity

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Here we report the synthesis and crystal structure of $[K(18\text{-crown-}6)]_2[Te_2As_2]$, **1**, the first four-membered ring Zintl anion of elements from groups XV and XVI. The anion has an unexpected planar parallelogram structure with alternating bonds, which prompted a study of the possible antiaromaticity or aromaticity of the compound.

Stable aromatic systems with $4n + 2$ π-electrons are ubiquitous in organic chemistry. Aromatic non-organic molecules are also known.[1] Some of the most common examples in Zintl anion chemistry are the Pn_4^{2-} (Pn = Sb, Bi),[2] as well as the planar pentagonal aromatic clusters such as Td_5^{6-} (Td = Sn and Pb).[3] However, crystal structures of non-organic antiaromatic compounds with $4n$ π-electrons do not appear to have been reported. The rectangular Al_4^{4-} in the $Li_3Al_4^-$ anion is the first proposed antiaromatic non-organic species and was observed in the gas phase by Kuznetsov et al. in 2003.[4]

The new compound, **1**, was isolated from an ethylenediamine solution of As, K, and As_2Te_3 at room temperature.[5] The compound crystallized in the monoclinic $P2(1)/n$ space group, and its solved crystal structure is shown in Figure 1.[6] The structure is a distorted square bipyramid, with the two K^+ ions "crowned" by 18-crown-6. Very significantly, the cations are out of the plane defined by the crown ether and point toward $[Te_2As_2]^{2-}$.

The most interesting aspect of the structure is the anion $[Te_2As_2]^{2-}$ (Figure 1b). It is a planar four-membered ring with alternating As−Te bonds of 2.690(1) and 2.807(1) Å and angles at the As and Te atoms of 107.23(3) and 72.77(3)°, respectively. The planar structure was unexpected. Square-planar rings of Bi_4^{2-} and Sb_4^{2-} can be explained by their $4n + 2$ π-electrons, which does not hold for **1**. Four-membered rings, formed with atoms of groups XV and XVI, have been the object of considerable interest, and butterfly-like shape has been predicted from theory.[7] However, in the calculations involving anions, no cation−anion interaction was considered. The importance of that interaction has been shown by Twamley and Power for square-planar gallium species,[8] of which we did our calculations on the entire structure.

First principles density functional calculations[9] were carried out to interrogate the geometry and the electronic structure of the $[Te_2As_2]^{2-}$ anion and the corresponding salt. Initially, the electronic structure of the cluster and crowned K^+ shown in Figure 1a was carried out. The results indicate that the cluster possesses a singlet configuration corresponding to a planar Te_2As_2 square with As−Te bond length of 2.70 Å as opposed to the observed parallelogram configuration (see Figure 2b). A careful analysis of the electronic structure revealed that the cluster also possesses a spin triplet state that is 0.01 eV more stable than the singlet but has a parallelogram ground state with As−Te bond lengths of 2.59 and 2.86 Å and a Te−As−Te angle of 93.7°, in reasonable agreement with the observed structure, indicating that spin effects are responsible for the observed distortion (see Figure 2a). Within the accuracy of the calculation, the two states can be regarded as degenerate. Since both As and Te are nonmagnetic, the existence of a triplet ground state raised the possibility of a ferromagnetic solid. To further examine this possibility, we carried out electronic structure calculations on the solid using the VASP code. A full unit cell that contains two $[K(18\text{-crown-}6)]_2[Te_2As_2]$ units was chosen to examine the possibility of nonmagnetic, ferromagnetic, and antiferromagnetic ground states. The ground state was a magnetic configuration where localized spins on the $[Te_2As_2]$ coupled ferromagnetically. The magnetic solution was 127 meV more stable per cluster than a nonmagnetic solution. A closer analysis of the spin density on $[Te_2As_2]$ units revealed that the spin density is distributed on both As and Te sites with more spin on the As site (see Figure S1).

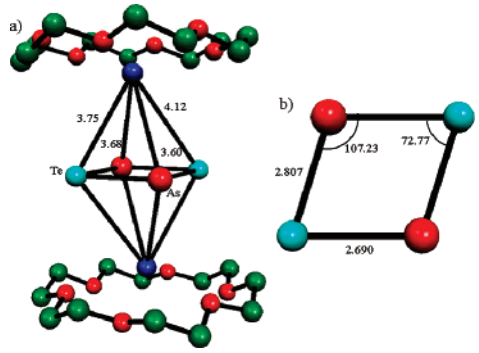

Figure 1. (a) Side view of $[K(18\text{-crown-}6)]_2[Te_2As_2]$, **1**. (b) Top view of $[Te_2As_2]^{2-}$. All distances are in Å.

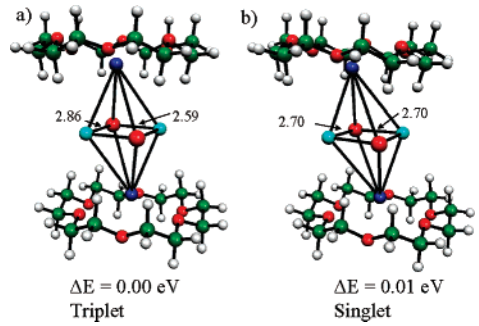

Figure 2. DFT optimization of (a) triplet $[K(18\text{-crown-}6)]_2[Te_2As_2]$, (b) singlet $[K(18\text{-crown-}6)]_2[Te_2As_2]$.

The planar structure and the observed alternation of the As−Te bonds of the $[Te_2As_2]^{2-}$ anion suggest the possibility of antiaromaticity. The observed bond distances of 2.690(1) and 2.807(1) Å are slightly elongated compared to the As−Te single bonds listed in the literature (2.611−2.623 Å).[10] The calculated alternating Al−Al bond lengths (2.55 and 2.68 Å) reported for the proposed non-organic antiaromatic system, Al_4^{4-},[4] are also somewhat elongated compared to the experimentally observed single Al−Al single bonds (2.49−2.62 Å) cited in the literature.[11] The difference of 0.12 Å

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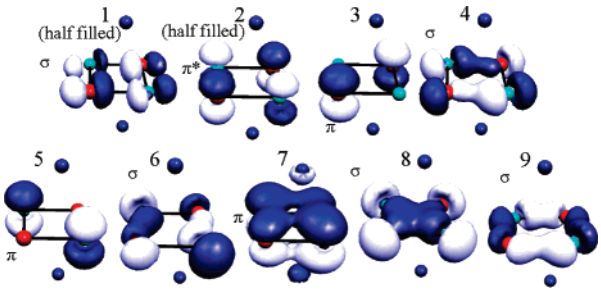

Figure 3. Molecular orbital plots of the nine HOMOs for triplet $K_2Te_2As_2$.

between the shorter and the longer bonds in our compound is essentially the same as the one (0.13 Å) reported for Al_4^{4-}.

MO analysis was performed for $K_2Te_2As_2$ (Figure 3) in order to better understand the structure and bonding. To make the arguments simple, we first consider the singlet configuration. There are 16 valence p-electrons (2×4 (from the Te) $+ 2 \times 3$ (from the As) $+$ 2 (from the charge)) in the $Te_2As_2^{2-}$ anion. The electron density distributions in the eight relevant occupied orbitals and the lowest unoccupied orbital are shown in Figure 3. For the singlet, they can be divided into two groups: 5 σ in-plane bonding orbitals (4, 6, 8, and 9 all bonding, 1 is unfilled antibonding in one direction and bonding in the other) and 4 π-orbitals. Consequently, all the π-orbitals, the bonding (7), nonbonding (3 and 5), and antibonding (2), are occupied, and the net bond order is zero. The occupied bonding σ-orbitals can be divided into radial (8) and tangential (4, 6, and 9) systems. By Hückel rule, both of them should be aromatic because they have 2 and 6 electrons, respectively. For quantitative estimation of the aromaticity, we calculated the nucleus-independent chemical shift (NICS) proposed by Schleyer and co-workers[12] that provides a magnetic criterion to identify the ring currents. Systems with negative NICS are aromatic, while those with positive NICS are antiaromatic. The NICS values, calculated based on optimized geometry and X-ray single diffraction, are given in the Supporting Figures S2b and S2c, respectively. The NICS value for the X-ray structure is negative at the ring center (-19.6) and changes to slightly positive above the plane, showing nonaromatic properties out of the plane but σ aromaticity in the plane. NICS of the optimized structure is slightly antiaromatic at the ring center ($+4.8$), which increases above the plane. The observed differences are probably based on the elongation of the As−As diagonal in optimized structure, which destabilizes the σ aromatic systems.

As pointed out, the observed cluster has parallelogram geometry, and our calculations indicate that it has a triplet ground state. The triplet formation involves a transfer of one electron from orbital 2 to 1 (Figure 3). Note that while the singlet HOMO (2) is a π^*-orbital the LUMO (1) is a σ as it involves bonding between individual pairs and antibonding between the two pairs. Consequently, its occupation leads to an elongation of the two As−Te bonds leading to the observed distortion. While Figure 2 shows this effect for a cluster model, Figure S1 gives the calculated bond lengths for infinite solid calculated using VASP. Figure S2a shows the calculated NICS for the triplet state, and it is interesting that the NICS at the center is negative (-5.1), indicating an aromatic system. The change from the optimized singlet to triplet can be linked to the increase in π aromaticity associated with a π^* to σ electron transfer. Thus, both the geometry and NICS of the X-ray structure is closer to the optimized triplet than the optimized singlet (Figure S2). Lower aromaticity of the triplet compared to the actual structure is presumably due to decreased σ-aromaticity of the radial system, a consequence of the same π^* to σ electron transfer. Clearly, modest distortions in the geometry result in different net ring currents. Calculations on the bulk system indicate that the ferromagnetic solution is more stable than the antiferromagnetic state by 87 meV per cluster. The possible existence of an aromatic ferromagnet is truly exciting.

In conclusion, we report the synthesis and electronic structure investigation of a new ionic compound, **1**. It possesses a triplet ground state whose spin configuration leads to a distortion of the square geometry into a parallelogram with alternating Te−As bond lengths. The triplet is more stable than an optimized singlet structure and better describes the observed X-ray geometry. NICS analysis shows both the triplet and actual structure to have net aromatic character. Calculations on the periodic solid show that the spin moments on the individual motifs order ferromagnetically.

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Supporting Information Available: Details of the theoretical calculations, the absolute energies and optimized geometries, and CIF file of compound **1**. This material is available free of charge via the Internet at http://pubs.acs.org.

References

(1) Boldyrev, A. I.; Wang, L. S. *Chem. Rev.* **2005**, *105*, 3716.
(2) (a) Critchlow, S. C.; Corbett, J. D. *Inorg. Chem.* **1984**, *23*, 770. (b) Cisar, A.; Corbett, J. D. *Inorg. Chem.* **1977**, *16*, 2482.
(3) Todorov, I.; Sevov, S. C. *Inorg. Chem.* **2004**, *43*, 6490.
(4) Kuznetsov, A. E.; Birch, K. A.; Boldyrev, A. I.; Li, X.; Zhai, H. J.; Wang, L. S. *Science* **2003**, *300*, 622.
(5) All manipulations were performed in a nitrogen-filled glovebox; 100 mg (2.56 mmol) of K (Alfa Aesar, 99.95%, ampouled under Argon) and 400 mg (5.33 mmol) of As (Alfa Aesar, polycrystalline lump 99.99999+%, grinded before use) were placed in a 20 mL vial, and 5 mL of ethylenediamine (Aldrich, 99.5%, purified by redistillation, packed under Ar) was added. The mixture was stirred overnight at room temperature. The red suspension was filtrated through an Acrodisc premium 25 mm syringe filter with GxF/0.2 μm pores, and the resulting transparent red solution was used for further reactions. Note: As and K metals did not completely dissolve; 50 mg (0.09 mmol) of As_2Te_3 (Aldrich, 99%) was added to 1 mL of the above solution. The mixture was stirred for 2 h at room temperature and then filtrated through a syringe filter. The obtained very dark red solution was carefully layered with 97 mg of 18-crown-6 (Alfa Aesar, 99%) dissolved in 3 mL of toluene. A few days later, red crystals were formed on the sides of the reaction vessel.
(6) X-ray diffraction data were collected with graphite-monochromated Mo Kα radiation at 100 K on a Bruker APEX diffractometer with CCD area detector. The structure was solved by direct method and was refined for F^2 using SHELXTL V6.14 package. Very dark red rod; $0.16 \times 0.12 \times 0.09$ mm; monoclinic $P2(1)/n$; $a = 10.307(4)$ Å, $b = 9.951(4)$ Å, $c = 18.585(7)$ Å, $\beta = 98.394(6)°$; $V = 1885.8(13)$ Å^3; $Z = 2$; $\mu = 3.559$ cm^{-1}; $\rho_{calcd} = 1.789$ g·cm^{-1}; $R1/wR2 = 5.99/19.72\%$ for 3006 observed reflections ($I \geq 2\sigma_I$).
(7) (a) Mercero, J. M.; Lopez, X.; Fowler, J. E.; Ugalde, J. M. *J. Phys. Chem. A* **1997**, *101*, 5574. (b) Cave, R. J.; Davidson, E. R.; Sautet, P.; Canadell, E.; Eisenstein, O. *J. Am. Chem. Soc.* **1989**, *111*, 8105.
(8) Twamley, B.; Power, P. P. *Angew. Chem., Int. Ed.* **2000**, *39*, 3500.
(9) Cluster calculations were performed using the deMon DFT code using dzvp basis and a GGA functional. Solid-state calculations were performed using VASP.
(10) (a) Eisenmann, B.; Zagler, R. *Z. Naturfosrch.* **1987**, *42B*, 1079. (b) Warren, C. J.; Haushalter, R. C.; Bocarsly, A. B. *Chem. Mater.* **1994**, *6*, 780.
(11) (a) Cui, C.; Li, X.; Wang, C.; Zhang, J.; Cheng, J.; Zhu, X. *Angew. Chem., Int. Ed.* **2006**, *45*, 2245. (b) Schiefer, M.; Reddy, N. D.; Roesky, H. W.; Vidovic, D. *Organometallics* **2003**, *22*, 3637.
(12) Schleyer, P. v. R.; Maerker, C.; Dransfield, A.; Jiao, H.; Hommes, N. J. R. *J. Am. Chem. Soc.* **1996**, *118*, 6317.

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