

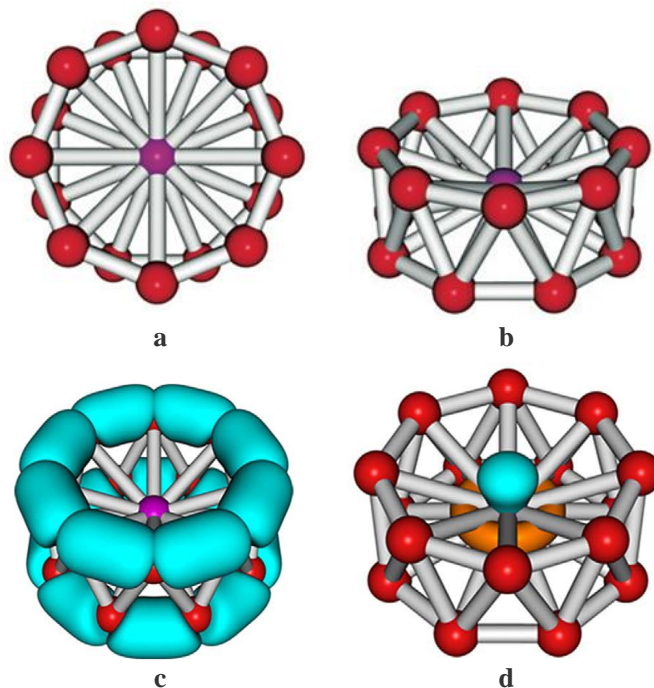
**NOTE**

## Coordination number attained a theoretical maximum in clusters and Werner-type complexes\*

### Cobalt-centered boron molecular drums

In October 2015, Alexander I. Boldyrev of Utah State University, Lai-Sheng Wang of Brown University, and their colleagues reported cobalt-centered boron and fluorine cluster  $\text{CoB}_{16}^-$  having the highest coordination number known heretofore in chemistry.<sup>1</sup> The drum-like structure is a molecular sandwich made of two  $\text{B}_8$  rings connected to the central cobalt

atom via 16 bonds (Figure 1), the theoretical maximum based on the number of available atomic orbitals. In the structure shown, the 'bonds' between atoms in the clusters do not represent classical B–B or Co–B bonds. The  $\text{CoB}_{16}^-$  clusters were made by laser vaporization of a target composed of Co and isotopically enriched  $^{11}\text{B}$ . The target clusters, isolated from the product mixture, were characterized by photoelectron spectroscopy and *ab initio* calculations.



**Figure 1.** (a, b) Two views of one of the isomers of  $\text{CoB}_{16}^-$  cluster. (c) Sixteen B–B sigma bonds, (d) Lone pair on Co. Sticks drawn between atoms do not necessarily represent classical B–B or Co–B bonds. Adapted from Reference [1] with permission. Popov *et al.*, *Nat. Commun.* **2015**, 6, 8654–8660 (open access). Copyright © 2015, Springer Nature.

Close to this report, it was already shown that anionic boron clusters are two-dimensional (2D) at  $\text{B}_{30}$ ,  $\text{B}_{35}$ , and  $\text{B}_{36}$ .<sup>2–4</sup> The 2D-to-3D transition was suggested to occur at  $\text{B}_{20}$  for neutral, and at  $\text{B}_{16}^+$  for cationic clusters. 2D to fullerene-like 3D structure transition is shown to occur in negatively charged boron clusters in  $\text{B}_{39}^-$  and  $\text{B}_{40}^-$ .<sup>5,6</sup> These clusters of nearly

spherical shapes are named as borospherenes. Various transition metal atoms can be placed inside of monocyclic boron rings to form  $(\text{M}\text{C}\text{B}_n)$ .<sup>7</sup> The monocyclic boron rings are beautiful molecular wheel-type structures. Doping of the boron rings with Ta and Nb results in  $\text{Ta}\text{C}\text{B}_{10}^-$  and  $\text{Nb}\text{C}\text{B}_{10}^-$ , respectively.<sup>8</sup> The clusters possess a record coordination number of 10.

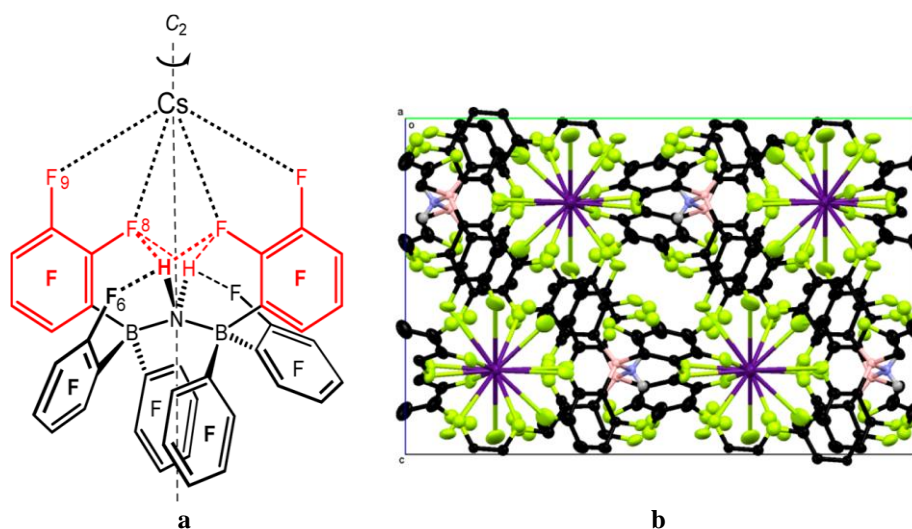
\* Contributed by S. Samal, Editor, CSR

Computational calculations for neutral  $B_{16}$  and  $CoB_{16}^-$  reveal that Co interacts with the tubular  $B_{16}$  host. The encapsulation of Co strengthens the B–B  $\sigma$ -bond within each  $B_8$  ring but weakens the inter-ring interaction in  $B_{16}$ . The authors conclude that the  $CoB_{16}^-$  molecular drum represents the highest coordination for a metal atom known in chemistry.

## Werner-type 16-coordinate Cs complex

In June 2016, Klaus-Richard Pörschke and coworkers of the Max Planck Institute reported their work ‘ $Cs[H_2NB_2(C_6F_5)_6]$

featuring an unequivocal 16-coordinate cation’.  $Cs[H_2NB_2(C_6F_5)_6]$  is a Werner-type molecule in which 16 fluorine atoms coordinate a central Cs atom from five anion units.<sup>9</sup> Singly charged  $Cs^+$  cation with the weakly coordinating  $[H_2NB_2(C_6F_5)_6]^-$  anion allowed to go beyond 12 bonds in a complex.  $Cs[H_2NB_2(C_6F_5)_6]$  has a  $C_2$  symmetrical conformation, which gives rise to the 16-coordinate  $Cs^+$  cation in a tetracosahedral arrangement of F atoms (Figure 2). It is for the first-time the Werner-type complex of 16-Coordination number to one metal is achieved.



**Figure 2.** Schematic presentation of (a) the molecular structure of  $Cs[H_2NB_2(C_6F_5)_6]$ , showing the novel conformation of the anion, and (b) the position and orientation of the molecular entities in the unit cell. Adapted from Reference [9] with permission. Pollak *et al. J. Am. Chem. Soc.* **2016**, *138*, 9444-9451. © 2016 American Chemical Society.

The Werner-type complexes are to be distinguished from the  $CoB_{16}^-$  cluster discussed above.<sup>1</sup> To achieve a high coordination number (CN) above 12 in Werner-type complexes requires a large metal center of low electrophilicity and small donor atoms of low donor strength.  $Cs^+$  is the largest monatomic cation of lowest electrophilicity and with high polarizability (ionic radius of 6-coordinate  $Cs^+$  is 1.67 Å). Covalently bonded fluorine is the second largest element next to hydrogen. It has a van der Waals radius of 1.47 Å. Distinct from the H atoms, fluorine atoms participate in coordination with a full electron pair. Coordination of  $Cs^+$  with an array of fluorine atoms present as substituents in weakly coordinating anions is a promising approach to obtain high coordination numbers. For  $Cs^+$  and

covalently bound fluorine, only CNs  $\leq 12$  were realized before. For example, for  $Cs[SbF_6]$  and  $Cs[Sb_2F_{11}]$ , the CN of Cs is 12. In  $[H_2NB_2(C_6F_5)_6]^-$  anion, the lattice stabilization effect was appropriate enough to furnish the 16-coordinate  $Cs^+$  complex. Typical salts of the anion are  $[Na(OEt_2)_4][H_2NB_2(C_6F_5)_6]$ ,  $[H(OEt_2)_2][H_2NB_2(C_6F_5)_6]$ ,  $[Ti(OEt_2)_4][H_2NB_2(C_6F_5)_6]$ , and  $[Ti(\text{toluene})_3][H_2NB_2(C_6F_5)_6]$ .<sup>10,11</sup> By stirring  $[Na(OEt_2)_4][H_2NB_2(C_6F_5)_6]$  with CsF salt in water, the desired 16-coordinate  $Cs^+$  complex was obtained in quantitative yield. A reaction is carried out with RbF instead of CsF, affording  $Rb[H_2NB_2(C_6F_5)_6] \cdot CH_2Cl_2$ . In this complex, the CN of  $Rb^+$  cation is 10. This highlights the unique CN of 16 by the larger, less electrophilic, and more polarizable  $Cs^+$ .

## References

1. I. A. Popov, T. Jian, G. V. Lopez, A. I. Boldyrev, L.-S. Wang, Cobalt-centred boron molecular drums with the highest coordination number in the  $CoB_{16}^-$  cluster. *Nat. Commun.* **2015**, *6*, 8654-8660.
2. T. Kondo, Recent progress in boron nanomaterials. *Sci. Technol. Adv. Mat.* **2017**, *18*, 780-804.
3. W.-L. Li, Q. Chen, W.-J. Tian, H. Bai, Y.-F. Zhao, H.-S. Hu, J. Li, H.-J. Zhai, S.-D. Li, L.-S. Wang, The  $B_{35}$  cluster with a double-hexagonal vacancy: a new and more flexible structural motif for borophene. *J. Am. Chem. Soc.* **2014**, *136*, 12257-12260.
4. Z. A. Piazza, H.-S. Hu, W.-L. Li, Y.-F. Zhao, J. Li, L.-S. Wang, Planar hexagonal  $B_{36}$  as a potential basis for extended single-atom layer boron sheets. *Nat. Commun.* **2014**, *5*, 3113-3118.
5. Q. Chen, W.-L. Li, Y.-F. Zhao, S.-Y. Zhang, H.-S. Hu, H. Bai, H.-R. Li, W.-J. Tian, H.-G. Lu, H.-J. Zhai,

- Experimental and theoretical evidence of an axially chiral borospherene. *ACS Nano* **2014**, *9*, 754-760.
6. H.-J. Zhai, Y.-F. Zhao, W.-L. Li, Q. Chen, H. Bai, H.-S. Hu, Z. A. Piazza, W.-J. Tian, H.-G. Lu, Y.-B. Wu, Observation of an all-boron fullerene. *Nat. Chem.* **2014**, *6*, 727.
  7. C. Romanescu, T. R. Galeev, W.-L. Li, A. I. Boldyrev, L.-S. Wang, Transition-metal-centered monocyclic boron wheel clusters ( $M@B_n$ ): a new class of aromatic borometallic compounds. *Acc. Chem. Res.* **2012**, *46*, 350-358.
  8. T. R. Galeev, C. Romanescu, W. L. Li, L. S. Wang, A. I. Boldyrev, Observation of the highest coordination number in planar species: decacoordinated  $Ta@B_{10}^-$  and  $Nb@B_{10}^-$  anions. *Angew. Chem. Int. Ed.* **2012**, *51*, 2101-2105.
  9. D. Pollak, R. Goddard, K.-R. Pörschke,  $Cs[H_2NB_2(C_6F_5)_6]$  Featuring an unequivocal 16-coordinate cation. *J. Am. Chem. Soc.* **2016**, *138*, 9444-9451.
  10. S. J. Lancaster, A. Rodriguez, A. Lara-Sanchez, M. D. Hannant, D. A. Walker, D. H. Hughes, M. Bochmann,  $[H_2N\{B(C_6F_5)_3\}_2]^-$ : A new, remarkably stable diborate anion for metallocene polymerization catalysts. *Organometallics* **2002**, *21*, 451-453.
  11. Y. Sarazin, D. L. Hughes, N. Kaltsoyannis, J. A. Wright, M. Bochmann, Thallium (I) sandwich, multidecker, and ether complexes stabilized by weakly-coordinating anions: A spectroscopic, structural, and theoretical investigation. *J. Am. Chem. Soc.* **2007**, *129*, 881-894.

## Remembering Alfred Werner



**Alfred Werner** (1866–1919) was born in Switzerland on 12 December 1866. He was a student at ETH Zurich and a professor at the University of Zurich. In 1893, Werner proposed the octahedral configuration of transition metal complexes for which he received the Nobel Prize in Chemistry in 1913. It was the first an inorganic chemist won the Nobel Prize. The next Nobel Prize for

work on inorganic chemistry was in 1973, awarded jointly to Ernst Otto Fischer and Geoffrey Wilkinson "for their pioneering work, performed independently, on the chemistry of the organometallic, so-called sandwich compounds." In 1893, Werner stated his theory of variable valence. For the first time, Werner proposed that inorganic complex compounds contain central atoms or ions around which a definite number of other atoms, radicals, or molecules are arranged. Werner called this number the coordination number of the central atom or ion. In

the process, a simple, spatial, geometric pattern emerged. This theory became the basis for modern coordination chemistry. In illustrating his theory, Werner proposed structures for hexamminecobalt(III) chloride,  $CoCl_3 \cdot 6NH_3$ . For this molecule, he proposed the structure  $[Co(NH_3)_6]Cl_3$ . In this complex, six  $NH_3$  molecules surround the  $Co^{3+}$  ion at the vertices of an octahedron. The three  $Cl^-$  are free ions. Werner confirmed this from conductivity measurement, and by chloride anion analysis using precipitation with silver nitrate. For this compound, Werner considered that the  $Co-Cl$  bonds correspond to a "primary" valence of 3, while the  $Co-NH_3$  bonds correspond to a "secondary" or weaker valence of 6. Werner rationalized the number of isomers observed for complexes with more than one type of ligand. He explained the existence of two geometric isomers of formula  $[Co(NH_3)_4Cl_2]Cl$  as *cis*- $[Co(NH_3)_4Cl_2]^+$  and *trans*- $[Co(NH_3)_4Cl_2]^+$ . The year in which he received Nobel Prize for Chemistry, he was diagnosed with suffering from arteriosclerosis. On November 15, 1919, he died at the early age of 53.

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