Cs[H$_2$NB$_2$(C$_6$F$_5$)$_6$] Featuring an Unequivocal 16-Coordinate Cation

David Pollak, Richard Goddard, and Klaus-Richard Pörschke*

Max-Planck-Institut für Kohlenforschung, Kaiser-Wilhelm-Platz 1, 45470 Mülheim an der Ruhr, Germany

S *Supporting Information*

ABSTRACT: Cesium bis(perfluoro-triphenylborane)amide, Cs-[H$_2$NB$_2$(C$_6$F$_5$)$_6$] (**1**), has been prepared by the reaction of sodium salt and CsF in dichloromethane and water. The compound is exceptional for a [H$_2$NB$_2$(C$_6$F$_5$)$_6$]$^-$ salt in that it contains a monatomic solute-free cation. Determination of the molecular structure revealed a novel C_2 symmetrical conformation of the weakly coordinating [H$_2$NB$_2$(C$_6$F$_5$)$_6$]$^-$ anion, which gives rise to an unprecedented 16-coordinate (CN 16) Cs$^+$ cation in a likewise unprecedented tetracosahedral arrangement of F atoms. The poor solubility of **1** allows nearly quantitative separation of Cs$^+$ from water, which suggests potential applications as an effective $^{134/137}$Cs remover from nuclear waste solutions, administration as an antidote for $^{134/137}$Cs poisoning, and use for $^{131/137}$Cs radiotherapy (brachytherapy). Rb-[H$_2$NB$_2$(C$_6$F$_5$)$_6$]·CH$_2$Cl$_2$ (**2**) has also been characterized, featuring two inequivalent Rb$^+$ cations having CN 10, one of which involves Rb$^+$(η^2-Cl$_2$CH$_2$)$_2$ coordination.
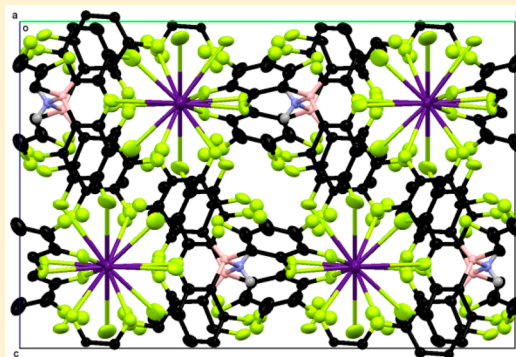
INTRODUCTION

The concept of coordination number (CN), first formulated by Werner in 1893, represents one of the organizing principles in chemistry. In coordination chemistry, CN designates the number of atoms (respective ions or molecules) that a central ion holds as its nearest neighbors by direct bonding. CNs typically range between 2 and 12[1] with the latter being exemplified by the structure of (NH$_4$)$_2$Ce(NO$_3$)$_6$.[2] CNs higher than 12 are extremely rare and are so far confined to metals with hydrogen neighbors coming from BH$_4$$^-$- or RBH$_3$$^-$-type anions. Isolated examples for CN 14 are Th(BH$_4$)$_4$, Pa(BH$_4$)$_4$, U(BH$_4$)$_4$, and U(BH$_4$)$_4$(thf)$_2$.[3a] For Th(H$_3$BNMe$_2$BH$_3$)$_4$, a neutron diffraction study revealed CN 15[3a] "just one bond short of a perfect 16".[3b] In fact, DFT calculations on this compound indicated that CN 16 should be stable in a D_{2d} symmetrical dodecahedral structure of the ThB$_8$ core with each Th···B unit bridged by two hydrogen atoms. For the alkali metal boronates, M[BD$_4$] (M = Na−Cs) up to 24 coordination sites, albeit with half occupancy, have been identified for the larger alkali metals in a neutron diffraction study.[4] In all isolated complexes, the boronate anions bind by multicenter bonding, thus sharing already bonded electrons.

Regarding other donor atoms than hydrogen "in the search for species with the highest CN", it is interesting to note that $_{82}$Pb(He)$_{15}$$^{2+}$ has been calculated as a stable structure.[5] Here, the Pb^{2+} ion formally attains the $_{110}$Ds (Eka-Pt) electron shell assuming that each He ligand serves as a 2-e donor. The Werner-type complexes are to be distinguished from the packing modes of pure metals (e.g., CN 14 for body-centered cubic structures) and alloys (e.g., CN 12-16 in Friauf−Laves polyhedra),[1,6] the structures of cage compounds such as Cs$_{8-n}$Si$_{46}$- and Cs$_8$Na$_{16}$Si$_{136}$-type clathrates,[7a] and the CoB$_{16}$$^-$

cluster.[8] In Cs$_8$Na$_{16}$Si$_{136}$, the Si atoms are all 4-bonded similar to carbon in diamond, thereby forming a framework of fused Si$_{20}$ and Si$_{28}$ cages, and the Na and Cs atoms are encapsulated in these cages as shown by X-ray structure analysis.[7b] For the CoB$_{16}$$^-$ species, which has been generated in the gas phase by laser vaporization of a Co−B target, a drum-like structure of 16 4-fold B−B bonded boron atoms around a central Co atom has been calculated.[8]

To achieve extremely high CNs > 12 in Werner-type complexes of non-hydrogen donors requires a large metal center of low electrophilicity and small donor atoms of low donor strength. Cs$^+$ is the largest singly charged monatomic cation and therefore of lowest electrophilicity.[9] Concomitantly, its polarizability is high.[10] According to van der Waals (vdW) radii, covalently bonded fluorine is the second largest element next to hydrogen (see below). Distinct from the H atoms in boronates, fluorine atoms participate in coordination with a full electron pair. Clearly, for ligand atoms other than hydrogen, coordination of Cs$^+$ with an array of covalently bonded fluorine atoms present as substituents in weakly coordinating anions (WCAs) seems a promising approach to obtain high CNs.

The most prominent and frequently applied WCAs include [B(C$_6$F$_5$)$_4$]$^-$, [(μ-H$_2$N)B$_2$(C$_6$F$_5$)$_2$]$^-$, [B{C$_6$H$_3$-3,5-(CF$_3$)$_2$}$_4$]$^-$, [Al{OC(CF$_3$)$_3$}$_4$]$^-$, and [(μ-F)Al$_2${OC(CF$_3$)$_3$}$_6$]$^-$. These anions are much larger than the classical complex anions such as PF$_6$$^-$, Sb$_2F_{11}$$^-$, or ClO$_4$$^-$, and the negative charge is distributed over a multitude of fluorine substituents, which renders the anions both extremely weakly basic and nucleophilic and at the same time relatively chemically inert.

Significant contributions to the field of WCAs have been made, among others, by the groups of Strauss, Piers, Reed, Marks, Krossing, and Bochmann.[11] Some time ago, our group reported the synthesis of $Tl[B(C_6F_5)_4]$,[12a] of which Piers et al. have determined the crystal structure,[12b] and more recently, we observed $[Al\{OC(CF_3)_3\}_4]^-$-facilitated "lattice stabilization"[13a,b] of the bis(piperidonium) dication held together merely by hydrogen bonds.[14]

In the context of these studies, we became interested in Bochmann's $[H_2NB_2(C_6F_5)_6]^-$ anion, for which we expected a similar lattice stabilization effect. Typical salts of the anion are $[Na(OEt_2)_4][H_2NB_2(C_6F_5)_6]$,[15a] $[H(OEt_2)_2]$-$[H_2NB_2(C_6F_5)_6]$,[15a] $[Tl(OEt_2)_4][H_2NB_2(C_6F_5)_6]$,[15c] and $[Tl$-$(toluene)_3][H_2NB_2(C_6F_5)_6]$,[15c] revealing its weakly coordinating nature. There are presently 43 crystal structures of $[H_2NB_2(C_6F_5)_6]$ salts included in the Cambridge Structural Database (CSD),[16] some of which contain several independent anions in the asymmetric unit. In all of the crystal structures reported, the anion adopts conformations **A** or **B** (Figure 1) or an intermediate thereof.
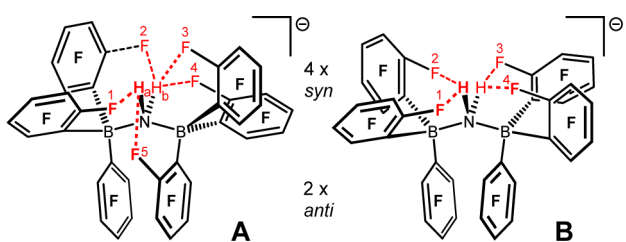

Figure 1. Commonly encountered conformations of the $[H_2NB_2(C_6F_5)_6]^-$ anion: **A**, when the anion is fully separated from cation; **B**, for the anion undergoing M···F or CH···F contacts with the cation.

In the quest for a simple and unsolvated reagent, we prepared hitherto unknown $Cs[H_2NB_2(C_6F_5)_6]$ (**1**). Unexpectedly, the anion in solute-free **1** adopted a novel C_2-symmetrical conformation. Moreover, the Cs^+ cation exhibited the highest CN ever observed for an isolated Werner-type complex[17] with an unprecedented tetracosahedral arrangement of the fluorine atoms. This must be seen as the consequence of an unforeseen conformational peculiarity of the $[H_2NB_2(C_6F_5)_6]^-$ anion.

■ RESULTS AND DISCUSSION

The title compound was first prepared by sonication of $[Na(OEt_2)_4][H_2NB_2(C_6F_5)_6]$[15a] and CsF in CH_2Cl_2 at 40 °C. After filtration to remove excess CsF and precipitated NaF, a clear solution was obtained, which was concentrated. The addition of pentane resulted in the separation of colorless cuboid crystals of solute-free $Cs[H_2NB_2(C_6F_5)_6]$ (**1**) in 74% yield over the course of several days. Subsequently, a much easier and quantitative synthesis of **1** was found by stirring $[Na(OEt_2)_4][H_2NB_2(C_6F_5)_6]$ with any soluble CsX salt in water and collecting precipitated **1** by filtration. The compound may then be recrystallized as described (eq 1).[18]
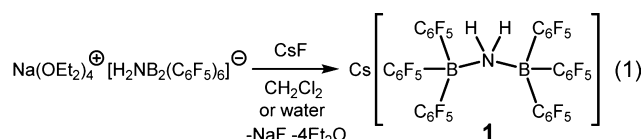
Compound **1** shows a sharp melting point at 125 °C. No obvious thermal anomaly was detected by differential scanning calorimetry (DSC). The compound dissolves well in CH_2Cl_2 (ε = 8.9) and THF (7.6) and even in solvents of low dielectric constant, such as chloroform, Et_2O, and toluene (4.9−2.4). It is only sparingly soluble in MeOH (32.7) and virtually insoluble in water (78.4) and alkanes (≤2.0). A solution of **1** in CD_2Cl_2 gives rise to the typical NMR signals for the $[H_2NB_2(C_6F_5)_6]^-$ anion, such as a broad ^1H signal for NH_2 ($\delta(H)$ 5.66), a singlet for boron ($\delta(^{11}B)$ −8.2), and in the ^{19}F NMR spectrum, the set of three multiplets at $\delta(^{19}F)$ −132.8, −160.1, and −165.6.[15a,c,19c] ^{133}Cs NMR of an utmost dilute solution of **1** in CD_2Cl_2 gives a sharp singlet at relatively low field, $\delta(^{133}Cs)$ 17.3, which shifts upfield to $\delta(^{133}Cs)$ 8.6 for a saturated solution.[20] Because downfield chemical shifts $\delta(^{133}Cs)$ are attributed to enhanced electron density at Cs^+, caused here by CD_2Cl_2 solvation of Cs^+ of the dissociated salt, the reverse upfield chemical shift points to reduced solvation and increased Cs^+−WCA ion-pairing of **1** at higher concentrations.[21a−c] No $^{133}Cs,^{19}F$ coupling is observed.

ESI mass spectroscopy of **1** displays almost exclusively the signals for Cs^+ (m/z = 133) and the intact anion $[H_2NB_2(C_6F_5)_6]^-$ (m/z = 1040). The IR spectrum of **1** (see Supporting Information) contains very few bands above 1715 cm^{-1} with weak resonances at 3375 cm^{-1} attributable to N−H stretching vibrations. Because the cation itself does not cause any bands, the series of bands at 1648(ms), 1517(s), 1461(vs), 1272(ms), 1082(vs), 976(vs), and 778(ms) cm^{-1} can be seen as characteristic for the $[H_2NB_2(C_6F_5)_6]^-$ anion in the C_2 conformation.

A single-crystal of **1** has been subjected to X-ray structure analysis (Table 1). The compound crystallizes in the monoclinic crystal system in the space group $C2/c$ (no. 15) with 4 equiv of molecular units in the unit cell (Figure 2). The four units are positioned on one of the 2-fold rotation axes that pass through the N and Cs atoms of a molecule and render both NH protons and the two $B(C_6F_5)_3$ entities equivalent. The anions adopt a chiral conformation, and **1** exists as pairs of enantiomers related by a center of symmetry. One pair of enantiomers is located in the middle of the unit cell, and an additional pair is located in the bc plane, centered on the c axis, and shared by four unit cells. A schematic drawing of the packing of cations and anions in the crystal structure of **1** is given in Figure 2b.

The conformation of the anion, **C**, is sketched in Figure 3. In contrast to all previously known salts of the $[H_2NB_2(C_6F_5)_6]^-$ anion, only two C_6F_5 groups are positioned "syn" with four "anti" to the NH_2 protons. Considering that conformation **B**, when ideal, would also be C_2 symmetrical, the inverse arrangement of the groups in **C** led us to denote this conformation as being "inverse C_2 symmetrical". The two syn-C_6F_5 rings are nearly coplanar to the central B,N,B^* plane and tilted away from that plane in opposite directions by 22°. The syn-C_6F_5 rings, with their edges and F8 atoms, adopt an approximately staggered conformation with respect to the NH_2 protons. The internal ortho and meta fluorine atoms of the syn-C_6F_5 rings, F8 and F9, enclose pairwise chelating and C_2-symmetrically the Cs^+ ion (Cs1···F8 = 3.200(2) Å and Cs1···F9 = 3.303(3) Å; F8−Cs1−F9 = 47.5(1)°).

Within the anion, the NH_2 protons extend unsymmetrically bifurcated hydrogen bonds to the ortho fluorine atoms F8 and F8*, N1H1···F8 = 2.30(4) Å (111°) and N1H1···F8* = 2.52(4) Å (95°), and markedly shorter bonds N1H1···F6 =

Table 1. Crystal Data and Structure Refinement of 1 and 2

compound (internal code)	1 (9342)	2 (9513)
CCDC number	1442824	1442825
empirical formula	$C_{36}H_2B_2CsF_{30}N$	$C_{37}H_4B_2Cl_2F_{30}NRb$
color	colorless	colorless
formula wt (g mol^{-1})	1172.92	1210.40
temp (K)	200(2)	100(2)
wavelength (Å)	0.71073	0.71073
cryst. syst.	monoclinic	orthorhombic
space group	$C2/c$ (No. 15)	$P2_12_12$ (No. 18)
Unit Cell Dimensions		
a (Å)	10.5035(16)	15.2711(5)
b (Å)	22.634(3)	22.003(4)
c (Å)	15.322(2)	11.5029(13)
α (deg)	90.0	90.0
β (deg)	102.826(3)	90.0
γ (deg)	90.0	90.0
V (Å^3)	3551.7(9)	3865.1(8)
Z	4	4
V/Z (Å^3)	887.9	966.3
calcd density (g cm^{-3})	2.194	2.080
abs coeff (mm^{-1})	1.236	1.600
$F(000)$ (e)	2240	2336
cryst. size (mm^3)	0.13 × 0.12 × 0.09	0.15 × 0.09 × 0.05
θ range for data collection (deg)	2.183−30.504	3.662−33.121
index ranges	$-14 \leq h \leq 14$	$-22 \leq h \leq 23$
	$-32 \leq k \leq 32$	$-33 \leq k \leq 33$
	$-21 \leq l \leq 21$	$-17 \leq l \leq 17$
no. of rflns collected	50553	79534
no. of indep. rflns	5418 (R_{int} = 0.040)	14652 (R_{int} = 0.0385)
no. of rflns with $I > 2\sigma(I)$	4780	12269
completeness (%)	100.0	99.6
abs correction	Gaussian	Gaussian
max/min transmission	0.94712/0.89715	0.92673/0.85000
full-matrix least-squares	F^2	F^2
no. of data/restraints/params	5418/0/310	14652/0/659
goodness of fit on F^2	1.666	1.087
Final R Indices ($I > 2\sigma(I)$)		
R1	0.0652	0.0479
wR2	0.2008	0.1276
R Indices (All Data)		
R1	0.0718	0.0656
wR2	0.2082	0.1420
abs struct. parameter		0.008(2)
largest diff. peak/hole (e Å^{-3})	1.17/−1.08	1.320/−1.973

Figure 2. (a) Unit cell of $Cs[H_2NB_2(C_6F_5)_6]$ (**1**). Selected bond lengths and an angle: B1−N1 = 1.646(3) Å, B1−C1 = 1.650(4) Å; B1−N1−B1* = 133.2(3)°. For Cs1···F distances, see the text. (b) Schematic presentation of the position and orientation of the molecular entities in the unit cell. The chirality of the anion is indicated in color.

Figure 3. Schematic presentation of the molecular structure of $Cs[H_2NB_2(C_6F_5)_6]$ (**1**), showing the novel conformation **C** of the anion.

2.13(4) Å (134°) with a more obtuse angle to the ortho-F6 atoms of two anti-C_6F_5 rings. The six N1−H1···F distances in conformation **C** generally appear longer and the angles at hydrogen accordingly smaller than for **A** and **B**. This suggests that in **1** the N−H···F bonding contacts contribute less to the stabilization of anion conformation **C** than is the case for conformations **A** and **B**.

In the crystal (Figure 2), each Cs$^+$ cation is bonded to five $[H_2NB_2(C_6F_5)_6]^-$ anions and each anion likewise to five Cs$^+$ cations. As a consequence of the C_2 symmetry at cesium, all Cs1···F contacts arise pairwise, and each Cs$^+$ ion is involved in a record-setting total of 16 such Cs1···F contacts, of which eight contacts (3.099(3), 3.196(5), 3.200(2), 3.303(3) Å) are relatively short and eight contacts (3.569(2), 3.591(3), 3.629(5), 3.799(1) Å) are long with a total mean distance of 3.423 Å.
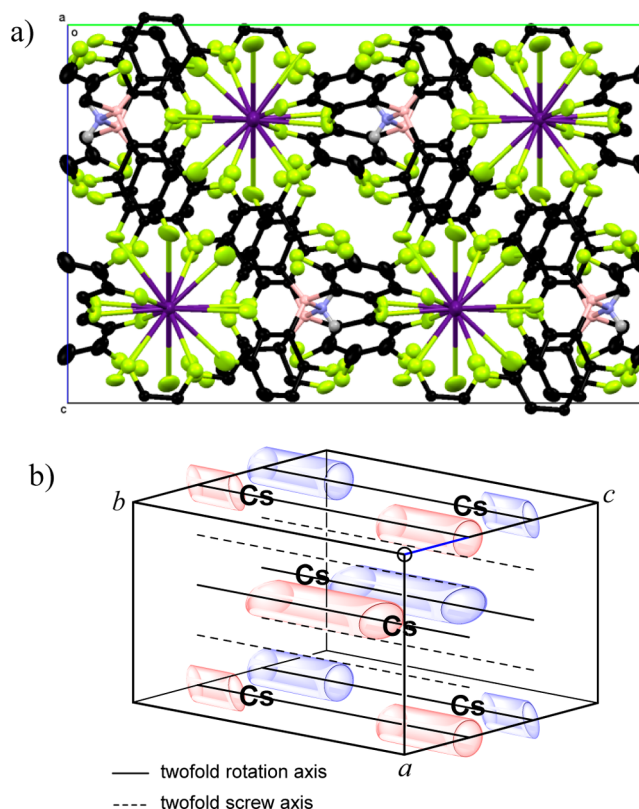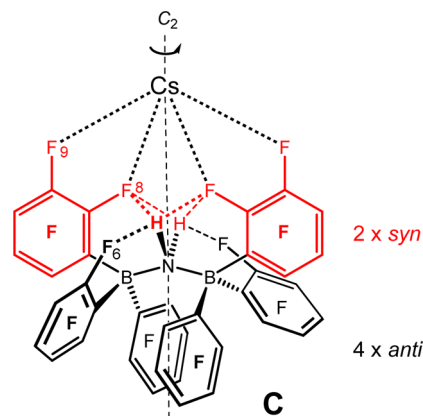
The Cs$^+$ ion is the largest stable monatomic cation (ionic radius for 6-coordinate Cs$^+$ is 1.67 Å),[22,23] and covalently bound fluorine atoms ($r_{ion}(F^-)$ = 1.37 Å, $r_{vdW}(F)$ = 1.47 Å) are the smallest atoms next to hydrogen ($r_{vdW}(H)$ = 1.20 Å).[24] For Cs$^+$ and covalently bound fluorine, only CNs $\leq$ 12 have been realized so far with Cs···F distances usually ranging between 3.05 and 3.55 Å; the mean of the values is generally larger than the sum of $r_{ion}(Cs^+)$ and $r_{vdW}(F)$ at 3.14 Å. For example, for $Cs[SbF_6]$ (mean of all Cs···F distances is 3.249 Å)[25] and $Cs[Sb_2F_{11}]$ (3.276 Å),[26] the CN is 12; for $Cs[Sb(OTeF_5)_6]$

(3.275 Å), the CN is merely 10,[27] and for $Cs[Al\{OC(CF_3)_3\}_4]$ (3.316 Å), the CN equals 11.[28b]

High coordination numbers imply a large coordination sphere and highly ionic bonding situations because only long and therefore weak bonds allow accommodation of many interactions about the central atom.[28a] Thus, **1**, with its record-setting 16 Cs···F bonding contacts and largest mean bond length, reflects an utmost ionic bonding situation. At the same time, we note that for the $_{55}Cs^+F_{16}$ coordination, the 32-e closed-shell electron configuration $[_{54}Xe]4f^{14}5d^{10}6s^2p^6$ of $_{86}Rn$ is achieved, which should contribute to stabilization.

At first glance, it appears counterintuitive that the least electrophilic of all monatomic cations, Cs^+, associates with the usually noncoordinating WCA so strongly that the latter even undergoes an unparalleled change of its conformation **A/B** to higher energetic mode **C**. Multiple key factors contribute to an explanation of the structure: (a) The low electrophilicity of Cs^+ means that its solvation enthalpy for diethyl ether and dichloromethane is also low. Hence, the otherwise non-coordinating $[H_2NB_2(C_6F_5)_6]^-$ can now outrival these solvents for binding to Cs^{+29} by electrostatic attraction,[21d] whereas more electrophilic cations retain the solvation. (b) With enthalpy becoming less important, entropic effects associated with the reduced ion solvation upon ion-pairing gain significance. (c) Although each single interaction of Cs^+ with fluorine appears to be weak, the many weak bonds add up to an overall strong association. This energy gain is in fact large enough to overcompensate the energy required for the necessary conformational reshaping of the $[H_2NB_2(C_6F_5)_6]^-$ anion, thus enabling the 16 F atoms from five anions to be placed in the Cs^+ coordination sphere and satisfying its subtle but distinct electronic demand. (d) An optimum geometrical match of alternating cations and anions allows for building of a strong 3D lattice. Some of these considerations may also provide a mechanistic rationale for explaining the "cesium effect" in organic chemistry.[30]

Polyhedron of the CsF$_{16}$ Coordination. To assign a polyhedron to the CsF_{16} coordination in **1**, a visual inspection of the distribution of F atoms suggests that there are pairs of equivalent quadrilaterals (F8, F8*, F5, F15) and envelope-folded pentagons (F4, F5, F15, F16, and F3). Thus, the 16 F atoms appear to be arranged in a tetracosahedron (24-hedron) geometry of 4 quadrilaterals and 20 triangles with 38 edges according to the Euler equation $N + F = E + 2$.

A list of prominent polyhedrons having 16 vertices is included in the Table S1. Although most of these polyhedrons can be excluded for obvious reasons, four deserve special attention: (a) The capped truncated tetrahedron (also named the Friauf polyhedron, 28-hedron; T_d symmetry) is present in many intermetallic phases.[6] (b) The related Thomson 28-hedron is calculated as the most stable distribution of 16 negative spherical charge points around a central 16+ charge with all charge points being identical. This polyhedron is similar to the Friauf polyhedron, albeit chiral and thus of lower symmetry (T).[31] However, both polyhedra have more faces (28, all triangles) than required by **1**. (c) The square gyrobicupola (Johnson solid J29, D_{4d} symmetry) has been established for the $Ag_{16}(PSi^tBu_3)_8$[32a] and $[Cu_{16}S_{10}]^{4-32b}$ clusters but features only 18 faces. (d) The disphenocingulum (J90; 4 squares, 20 triangles, 38 edges; D_{2d} symmetry) agrees with **1** in that it represents a 24-hedron, but the spatial arrangement of the faces does not meet the situation given in **1**.

In fact, there appears to be no example for a disphenocingulum cluster (D_{2d} tetracosahedron) in solid-state chemistry.[33]

For clarity, the geometrical situation in **1** is sketched in Figure 4. The coordination geometry of the CsF_{16} tetracosahe-
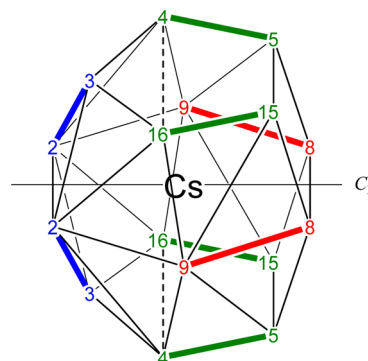

Figure 4. Tetracosahedral coordination geometry of 16-coordinate Cs^+ in **1**. Dotted lines indicate envelope folding of the pentagons forming quatrilaterals and triangles. Numbering denotes the location of proximate fluorine atoms identified in the X-ray structure analysis. F atoms connected by bold lines indicate the positions of the chelating pairs. Coloring: red, anion 1 positioned on C_2 axis; green, anions 2 and 3 related to anion 1 by inversion; and blue, anions 4 and 5 related to anion 1 by screw axes. Drawing is not to scale; for the same figure including geometrical data, see Figure S1.

dron approximates to capping a hexagon on both faces by a pentagon. The same result can be achieved by inserting a hexagon as the central deck into a pentagonal prism. An alternative view of the structure is that it is based on a hexagonal prism whose two opposing equivalent hexagons (F2, F4, F5, F8, F15, F16) and two neighborly equivalent squares (F2, F2*, F4, F16) are each capped. Although the ideal symmetry of such tetracosahedron is C_{2v}, it is lowered to C_2 in **1** due to the 8-fold pairwise binding of F atoms, the specific C_2 symmetrical conformation **C** of the anion, and the given mode of five binding anions to the central Cs^+. The given tetracosahedral arrangement of atoms appears to be unprecedented.

Utilizing the Insolubility of 1 in Water for Trapping $^{134/137}$Cs. The insolubility of **1** in water[34] suggests various applications of the $[H_2NB_2(C_6F_5)_6]^-$ anion with respect to the radioactive isotopes of cesium, namely, ^{131}Cs, ^{134}Cs, and ^{137}Cs. For illustration, we have carried out the following reactions (the IR spectra of all products agreed with that of pure **1**). (a) To an $\sim10^{-4}$ M aqueous solution of $Na[H_2NB_2(C_6F_5)_6]$ was added 1.04 equiv of CsCl. After brief mixing, a clear solution resulted from which crystals of **1** soon separated in 66% yield. Extraction (once) of the aqueous phase with CH_2Cl_2 and evaporation of the solvent gave a further crop of **1** with a total yield of 98%. (b) A suspension of $Na[H_2NB_2(C_6F_5)_6]$ in water was stirred overnight. The crystals of $Na[H_2NB_2(C_6F_5)_6]$ disappeared and were replaced by slimy material (possibly a hydronium salt) covering the glass wall. When CsCl was added, this material disappeared almost instantaneously, and after some time, solid **1** began to separate out. (c) The experiment according to (a) was repeated using water containing additional salts (KCl, $PbCl_2$, $CrCl_3$, $CaCl_2$, and $FeCl_3$). A brown precipitate was formed, which was considered to be a mixture of **1** and $Fe(OH)_3$. After filtration, the solid was extracted with CH_2Cl_2. Removal of the solvent left a colorless residue of **1** (76%); thus,

Cs$^+$ was selectively separated from the initial solution. Precipitation of **1** from water is distinctly different from the separation of Cs salts by ion exchange resins or complexation with polyether ligands. The driving force for the separation of **1** appears to be hydrophobicity of the [H$_2$NB$_2$(C$_6$F$_5$)$_6$]$^-$ anion and the favorable formation of the 3D lattice based on Cs$^+$F$_{16}$ coordination. There appears to be 100% specificity of the [H$_2$NB$_2$(C$_6$F$_5$)$_6$]$^-$ anion for the Cs$^+$ ion in aqueous solutions.

We see possible applications for Na[H$_2$NB$_2$(C$_6$F$_5$)$_6$] (i) with the formation of **1** as a $^{134/137}$Cs remover from nuclear waste solutions[35] and (ii) as an antidote for humans and animals in the case of $^{134/137}$Cs contamination, similar to the current administration of Prussian blue (Radiogardase, supplier Heyl, Berlin, Germany).[36] (iii) Direct utilization of **1** incorporating radioactive isotopes ^{131}Cs or ^{137}Cs might occur in brachytherapy of various cancers, taking advantage of the insolubility of such compounds in water and their easy preparation by precipitation from aqueous solutions.

Rb[H$_2$NB$_2$(C$_6$F$_5$)$_6$]·CH$_2$Cl$_2$ (2). A reaction related to eq 1 has been carried out in CH$_2$Cl$_2$ with RbF instead of CsF, affording the crystalline solid Rb[H$_2$NB$_2$(C$_6$F$_5$)$_6$]·CH$_2$Cl$_2$ (**2**). X-ray structure analysis of **2** (space group P2$_1$2$_1$2 (No. 18), Z = 4; Table 1) reveals the presence of two independent Rb$^+$ cations, Rb1 and Rb2, both lying on 2-fold rotational axes parallel to c (Figure 5 and Figures S2 and S3). Rb1 assumes CN 10 and is
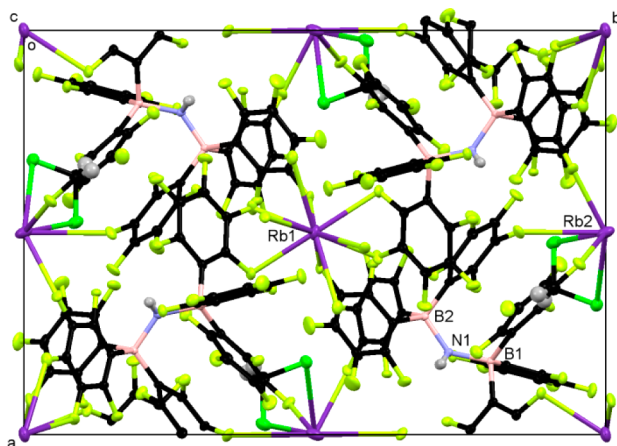

Figure 5. Molecular structure of Rb[H$_2$NB$_2$(C$_6$F$_5$)$_6$]·CH$_2$Cl$_2$ (**2**).

bonded to four pairs of vicinal F atoms of C$_6$F$_5$ groups (F11/F12 and F22/F23 with F−Rb1−F = 54.0 and 51.1°) and two single F atoms (F35−Rb1−F35* = 47.7°) from a total of six surrounding anions (Rb1−F = 2.836−3.247(3) Å with a mean of 3.051 Å). Rb2 also assumes CN 10 but appears to bond to only six single F atoms of four anions (F17, F21, and F29; Rb2−F = 2.809−3.292(3) Å with a mean of 3.048 Å), preferring to chelate two additional CH$_2$Cl$_2$ ligands (Rb2−Cl1 = 3.5973(14) Å, Rb2−Cl2 = 3.4986(16) Å). Whereas the Rb$^+$ cation exhibits two coordination spheres in **2**, the [H$_2$NB$_2$(C$_6$F$_5$)$_6$]$^-$ anion adopts just one asymmetric conformation of type **A**. The four equivalent anions of the unit cell are related to one another by 2-fold screw axes parallel to a and b. The difference in the structures of **1** and **2** can be attributed to the smaller ionic radius of the Rb$^+$ cation (r_{ion}(Rb$^+$) = 1.52 Å) compared to that of Cs$^+$, leading to a smaller CN for Rb$^+$ and a higher electrophilicity[9] of the Rb$^+$ cation, resulting in the binding of two solvent molecules to Rb2. Compound **2** appears to be the first example of structurally characterized Rb(η-Cl$_2$CH$_2$) coordination.

Effective Volume of the [H$_2$NB$_2$(C$_6$F$_5$)$_6$]$^-$ Anion and Lattice Potential Energy of 1. The structures of Cs[H$_2$NB$_2$(C$_6$F$_5$)$_6$] (**1**) and Rb[H$_2$NB$_2$(C$_6$F$_5$)$_6$]·CH$_2$Cl$_2$ (**2**) allowed us to determine the effective volume of the [H$_2$NB$_2$(C$_6$F$_5$)$_6$]$^-$ anion and the lattice potential energy of **1** by applying the Jenkins−Passmore volume-based thermodynamics (VBT) approach.[13] Calculating the volume of a molecule or ion from the vdW radii of the atoms generally creates voids that remain inaccessible for other species (solvents, counterions) but actually add to the space requirements of the molecule or ion. Thus, vdW volumes are generally smaller than the actual space required by the molecules or ions. To solve this problem for purely ionic compounds, Jenkins et al. have suggested determining the "effective" or "thermochemical volume" of the ion by assuming that the region of the crystal not occupied by the cation is assigned to the anion and vice versa. Thus, when molecular volume V_m = V/Z is determined from the crystal structure data, and the volume of the counterion is also known, the volume of an ion in question can be easily determined by subtraction. Most conveniently, the structures of Cs salts are studied as (i) Cs$^+$ represents the largest and least electrophilic[9] monatomic cation, (ii) its salts are usually free from other molecules such as solute molecules that therefore do not have to be accounted for, (iii) its volume can be determined from

Table 2. Effective Volume of Some Fluorinated Anions and their Tl or Cs Salts
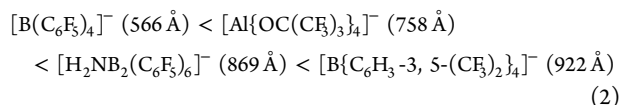
compound	V_m, Å^3	V(cation), Å^3	V_{therm}(anion), Å^3	V_{vdW}(anion), Å^3
Cs[AsF$_6$]	138.6[40]	19	120[a]	
Cs[SbF$_6$]	149.0[25]	19	130[a]	
Cs[Sb$_2$F$_{11}$]	241.2[26]	19	222[a]	
Cs[B(CF$_3$)$_4$]	249.4[41]	19	230	
Tl[B(C$_6$F$_5$)$_4$]	580.2[12b]	14	566[b]	349,[15b] 405[11g]
Cs[Sb(OTeF$_5$)$_6$]	743.2	19	724[27]	
Cs[Al{OC(CF$_3$)$_3$}$_4$]	777.3	19	758[28b]	
Cs[H$_2$NB$_2$(C$_6$F$_5$)$_6$]	888	19	869[b]	538,[15b] 621[11g]
Tl[B{C$_6$H$_3$-3,5-(CF$_3$)$_2$}$_4$][d]	936[42]	14	922	
[CI$_3$][(μ-F)Al$_2${OC(CF$_3$)$_3$}$_6$]	1222.7	109.4[c]	1113[38b,38c]	

^{a}Somewhat lower values by averaging the values from several structures with different alkali metals have previously been reported. For a better comparison, the data in this table refer exclusively to Cs and Tl salts. ^{b}These works. ^{c}Determined by comparing the molecular volumes of Cs[Al{OC(CF$_3$)$_3$}$_4$], [CI$_3$][Al{OC(CF$_3$)$_3$}$_4$], and [CI$_3$][(μ-F)Al$_2${OC(CF$_3$)$_3$}$_6$].[38b,c] ^{d}The compound is suspected to contain in the crystal 0.33 molecules of CH$_2$Cl$_2$ per molecular formula unit, which could not however be unambiguously located from the data.

the reliably known ionic radius, and (iv) any error in the assessment of the volume of Cs^+ remains insignificant owing to the much larger volume of the anions. Using $_{55}Cs^+$ ($r_{ion}(Cs^+) = 1.67$ Å)[22,23a] is preferable to $_{47}Ag^+$ (1.15 Å), $_{37}Rb^+$ (1.52 Å), and $_{81}Tl^+$ (1.50 Å) as the latter cations are substantially smaller and more electrophilic with Ag^+ mostly, and Tl^+ frequently, giving rise to solvent donor adducts. In the cases where no crystalline Cs salts but solvent-free Tl salts are available, the latter can be taken as a substitute. From the established ionic radius of Cs^+, the volume of the cation is $V(Cs^+) = 19$ Å^3, and the corresponding values for Tl^+ are $r_{ion}(Tl^+) = 1.50$ Å and $V(Tl^+) = 14$ Å^3.

The effective (thermochemical) volumes V_{eff} of some frequently used fluorinated WCAs are listed in Table 2. From the crystal data of $Tl[B(C_6F_5)_4]$ ($V_m = 580.2$ Å^3,[12b] $V(Tl^+) = 14$ Å^3), we calculated for the $[B(C_6F_5)_4]^-$ anion $V_{eff} = 566$ Å^3. This value is appreciably larger than its calculated vdW volume and represents a multiple of those of the classical complex anions such as $[AsF_6]^-$, $[SbF_6]^-$, and $[Sb_2F_{11}]^-$. Nevertheless, the space required by $[B(C_6F_5)_4]^-$ is still only moderate when compared with $[Sb(OTeF_5)_6]^-$ ($V_{eff} = 724$ Å^3) and $[Al\{OC-(CF_3)_3\}_4]^-$ ($V_{eff} = 758$ Å^3).[28b] Regarding $[H_2NB_2(C_6F_5)_6]^-$, from the structure of 1 ($V_m = 888$ Å^3) and $V(Cs^+) = 19$ Å^3, the volume of the anion in its C_2 symmetrical conformation **C** is determined to be $V_{eff} = 869$ Å^3. Thus, the anion is found to be considerably larger (by roughly 50%) than previously assumed on the basis of the calculated vdW volume, and it is also appreciably larger than that of $[Al\{OC(CF_3)_3\}_4]^-$, as determined by the same method. As a cross-check, V_{eff} of the $[H_2NB_2(C_6F_5)_6]^-$ anion, now in its C_1 symmetrical conformation **A**, can also be determined from the molecular volume of 2, $V_m = 966$ Å^3, $V(Rb^+) = 15$ Å^3, and $V(CH_2Cl_2) = 82$ Å^3,[37] arriving at exactly the same value of $V_{eff} = 869$ Å^3. This suggests that the volume of the $[H_2NB_2(C_6F_5)_6]^-$ anion is largely independent of its conformation. $[H_2NB_2(C_6F_5)_6]^-$ is surpassed in its volume by the "BARF" anion $[B\{C_6H_3-3,5-(CF_3)_2\}_4]^-$ ($V_{therm} = 922$ Å^3) and by $[(\mu-F)Al_2\{OC(CF_3)_3\}_6]^-$ ($V_{therm} = 1113$ Å^3).[38] Interestingly, estimating the volumes of the anions by the Hofmann atom volume increments[39] leads for $[B(C_6F_5)_4]^-$ (569 Å^3) and $[H_2NB_2(C_6F_5)_6]^-$ (883 Å^3) to values in close agreement with those determined by the VBT method, whereas for the other anions in Table 2, deviations of the estimated volumes are more pronounced.

When choosing an anion for crystallizing a salt of an organic, inorganic, or organometallic cation, the relative sizes of cations and anions are often neglected. It is our feeling that for effective crystallization of a WCA salt a proper matching of cations and WCAs with respect to their relative sizes is an important criterion. Thus, in practical terms, to find a fitting anion for a given cation, it seems advisable to test out a standard assortment of the most significant WCAs of different sizes. For this purpose, it might be helpful to resort to the sequence of the most prominent WCAs with the now known increasing effective volumes.

$$[B(C_6F_5)_4]^-\ (566\,\text{Å}) < [Al\{OC(CF_3)_3\}_4]^-\ (758\,\text{Å})$$
$$< [H_2NB_2(C_6F_5)_6]^-\ (869\,\text{Å}) < [B\{C_6H_3\text{-}3,5\text{-}(CF_3)_2\}_4]^-\ (922\,\text{Å})$$
$$(2)$$

complemented by further compounds in Table 2. The new data extend and correct the existing volume data for some useful WCAs.

On the basis of the molecular volume of 1, the lattice potential energy was calculated by the elegant Jenkins–Passmore VBT approach to be $U_{POT} = 348$ kJ mol^{-1}. This value is appreciably smaller than that of $Tl[B(C_6F_5)_4]$[12] at 385 kJ mol^{-1} (see Supporting Information). The rather low value of 1 reflects the large volume of the anion and also explains the high solubility of 1 in solvents of low dielectric constant such as diethyl ether and toluene. Similar calculations have been performed previously for $Cs[Sb(OTeF_5)_6]$[27] and $Cs[Al\{OC-(CF_3)_3\}_4]$.[28b]

CONCLUSIONS

We have reported the synthesis and structural properties of $Cs[H_2NB_2(C_6F_5)_6]$ (1) in which Cs^+ as the largest monatomic and least electrophilic cation is ion-paired with the weakly coordinating anion $[H_2NB_2(C_6F_5)_6]^-$. For comparison, the structure of $Rb[H_2NB_2(C_6F_5)_6]\cdot CH_2Cl_2$ (2) is also reported. The results are relevant to the fields of coordination chemistry and weakly coordinating anions in numerous aspects: (i) $Cs[H_2NB_2(C_6F_5)_6]$ (1) is the first simple solute-free salt of the $[H_2NB_2(C_6F_5)_6]^-$ anion combined with a monatomic cation. The more electrophilic Na^+, Tl^+, and Rb^+ are all at least partially solvated (see 2). (ii) In addition to the previously established conformations **A** and **B** of the $[H_2NB_2(C_6F_5)_6]^-$ anion, compound 1 reveals a novel strictly C_2 symmetrical conformation **C**, in which only two (instead of the usual four) C_6F_5 groups are in the "syn" position ("inverted C_2 symmetry"). (iii) For ligand atoms other than hydrogen, the ultimate Werner CN 16 has been achieved for the first time, exceeding the so far highest accepted CN 12 in magnitude. For the observed CsF_{16} coordination geometry, a likewise novel tetracosahedral arrangement of F atoms is observed. (iv) High coordination numbers imply a large coordination sphere and highly ionic bonding situations because only long and therefore weak bonds allow the accommodation of many interactions about the central atom. Thus, 1, with its record-setting 16 $Cs\cdots F$ bonding contacts and largest $Cs\cdots F$ mean bond length, reflects an utmost ionic bonding situation. Interestingly, Cs^+ in CsF_{16}^+ appears to adopt the formal 32-e closed-shell electron configuration $[_{54}Xe]4f^{14}5d^{10}6s^2p^6$ of $_{86}Rn$. (v) Counterintuitively, the least electrophilic monatomic cation associates so strongly with the WCA that it imposes a novel and higher energetic conformation to the anion. Because solvation energy of Cs^+ is low and no durable solvation takes place, Cs^+ can associate optimally with the WCA in the solid in contrast to the situation for the more electrophilic Tl^+ and Rb^+, which become more strongly shielded by solvation with Et_2O or CH_2Cl_2. (vi) The effective volume of the $[H_2NB_2(C_6F_5)_6]^-$ anion has been determined from the structural data by the VBT method. Thus, on the basis of experimental data, an ordering of $[H_2NB_2(C_6F_5)_6]^-$ together with other prominent WCAs of high practical usage in a series of increasing anion volumes has become possible (eq 2). (vii) The sequence of eq 2 assists a size-based matching of cations and anions for ion-pairing considered important for successful crystallization in many instances. (viii) The structure of 2, which features a CN of only 10 for both Rb^+ cations, highlights the unique and record-setting coordination mode adopted by the larger, less electrophilic, and more polarizable Cs^+ in 1.

EXPERIMENTAL SECTION

Synthesis of $Cs[H_2NB_2(C_6F_5)_6]$ (1). (a) A two-necked round-bottom flask, equipped with a reflux condenser, was filled with

$[Na(OEt_2)_3][H_2NB_2(C_6F_5)_6]$ (2.57 g, 2.00 mmol), CsF (0.32 g, 2.1 mmol), and CH_2Cl_2 (50 mL). The flask was placed in an ultrasonic bath, and the suspension was sonicated for 14 h; by cooling, the bath temperature was kept at 40 °C. The excess of CsF and the precipitated NaF were removed by filtration, and the volume of the solution was reduced to approximately 25 mL. Admixing pentane to the solution afforded separation of colorless crystals with a yield of 1.74 g (74%). (b) $[Na(OEt_2)_3][H_2NB_2(C_6F_5)_6]$ (2.57 g, 2.00 mmol) and CsCl (0.34 mg, 2.02 mmol) were mixed in 30 mL of water. After some time, the precipitate was collected by filtration, washed with water, and dried under a vacuum, resulting in a yield of 2.25 g (96%). ^1H NMR (CD_2Cl_2): δ 5.66 (broad, NH_2). ^{11}B NMR (CD_2Cl_2): δ −8.2 (s). ^{19}F NMR (CD_2Cl_2): δ −132.8 (d, 2C, F_{ortho}), −160.1 (t, 1C, F_{para}), −165.6 ("t", 2C, F_{meta}). ESIpos MS (CH_2Cl_2) m/z (%): 133 $([Cs]^+$, 100). ESIneg MS (CH_2Cl_2) m/z (%): 528 $([H_2NB(C_6F_5)_3]^-$, 2), 1040 $([H_2NB_2(C_6F_5)_6]^-$, 100). Anal. Calcd for $C_{36}H_2B_2CsF_{30}N$ (1172.9): C, 36.87; H, 0.17; B, 1.84; Cs, 11.33; F, 48.59; N, 1.19. Found: C, 36.77; H, 0.10; B, 1.64; Cs, 10.29; F, 47.15; N, 2.19. Rb-$[H_2NB_2(C_6F_5)_6]\cdot CH_2Cl_2$ (2) has been prepared accordingly in CH_2Cl_2 solution.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/jacs.6b02590.

Calculation of U_{POT} of **1** by the VBT method (PDF)
IR specra of **1** (CIF)
IR specra of **2** (CIF)

■ AUTHOR INFORMATION

Corresponding Author

*poerschke@kofo.mpg.de

Notes

The authors declare no competing financial interest.

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here as it affects the derived volume of the anion by only ∼1% of the value. (b) The metallic radius of Cs is 2.65 Å, and the vdW radius of Cs has been suggested as an exceedingly large 3.43 Å.[24b]

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(34) For a suspension of $Cs[H_2NB_2(C_6F_5)_6]$ (**1**) in deionized water, stirred for several hours, no change in electric conductivity as compared to that in pure water ($\sigma = 2\ 10^{-3}$ S/m at 23.6 °C) is found. The unchanged **1** is virtually quantitatively recovered (e.g., 10 mg of **1** from 100 mL of water), excluding dissolution of **1** as an ion-pair. Thus, solubility of isolated **1** in water can be assessed at <1 ppm.

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