Inorganic Chemistry

Cyanido Antimonate(III) and Bismuthate(III) Anions

Sören Arlt,[†] Jörg Harloff, Axel Schulz,^{*,†,‡} Alrik Stoffers,[†] and Alexander Villinger[†]

[†]Institut für Chemie, Universität Rostock, Albert-Einstein-Straße 3a, 18059 Rostock, Germany

[‡]Leibniz-Institut für Katalyse e.V. an der Universität Rostock, Albert-Einstein-Straße 29a, 18059 Rostock, Germany

Supporting Information

ABSTRACT: The reaction of in situ generated $E(CN)_3$ (E = Sb, Bi) with different amounts of [Ph₄P]CN and [PPN]CN ([PPN]⁺ = [Ph₃P-N-PPh₃]⁺) was studied, affording salts bearing the novel ions $[E(CN)_5]^{2-}$, $[Bi_2(CN)_{11}]^{5-}$, and $[Bi(CN)_6]^{3-}$. The valence lone pair of electrons on the central atom of antimony and bismuth(III) compounds can be either sterically active in an unsymmetric fashion (three shorter bonds + x longer bonds) or symmetric (with rather long averaged bonds). In the presence of weakly coordinating cations (e.g., $[Ph_4P]^+$ and $[PPN]^+$), the solid-state structures of salts with [E(CN)₅]²⁻ anions contain well-separated cations and monomeric anions, which display a sterically active lone pair and a monomeric square-based pyramidal (pseudo-octahedral) structure. The [Bi(CN)₅· MeCN]²⁻ acetonitrile adduct ion exhibits a strongly distorted



octahedral structure, which is better understood as a [5+1] coordination. The intriguing $[Ph_4P]_6[Bi_2(CN)_{11}]CN$ salt consists of separated cations and anions as well as well-separated $[Bi_2(CN)_{11}]^{5-}$ and CN^- ions. The structure of the molecular [Bi₂(CN)₁₁]⁵⁻ ion can be described as two square-based-pyramidal [Bi(CN)₅]²⁻ fragments connected by a disordered bridging CN⁻ ion, thereby leading to a distorted-octahedral environment around the two Bi centers. Here the steric effect of the lone pair is much less pronounced but still present.

INTRODUCTION

The interest in cyano-pnictogen chemistry began in 1863, when Hübner and Werhane discovered that $P(CN)_3$ is formed in the reaction of PCl₃ and three equivalents of AgCN.¹ Knoth et al. used Me₃SiCN as a cyanide source and treated the pnictogen trichlorides ECl_3 (E = P, As, Sb, Bi), with Me₃SiCN, yielding the corresponding $E(CN)_3$ species (Scheme 1).² Structural

Scheme	1.	Synthesis	of I	E(CN))3 ($(\mathbf{E} =$	Sb,	Bi)
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EX ₃ +	3 Mo. SiCN	xylene	E(CN) _e	+	3 Me ₃ SiX
	0 1010301014	reflux			
		X = F, CI			

characterization was only successful for $P(CN)_3$ and As- $(CN)_{3}$.^{3,4} In a series of spectroscopic and theoretical papers, the structure and vibrational spectra of $E(CN)_3$ species have been discussed.^{1,3–19}

Dronskowski et al. pointed out that cooperativity amplifies pnictogen bonds which are mainly responsible for the formation of polymeric structures. These noncovalent interactions increase the heavier the pnictogen atom is, which nicely explains that $Sb(CN)_3$ and $Bi(CN)_3$ feature a network structure and a very low solubility in organic and inorganic solvents. Molecular units of Sb(CN)₃ and Bi(CN)₃ were isolated recently when ionic liquids were utilized as reaction media, which prevented oligomerization.²⁰ Only two ternary P-CN anions have been reported so far: (i) the dicyanophosphide

 $[P(CN)_2]^-$ and the unusual $[(NC)_2P-NC(CN)_2-P(CN)_5]^{2-}$ ion which were both described by Schmidpeter et al. 21-24Ternary pnictogen(V) cyanides are not yet known. Recently, the isolation and full characterization of salts bearing the fluorido-cyanido phosphate anions of the type $[PF_{6-n}(CN)_n]^-$ (with n = 1-5) were reported.^{25,26} To the best of our knowledge, there have been only four reports on antimony and bismuth cyanide complex compounds: however, all without any structural characterization: $^{27-30}$ Allman et al. described the formation of anionic $[Ph_2Bi(CN)_2]^-$ complexes in the reaction of [Ph₂BiCl₂]⁻ with NaCN on the basis of IR and elemental analysis data.²⁷ Alkali salts, containing the [SbCl₅(CN)]⁻ anion, were discovered by Müller upon addition of MCN (M = Na, K) to a solution of $SbCl_5$ in SO_2 .²⁸ Rastogi studied the reaction of $SbCl_3$ with KCN, which afforded the formation of K₂[SbCl₃(CN)₂].²⁹ In 2009 Renz and co-workers reported the isolation of an iron salt containing the $[Sb(CN)_6]^-$ ion from the reaction of $[SbCl_6]^-$ with KCN in acetone under reflux for 6 days.³⁰ In light of the rather poor analytical data (ESI-MS and IR data, Mössbauer spectra) the formation of the $[Sb(CN)_6]^-$ ion seems to be rather doubtful. Actually, we could not find the mentioned ESI-MS and IR data in the paper, or any elemental analysis data at all. Our own studies clearly showed that it is impossible to get a complete Cl/CN exchange by this procedure starting from $[SbCl_6]^-$.

Received: September 9, 2016

Scheme 2. Synthesis Protocol for $[WCC]_n[E(CN)_{3+n}]$ $(n = 1-3)^a$.

$$EF_3 + 3 Me_3SiCN + n[WCC]CN \longrightarrow [WCC]_n[E(CN)_{3+n}] + 3 Me_3SiX$$

^aIt should be noted that in all cases side products such as insoluble $E(CN)_3$ were observed.

Table 1. Product Distribution of the Reaction of EF_3 with *n* equiv of [WCC]CN in an Excess of Me_3SiCN ($[WCC]^+ = [Ph_4P]^+$, $[PPN]^+$)

	amt of [WCC]CN, equiv				
compd	1	2	3		
$[Ph_4P]^+, E = Sb$	$Sb(CN)_3/[Sb(CN)_5]^{2-}$	$Sb(CN)_{3}/[Sb(CN)_{5}]^{2-}$	$Sb(CN)_3/[Sb(CN)_5]^2/CN^-$		
$[PPN]^+, E = Sb$ $[Pb, P]^+, E = Bi$	$Sb(CN)_3/[Sb(CN)_5]^{2-}$ B;(CN)_/[B;(CN)_1]^2-	$Sb(CN)_{3}/[Sb(CN)_{5}]^{2-}$ B;(CN) /[B;(CN)] ²⁻ /[B;(CN)] ³⁻ /CN ⁻	$Sb(CN)_3/[Sb(CN)_5]^{2-}/CN^{-}$ B;(CN)/[B;(CN)] ⁵⁻ /CN ⁻		
$[PPN]^+$, E = Bi	$Bi(CN)_3/[Bi(CN)_5]^{2-}$	$Bi(CN)_{3}/[Bi(CN)_{5}]^{2}/[Bi(CN)_{6}]^{3}/CN^{-1}$	$Bi(CN)_3/[Bi(CN)_5]^2/[Bi(CN)_6]^3/CN^-$		

With respect to antimony and bismuth pseudohalide complexes, e.g. azides, it is noteworthy to mention that for both pnictogen atoms a variety of azido species have been isolated and fully characterized.^{31–42} To fill the gap with respect to antimony and bismuth cyanide compounds, we have studied the reaction of $E(CN)_3$ (E = Sb, Bi) with CN^- ions, and we report here on the synthesis and structural characterization of cyanido antimonates(III) and bismuthates(III).

RESULTS AND DISCUSSION

Synthesis. In a first series of experiments we prepared $E(CN)_3$ from EF_3 and Me_3SiCN (Scheme 1; E = Sb, Bi) and treated these highly insoluble polymeric $E(CN)_3$ compounds with [WCC]CN ($[WCC]^+ =$ weakly coordinating cation = $[Ph_4P]^+$, $[PPN]^+$ (= $[Ph_3P-N-PPh_3]^+$)). Regardless, no matter which organic solvent (e.g., acetonitrile) we used, no reaction was observed even after several days of reaction time and under reflux. For this reason, we changed our approach and reacted EF_3 with 3 equiv of Me_3SiCN in the presence of *n* equiv of [WCC]CN (*n* = 1–3) in acetonitrile (Scheme 2 and Table 1).

In the case of SbF₃ all three experiments led exclusively to the formation of $[WCC]_2[E(CN)_5]$ salts. In addition to $[WCC]_2[Sb(CN)_5]$ amounts of Sb(CN)₃ were always detected depending on the utilized stoichiometry of [WCC]CN, which is the reason the yields were rather poor (between 20 and 30%). Therefore, when only 1 equiv of [WCC]CN was used, mixtures of Sb(CN)₃ and $[Sb(CN)_5]^{2-}$ were always observed. It was impossible to isolate or even observe the desired $[WCC][Sb(CN)_4]$ salts. Upon addition of 3 equiv of [WCC]CN also only $[WCC]_2[Sb(CN)_5]$ salts could be isolated in addition to excess [WCC]CN. No formation of $[WCC]_3[Sb(CN)_6]$ was observed.

A similar situation was found for the reaction of BiF₃ with 3 equiv of Me₃SiCN in the presence of *n* equiv of [WCC]CN (n = 1-3) in acetonitrile (Scheme 2 and Table 1). With 1 equiv of [WCC]CN also only the formation of [WCC]₂[Bi(CN)₅] and Bi(CN)₃ was detected. Moreover, as expected, [WCC]₂[Bi(CN)₅] salts were obtained when BiF₃ was treated with 3 equiv of Me₃SiCN and 2 equiv of [WCC]CN. However, we also observed side products such as [WCC]₃[Bi(CN)₆] and [WCC]CN. For example, [PPN]₂[Bi(CN)₅·MeCN] always crystallized as the main product in addition to small amounts of [PPN]₃[Bi(CN)₆] or unreacted [PPN]CN, which also could be isolated by fractional crystallization. On one occasion we were able to isolate pure, acetonitrile-free [PPN]₂[Bi(CN)₅]. Moreover, also only on one occasion were we able to observe a difference between the two utilized WCCs, namely in the

reaction of BiF₃ with 3 equiv of [PPN]CN and an excess of Me₃SiCN, which led to the formation of a double salt, containing the unusual $[Bi_2(CN)_{11}]^{5-}$ and the "uncoordinated" naked CN⁻ ion. Hence, this double salt is best understood as a mixed crystal of $[Ph_4P]_5[Bi_2(CN)_{11}]$ and $[PPh_4]CN$.

It can be assumed that the bismuth reaction mixture is highly dynamic with respect to the CN ligand sphere around the formal Bi^{3+} cation and that, depending on solubility, concentration, and temperature, different products can be isolated. Therefore, only small isolated yields between 10 and 30% were possible. All antimony and bismuth cyanido complexes are rather labile with respect to moisture and decompose without melting above 170 °C.

It should be noted that, instead of acetonitrile, we also used ionic liquids (e.g., [BMIm][OTf], $[BMIm][N(Tf)_2]$, and $[P_{6,6,6,14}][N(Tf)_2]$ with $[P_{6,6,6,14}] =$ trihexyltetradecylphosphonium, $[OTf] = [CF_3SO_3]^-$, $[NTf]^- = [N(CF_3SO_3)_2]^-$) as solvents but in all these cases we were only able to isolate $[WCC]_2[E(CN)_5]$ (E = Sb, Bi); it was very difficult to isolate/ crystallize pure products from the rather viscous ionic liquids.

In particular, Raman spectroscopy is well-suited to detect uncoordinated CN^{-} $(
u_{\mathrm{CN}}$ 2051 cm $^{-1})$ and remaining MeCN (2247 cm^{-1}) from the synthesis process (Figure S5 in the Supporting Information). In addition, in the case of the $[E(CN)_5]^{2-}$ species always two well-resolved CN stretching modes were detected which could be assigned to the apical CN group appearing at higher wavenumber (Sb, 2180–2170 cm⁻¹; Bi, 2173 cm⁻¹) and the four basal CN groups (Sb, 2130–2100 cm⁻¹; Bi, 2119–2102 cm⁻¹) at slightly lower wavenumber in accord with computed wavenumbers (Figure S5). The latter mode appeared as a broad peak, but on some occasions further splitting was observed. Interestingly, for the $[Bi(CN)_6]^{3-}$ ion only one rather broad peak was observed at 2109 cm⁻¹. For the $[Ph_4P]_5[Bi_2(CN)_{11}]$ species we observed two broad peaks in the expected area for the two $[Bi(CN)_5]$ units (2115–2107 cm⁻¹) but in addition also the uncoordinated CN⁻ ion was detected at 2048 cm⁻¹ (cf. 2051 cm⁻¹ for [PPh₄CN]; Figure S5).

In addition, IG-¹³C NMR techniques (IG = inverse gate with D1 = 60 s) were utilized to detect the number of CN groups for all dissolved species. In all cases we always observed only the presence of $[E(CN)_5]^{2-}$ species (E = Sb, 139.0 ppm; Bi, 147.9 ppm; Figures S1 and S2 in the Supporting Information). Free CN⁻ was only detected upon significantly prolonged accumulation time as a broad signal at 165 ppm due to an increased dynamic. Probably, $[Bi(CN)_6]^{3-}$ or the bridged ion $[Bi_2(CN)_{11}]^{5-}$ is only formed upon the crystallization process

Table 2. Experimentally Observed, Selected Bond Lengths (Å) and Angles (deg) of All Considered Pnictogen Cyanide Species(E = Sb, Bi)representation of the second secon

compound	E-C	cis-C–E–C	trans-C-E-C	E-C-N
$[PPh_4]_2[Sb(CN)_5]$	2.142(4), 2.305(4), 2.351(4), 2.411(4), 2.479(5)	$78.7(1),79.9(1),80.3(1),80.3(1),84.1(1),84.9(1),85.8(1),\\86.6(1)$	158.3(1), 163.0(1)	166.0(3), 169.8(4), 174.3(3), 174.5(4), 178.8(4)
[PPN] ₂ [Bi(CN) ₅]	2.213(4), 2.47(1), 2.475(9), 2.483(6), 2.557(8),	77.0(2), 78.1(2), 82.2(2), 83.7(2), 84.8(2), 87.6(2), 90.5(2), 91.9(3)	159.2(2), 161.5(2)	173.4(4), 174(2), 174.4(7), 175.5(6), 179.4(3),
[PPN]₂[Bi(CN)₅· MeCN]	2.23(2), 2.47(2), 2.48(2), 2.51(2), 2.57(2)	79.4(5), 80.2(5), 80.3(5), 82.9(4), 84.2(5), 85.7(4), 87.9(5), 96.2(5)	161.6(5), 160.2(4)	168(1), 170(1), 176(1), 179(1), 180(1)
[PPN] ₃ [Bi(CN) ₆]	2.342(6), 2.414(6), 2.467(6), 2.615(6), 2.688(7), 2.798(6)	78.8(2), 82.1(2), 83.4(2), 83.5(2), 84.1(2), 84.4(2), 84.8(2), 86.8(2), 90.6(2), 94.4(2), 105.4(2), 115.1(2)	161.4(2), 162.3(2), 166.01(2)	160.7(5), ^c 164.0(5), ^c 173.6(5), ^c 175.4(5), 176.8(5), 179.3(6)
[PPh ₄] ₆ [Bi ₂ (CN) ₁₁] CN	2.312(2), ^{<i>a</i>} 2.484(2), 2.505(6), 2.551(2), 2.605(3), 2.960(9) ^{<i>b</i>}	$\begin{array}{l} \$1.9(1), \$3.0(1), \$3.18(7), \$3.81(6), \$4.73(6), \$6.88(6), \\ \$9.60(6), \$1.8(2), {}^{b} \ 96.1(2), {}^{b} \ 97.5(1), \$9.6(2), {}^{b} \ 99.7(3) {}^{b} \end{array}$	162.6(1), 168.33(6), $174.8(2)^{b}$	166.3(9), ^b 172.4(2), 173.6(3), 174.4(3), 175.9(2), 179.4(2)

 a C5–Bi1 (in Figure 4) featuring the position trans to the bridging C6–N6 unit. b Involving the bridging C6 atom. c Involving a C atom with a long Bi–C bond length.



Figure 1. (left) Molecular structure of the anion in $[Ph_4P]_2[Sb(CN)_5]$. Displacement ellipsoids are drawn at 50% probability (173 K). Selected bond lengths (Å) and angles (deg) are summarized in Table 2. (right) Ball-and-stick representation of the unit cell, with a view along the *a* axis showing separated ions.

or the dynamics in solution is too fast to be visualized by NMR methods. At any rate, it was impossible to detect these species in solution. According to these NMR results, the formation of considerable amounts of $[E(CN)_4]^-$ ions in solution is rather unlikely, in accord with the fact that on crystallization no salt formation with these ions was observed even when the exact stoichiometry was used.

Crystal Structures. The structures of $[PPN]_2[Sb(CN)_5]$, $[Ph_4P]_2[Sb(CN)_5]$, $[PPN]_2[Bi(CN)_5]$, $[PPN]_2[Bi(CN)_5]$, $[PPN]_2[Bi(CN)_5]$, MeCN], $[PPN]_3[Bi(CN)_6]$, and the double salt $[Ph_4P]_6[Bi_2(CN)_{11}]CN$ have been determined. Moreover, the structures of the starting material (pure) $[Ph_4P]CN$, as well as $[PPN]CN \cdot 2MeCN$ and $[PPN]CN \cdot (toluene)$ can be found in Table S1 in the Supporting Information. Tables S1–S3 in the Supporting Information present the X-ray crystallographic data. Selected molecular parameters of all discussed cyanide pnictogen compounds are given in Table 2.

 $[PPN]_2[Sb(CN)_5]$ crystallizes in the orthorhombic space group *Pbca* with four formula units per cell, while $[PPh_4]_2[Sb-(CN)_5]$ crystallizes in the monoclinic space group $P2_1/n$ also with four formula units per cell (Figure 1). Both structures consist of well-separated cations and $[Sb(CN)_5]^{2-}$ anions with no significant cation…anion contacts. As expected, $[Sb-(CN)_5]^{2-}$ adopts a strongly distorted square pyramidal geometry. There are no significant interactions between the anions (smallest interanionic Sb···N distance: $[Ph_4P]_2[Sb-(CN)_5]$, 5.771(4) Å; $[PPN]_2[Sb(CN)_5]$, 6.77(3) Å). Since the structure of $[PPN]_2[Sb(CN)_5]$ displays a strong disorder within the $[Sb(CN)_5]^{2-}$ ion, we wish to focus on $[Ph_4P]_2[Sb-(CN)_5]$ in the discussion but want to stress that the metrical parameters of both salts are rather similar. The basal Sb–C distances lie in the range between 2.305 and 2.479(5) Å (Table 2), while the apical Sb–C5 distance is considerably shorter at 2.142(4) Å (cf. $\sum r_{cov}(Sb-C) = 2.15$ Å).⁴³ Interestingly, all C5–Sb–C angles are smaller than 90°, since the Sb atom sits slightly inside the pyramid due to the steric demand of the lone pair (vide infra). All cyanido ligands are rather flexible, as shown by the Sb–C–N angles which are all smaller than the expected 180°.

[PPN]₂[Bi(CN)₅] crystallizes isotypically with [PPN]₂[Sb-(CN)₅] also in the orthorhombic space group *Pbca* with four formula units per cell. As discussed before, neither significant interactions between the cations and anions nor between the anions are found. [PPN]₂[Bi(CN)₅·MeCN] crystallizes in the monoclinic space group *Cc* with four units per cell. The molecular structural features of the $[Bi(CN)_5]^{2-}$ ion are very similar in comparison to those of the antimony analogue (vide supra), in addition to the fact that the Bi–C distances are slightly longer (basal 2.47–2.56 Å, apical 2.21 Å, cf. $\sum r_{cov}(Bi-C) = 2.26 Å_5^{43}$ Table 2). Interestingly, upon adduct formation

with acetonitrile these metrical parameters do not change much. The acetonitrile molecule (Figure 2, bottom) is loosely



Figure 2. (left) Molecular structure of the anion in $[PPN]_2[Bi(CN)_5]$. (right) Molecular structure of the anion in $[PPN]_2[Bi(CN)_5 \cdot MeCN]$. Displacement ellipsoids are drawn at 50% probability (173 K). Selected bond lengths (Å) and angles (deg) are summarized in Table 2. Donor-acceptor distance $d(N8 \cdots Bi1) = 3.14(1)$ Å.

connected by means of a weak Bi–N donor–acceptor bond (3.14(1) Å; cf. $\sum r_{cov}(Bi-N) = 2.22 Å,^{43} \sum r_{vdW}(Bi\cdots N) = 3.62 Å^{44}$ and 2.81(1) Å in MeCN·Bi(N₃)₃).³¹ Hence, the coordination geometry around bismuth is strongly distorted with respect to octahedral coordination (e.g., C5–Bi1–N8 157.5(4)°) but is better referred to as a [5 + 1] coordination mode.

 $[PPN]_3[Bi(CN)_6]$ crystallizes in the orthorhombic space group $Pna2_1$ with four formula units per cell. In the crystal there are no anion—anion contacts, as they are completely separated by $[PPN]^+$ cations. Figure 3 displays the C_1 -



Figure 3. Molecular structure of the anion in $[PPN]_3[Bi(CN)_6]$. Displacement ellipsoids are drawn at 50% probability (173 K). Selected bond lengths (Å) and angles (deg) are summarized in Table 2.

symmetric molecular structure of the $[Bi(CN)_6]^{3-}$ ion at 173 K with a strongly distorted octahedral BiC_6 skeleton. Interestingly, three shorter (2.342(6), 2.414(6), 2.467(6) Å) and three longer Bi–C distances (2.615(6), 2.688(7), 2.798(6) Å) are found (cf. $\sum r_{cov}(Bi-C) = 2.26$ Å,⁴³ $\sum r_{vdW}(Bi\cdots C) = 3.77$ Å⁴⁴). Hence, the coordination around the Bi center in $[Bi(CN)_6]^{3-}$ can be best described as a [3 + 3] coordination similar to the known low-temperature structure of $[Bi(N_3)_6]^{3-31}$

According to the traditional VSEPR description,⁴⁵ the $[Bi(CN)_6]^{3-}$ ion belongs to the class of AB₆X molecules (X = lone pair). Most known AB₆X molecules have an octahedral structure with the lone pair centered on the nucleus, but a few

(e.g., $[SeF_6]^{2-}$, $[TeF_6]^{2-}$, $[IF_6]^{-}$, XeF_6) have a distortedoctahedral structure ($C_{3\nu}$ symmetry) with a slightly off-centered lone pair. In such cases, in solids there are usually three or even four longer secondary bonds surrounding the position of the lone pair in accord with the formal [3 + 3] coordination description in $[Bi(CN)_6]^{3-}$ (vide supra).⁴⁶ The $C_{3\nu}$ distortion can also be attributed to a pseudo-Jahn-Teller effect. As discussed by Bersuker,⁴⁷ interatomic and molecular interactions generate bonded states of lower symmetry, which can be referred to as induced by a Jahn-Teller distortion. All these AB₆X species have in common that they have very flat potential energy surfaces (vide infra): that is, small effects in the solid state may have a strong influence on the molecular structure. In addition to the $[Bi(CN)_6]^{3-}$ ion, experimental structure data are also available of the pseudohalide complex ions $[BiY_6]^{3-}$ (Y $= N_{3,}^{31}$ SCN).⁴⁸ For $[Bi(N_3)_6]^{3-}$ variable-temperature single-crystal X-ray studies revealed a strongly distorted lowtemperature isomer with a stereochemically active lone pair localized at the Bi^{III} center ([3 + 3] coordination) and a hightemperature isomer with an approximate O_h-symmetric BiN₆ core and six rather long Bi-N distances due to the symmetric repulsive effect of the lone pair. For $[Bi(SCN)_6]^{3-}$ also a rather complicated structure was observed, since the structure consists of ions at sites of crystallographic inversion symmetry leading to an octahedral BiS_6 core.⁴⁸ However, the authors discuss distortion to D_{3h} symmetry and assume that this geometry is a result of a dynamic disorder between at least two $C_{3\nu}$ BiS₆ geometries.

The double salt $[Ph_4P]_6[Bi_2(CN)_{11}]CN$ crystallizes in the triclinic space group $P\overline{1}$ with two formula units per unit cell. Formally, this double salt can be dismantled into $[Ph_4P]CN$ and $[Ph_4P]_5[Bi_2(CN)_{11}]$. With respect to the anion the latter salt bearing the $[Bi_2(CN)_{11}]^{5-}$ ion can be considered as a Lewis acid $([Bi(CN)_5]^{2-})/Lewis$ base $([Bi(CN)_6]^{3-})$ complex with one bridging cyanide ligand of the $[Bi_2(CN)_6]^{3-}$ ion linking to the $[Bi(CN)_5]^{2-}$ ion (Figure 4). A similar bonding situation is



Figure 4. Molecular structure of the $[Bi_2(CN)_{11}]^{5-}$ ion in $[PPh_4]_6[Bi_2(CN)_{11}]CN$. Displacement ellipsoids are drawn at 50% probability (173 K). Selected bond lengths (Å) and angles (deg) are summarized in Table 2 and Table S6 in the Supporting Information. The disorder of the bridging N6–C6 ion is not shown here (but in Figure 5). Symmetry code: (i) 1 - x, 1 - y, 2 - z.

found in the well-known weakly coordinating anion $[Sb_2F_{11}]^$ ion;⁴⁹ however, both antimony atoms are in the oxidation state +V, whereas the bismuth atoms in $[Bi_2(CN)_{11}]^{5-}$ are in the oxidation state +III. Interestingly, this double salt represents a formal isomer of the analogous $[Ph_4P]_3[Bi(CN)_6]$ salt, since they have the same empirical formula $([Ph_4P]_6[Bi_2(CN)_{11}]CN$ = 2 $[Ph_4P]_3[Bi(CN)_6]$). However, so far it has been impossible to crystallize $[Ph_4P]_3[Bi(CN)_6]$; we always obtained $[Ph_4P]_6[Bi_2(CN)_{11}]CN$. It can be assumed that the larger $[PPN]^+$ counterion favors the crystallization of a salt with the isolated $[Bi(CN)_6]^{3-}$ ion while the smaller $[Ph_4P]^+$ ion allows more intermolecular interaction, thereby allowing the formation of a double salt containing the dinuclear $[Bi_2(CN)_{11}]^{5-}$ ion comprising a weakly interacting $(CN)^-$ bridge.

As shown in Figure 5, there are no significant interactions between the isolated CN^{-} ion and the $[Bi_{2}(CN)_{11}]^{5-}$ (distance



Figure 5. View along the *a* axis in $[Ph_4P]_6[Bi_2(CN)_{11}]CN$. Color code: Bi, violet; N, blue; C, gray; P, orange; isolated CN^- ion for which C and N cannot be distinguished, green. Hydrogen atoms are omitted for clarity. Not all bonds of the disordered CN groups to the Bi atoms are shown.

>8 Å) or between the $[Bi_2(CN)_{11}]^{5-}$ ions, since they are wellseparated by the $[Ph_4P]^+$ ions. The naked CN^- ion sits at the center of inversion in the middle of the unit cell and displays a disorder over two positions, which does not allow us to distinguish between carbon and nitrogen. In addition, the bridging CN^- ion (N6–C6 1.006(6) Å) is orientationally disordered with two CN units which coordinate either by the N or the C atom to both Bi³⁺ ions (for details see the Supporting Information).

A closer look at the bond lengths and angles reveals strong similarities to the structure of the $[Bi(CN)_5]^{2-}$ or $[Bi(CN)_5]^{2-}$ MeCN²⁻ ions rather than to the $[Bi(CN)_6]^{3-}$ ion. (i) Neglecting the bridging CN⁻ ion for a moment, each formal Bi³⁺ ion is square pyramidal with one short apical Bi-C distance (Bi1–C5 2.312(2) Å; cf. 2.213(4) Å in $[Bi(CN)_5]^{2-}$) and significantly longer basal Bi-C distances (between 2.484(2) and 2.605(3) Å; cf. 2.47(1)-2.557(8) Å in [Bi- $(CN)_{5}^{2-}$. (ii) The short Bi-C distance is opposite to the position of the lone pair (vide infra) and all C-Bi-C5 angles are smaller than 90°, thereby providing more space for the lone pair. (iii) There are not three distinctly shorter and three longer Bi–C distances as found for the $[Bi(CN)_6]^{3-}$ ion. As expected, the distances to the bridging CN⁻ ion are rather long (Bilⁱ-C6 2.960(9) Å and Bi1–N6 2.819(8) Å); cf. 3.14(1) Å in $[Bi(CN)_5 \cdot MeCN]^{2-}$ ($\sum r_{cov}(Bi-N) = 2.22$ Å and $\sum r_{cov}(Bi-C) = 2.26$ Å).⁴³ Hence, it might be more appropriate to consider the complex $[Bi_2(CN)_{11}]^{5^-}$ ion as two $[Bi(CN)_5]^{2^-}$ ions linked by weak donor-acceptor interactions with one CN⁻ ion in a [5 + 1] coordination mode.

Structure, Lone Pair Activity, and Thermodynamics. Gas-phase computations have been carried out for $E(CN)_3$ and the $[E(CN)_4]^{-1}$, $[E(CN)_5]^{2-}$, and $[E(CN)_6]^{3-}$ anions $(E = Sb, CN)^{-1}$ Bi) utilizing the density functional M06-2X, an aug-cc-pvTZbasis set for the C and N atoms, and for the pnictogen E a fully relativistic pseudopotential (Sb, ECP28MDF; Bi, ECP60MDF) and an aug-cc-pVTZ basis set. Solvent effects, which are essential to stabilize highly charged ions, are incorporated using the integral equation formalism version of the polarizable continuum model (PCM; solvent acetonitrile). For E(CN)₃, $[E(CN)_4]^-$, and $[E(CN)_5]^{2-}$ the expected $C_{3\nu}$ (trigonal pyramidal), $C_{2\nu}$ (bisphenoidal), and $C_{4\nu}$ (square pyramidal) symmetric structures were found to be the global minima, in accord with the experimental data. For the $[Sb(CN)_6]^{3-}$ anion the global minimum has $C_{3\nu}$ symmetry, while the octahedral species represents no minimum (number of imaginary frequencies 3) and lies 14.3 kcal mol⁻¹ above the C_{3v} -symmetric minimum. For the softer $[Bi(CN)_6]^{3-}$ ion a very flat potential energy surface (PES) was observed (C_{3v} , C_{4v} , and O_h -symmetric structure lie all within 1 kcal mol⁻¹). The only minimum structure, which could be detected, is also a C_{3v} symmetric structure with three short (2.426 Å) and three significantly longer Bi-C distances (2.721 Å) in accord with the experimental data found in the solid state. As depicted in Figure 6, the ELF (electron localization function) of the



Figure 6. Electron localization function of the $[Bi(CN)_6]^{3-}$ ion at 0.85 displaying the active lone pair localized at the Bi atom.

 $[Bi(CN)_6]^{3-}$ ion features a stereochemically active lone pair localized at the Bi atom pointing directly to the center of the triangle composed of the three carbon atoms with the longer Bi–C distance. A comparison with the ELF of Bi(CN)₃ (Figure S7 in the Supporting Information) underlines the idea of a [3 + 3] coordination mode in $[Bi(CN)_6]^{3-}$ (and $[SbCN)_6]^{3-}$). It should be noted that the ELF displaying the lone pair does not necessarily indicate electron density sitting in a 6s valence orbital. It is also feasible that electron density from 6p orbitals, which are involved in the Bi–CN bonding, is depicted. In any case this localized density is stereochemically active.

It is interesting to note that the deviation of the $C_{3\nu}$ symmetric $[\text{Bi}(\text{CN})_6]^{3-}$ structure to C_3 -symmetric (0.08 kcal mol⁻¹) or O_h -symmetric geometries (1.04 kcal mol⁻¹) is very small, but these are nonminimum structures (see Table S11 in the Supporting Information). We do want to stress that the known DFT methods were neither developed nor validated for triply negatively charged anions; hence, the quality of the results cannot be judged. The computational problem is even more complex, since the PES of the $[\text{Bi}(\text{CN})_6]^{3-}$ anion is extremely flat, so that dispersion, electron correlation, polarization effects, and basis set effects including relativistic effects must be considered. Therefore, solid-state effects such as cation—anion interactions may have a huge influence, which was recently demonstrated for the $[Bi(N_3)_6]^{3-}$ ion.³¹ As shown in Tables S10 and S11 in the Supporting Information, solvent effects also play an essential role, especially in stabilizing highly charged ions in solution. Nevertheless, experimental structural data obtained from X-ray studies are available and compare well with the experimental data. Hence, we can conclude that in all considered species including the $[E(CN)_6]^{3-}$ ion the lone pair is active, which is supported by ELF computations (see Figures 6–8).^{50–54} Moreover, the ionic bonding between the E³⁺ ions and the cyanido ligands becomes clearly visible in the electron localization function. The ELFs of $[Bi_2(CN)_{11}]^{5-}$ and $[Bi-(CN)_5\cdotMeCN]^{2-}$ are shown in Figures 7 and 8, also clearly



Figure 7. Electron localization function at 0.85 displaying the active lone pair localized at the Bi atom: (top) $[Bi_2(CN)_{11}]^{5-}$; (bottom) $[Bi(CN)_{5}$ ·MeCN]²⁻. Experimental structures were used.



Figure 8. 2D cross section of the electron localization function (ELF) depicted in a plane through atoms Bi, N, and C: (top) $[Bi_2(CN)_{11}]^{5-}$; (bottom) $[Bi(CN)_5 \cdot MeCN]^{2-}$. Experimental structures were used.

displaying an active lone pair at the bismuth ion. Interestingly, the ELF also displays distorted lone pairs located on the

 N_{MeCN}/C_{CN} donor atom and the Bi^{3+} ion in $[Bi(CN)_{5}\cdot$ $MeCN]^{2-}$ as well as in $[Bi_{2}(CN)_{11}]^{5-}$. Furthermore, the lone pair of the coordinating atom of the cyanide ion is always strongly compressed.

Natural bond orbital analysis (NBO analysis)^{55,56} also clearly indicates ionic bonding between formal E^{3+} and CN^- ions (Table S12 in the Supporting Information). The charge distribution for all species is characterized by a positive net charges at the pnictogen atom (Sb, 1.25–1.35e; Bi, 1.41– 1.45e) which hardly changes upon increasing the number of cyanido ligands. A closer look at the computed s character of the lone pair localized at the E atom and the occupation of the *ns* orbitals (n = 5 for Sb and n = 6 for Bi) exhibits small but significant differences (Table S12). (i) In comparison to the Sb species all Bi species always display a larger s character of the localized lone pair and the s character increases along the series $E(CN)_3 < [E(CN)_4]^- < [E(CN)_5]^{2-} < [E(CN)_6]^{3-}$. (ii) Analogously, the occupation of the *ns* valence orbital increases.

Thermodynamic data including solvent effects (PCM, solvent acetonitrile) of the successive anion formation upon adding CN^- to $E(CN)_3$ was also computed (eqs 1-3, Tables S10 and S11 in the Supporting Information). While the first two addition steps were computed to be exergonic for both species (eq 1, Sb -14.8 and Bi -13.5 kcal mol⁻¹; eq 2, Sb -2.7and Bi -7.3 kcal mol⁻¹), leading to the formation of $[E(CN)_4]^-$ and $[E(CN)_5]^{2-}$, respectively, the third step (formation of $[E(CN)_6]^{3-}$) is slightly endergonic (eq 3, Sb 8.7 and Bi 1.9 kcal mol^{-1}). Interestingly, the formation of $[Bi(CN)_6]^{3-}$ is much less endergonic and close to zero, in accord with experimental observation. Since at least salts bearing the $[E(CN)_5]^{2-}$ ion (E = Sb, Bi) and $[Bi(CN)_6]^{3-}$ were synthesized, it can be assumed that solid-state effects such as electrostatic interactions between cations and anions significantly stabilize salts containing these dianions or even trianions such as $[Bi(CN)_6]^{3-}$.

$$E(CN)_3 + CN^- \rightarrow [E(CN_3)_4]^-$$
(1)

 $[E(CN)_4]^- + CN^- \rightarrow [E(CN)_5]^{2-}$ (2)

$$[E(CN)_5]^- + CN^- \rightarrow [E(CN)_6]^{3-}$$
 (3)

CONCLUSIONS

EF₃ was treated with Me₃SiCN in the presence of [Ph₄P]CN and [PPN]CN ([PPN]⁺ = $[Ph_3P-N-PPh_3]^+$) to synthesize salts bearing the novel ions $[E(CN)_5]^{2-}$ (E = Sb, Bi), $[Bi_2(CN)_{11}]^{5-}$, and $[Bi(CN)_6]^{3-}$. With an excess of cyanide salt, the smaller weakly coordinating cation $[Ph_4P]^+$ allows more intermolecular interaction between the formal Bi^{III} atoms, resulting in the formation of $[Bi_2(CN)_{11}]^{5-}$ ions, which can be understood best as two $[Bi(CN)_5]^{2-}$ ions linked by one bridging CN⁻ ion, while for the larger [PPN]⁺ cation only the formation of the $[Bi(CN)_6]^{3-}$ ion was observed. The solid-state structures of all considered species contain well-separated cations and monomeric anions, which display a sterically active lone pair at the pnictogen atom. The $[Bi(CN)_{5} \cdot MeCN]^{2-}$ acetonitrile adduct ion features a formal distorted-octahedral structure, which, however, is better understood as a [5 + 1]coordination due to a rather long MeCN…Bi distance indicating also a sterically active lone pair at the Bi center. The experimentally observed structure of a salt containing the $[Bi(CN)_6]^{3-}$ ion shows three long and three short Bi–C bonds due to a sterically active lone pair at the Bi^{III} atom. Hence, the

coordination mode is best described as a [3 + 3] binding mode, in agreement with theoretical observations displaying a $C_{3\nu}$ symmetric geometry as the only minimum on the very flat PES. Thermodynamic data indicate an exergonic formation of the $[E(CN)_4]^-$ and $[E(CN)_5]^{2-}$ ions but slightly endergonic reactions for the formation of $[E(CN)_6]^{3-}$. It is obvious that in the condensed phase solid state/solvent effects such as electrostatic interaction between cations and anions or ions and solvent molecules stabilize salts containing such doubly/triply negatively charged ions with highly dynamic cyanide ligands.

ASSOCIATED CONTENT

S Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.inorg-chem.6b02174.

Experimental procedures and spectral data for all discussed compounds including starting materials, detailed X-ray data and discussion of disorder problems, additional analytical data, and computational data (PDF) Crystallographic data (CIF)

AUTHOR INFORMATION

Corresponding Author

*E-mail for A.S.: axel.schulz@uni-rostock.de.

ORCID ⁽⁶⁾

Axel Schulz: 0000-0001-9060-7065

Notes

The authors declare no competing financial interest.

ACKNOWLEDGMENTS

The authors thank the DFG (SCHU 1170/9-1), especially the priority program SPP 1708, for financial support.

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