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Pseudohalide HCN aggregate ions:  $[N_3(HCN)_3]^-$ ,  $[OCN(HCN)_3]^-$ ,  $[SCN(HCN)_2]^-$  and  $[P(CN \cdot HCN)_2]^-$  †

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In the presence of  $\mu$ -nitridobis(triphenylphosphonium) cation, [PPN]<sup>+</sup>, it was possible to stabilize and isolate [PPN]<sup>+</sup>-salts bearing the highly labile hydrogen cyanide aggregate anions of pseudohalides X (X = N<sub>3</sub>, OCN and SCN). From a concentrated solution of the [PPN]X salts in HCN, crystals of [PPN][X(HCN)<sub>3</sub>] (X = N<sub>3</sub>, OCN) or [PPN][SCN(HCN)<sub>2</sub>] could be obtained, when the crystallization was carried out fast and at low temperatures. The reaction of liquid HCN with the PCO<sup>-</sup> salt led to formation of dicyanophosphide, which crystallized as HCN disolvate [P(CN·HCN)<sub>2</sub>]<sup>-</sup>. All synthesized salts with hydrogen-bridged pseudohalide solvate anions are thermally unstable. Immediate loss of HCN was observed in the crystals outside the HCN solution. Oligomerization begins at ambient temperature, even in HCN solution. All discussed species were characterized by means of Raman spectroscopy, single crystal X-ray analysis and quantum-chemical calculations.

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### Introduction

The term "Pseudohalogen" was already introduced in 1925 by Birckenbach and Kellermann and describes heteroatomic molecules that are very similar in their chemical behaviour to halogens.<sup>1-5</sup> The most prominent features of pseudohalogen compounds are probably the formation of (i) single negatively charged anions, such as  $X^- = CN^-$ ,  $OCN^-$ ,  $SCN^-$ ,  $N_3^-$  or  $OCP^-$ , (ii) poorly soluble silver or mercury salts (AgX,  $Hg_2X_2$ ), dimers (X-X, e.g. NC-CN) as well as Brønsted acids HX. In addition, some pseudohalogens exist as neutral inter(pseudo)halogens (e.g. BrCN) and form covalent non-metal compounds (e.g. P(CN)<sub>3</sub>) as well as salts, containing pseudohalogenido complexes, such as [Si(CN)<sub>6</sub>]<sup>2-.6-8</sup> Moreover, some disproportionate in basic water solution (e.g. NC-CN + 2  $OH^- \rightarrow OCN^- +$  $CN^{-} + H_2O$ ). This concept can be extended to further characteristic features with respect to solvate cations  $([H_nX_{n-1}]^+)$  and anions ( $[X(HX)_n]^-$ ), which can also exist as mixed halogen/ pseudohalogen ions, for example  $[Y(HX)_n]^-$  (X and Y = halide and/or pseudohalide).

Solvate anions containing the same halides have been known for almost two centuries. It dates back to 1856, when Edmond Frémy described the synthesis of anhydrous HF start-

ing from K[FHF].9 Nearly 80 years later, Bozorth determined the X-ray structure of the potassium salt for the first time.<sup>10</sup> Later on, the solid state structures of higher aggregates of the type  $[F(HF)_n]^-$  (*n* = 2–5, 7) were determined.<sup>11–18</sup> Furthermore, the molecular structures of  $[Cl(HCl)_n]^ (n = 1-5)^{19-23}$  and [Br $(HBr)_n$   $[n = 1, 2)^{21,24,25}$  were investigated by single crystal X-ray diffraction, while the iodides could not be crystallized so far. In 1965, Dove synthesized the first hydrogen dipseudohalide salt, [Ph<sub>4</sub>As][H(NCS)<sub>2</sub>], starting from [Ph<sub>4</sub>As][HCl<sub>2</sub>] and two equivalents of KSCN in SO<sub>2</sub> (Scheme 1).<sup>26</sup> By means of X-ray crystallography a slightly bent structure of the anion in the solid state could be observed.<sup>27,28</sup> Dehnicke et al. were able to synthesize  $[Ph_4P][H(N_3)_2]$  with *in situ* generated HN<sub>3</sub>, which was treated with [Ph<sub>4</sub>P]N<sub>3</sub> (Scheme 1).<sup>29</sup> Salthouse and Waddington described the attempted synthesis of [nPr<sub>4</sub>N][H  $(CN)_2$ , which led to an oily residue with the characteristics (according to IR analysis) of the mono-solvate anion [H (CN)<sub>2</sub>]<sup>-.30</sup> However, the determination of its molecular structure is still missing.

Less is known about mixed aggregate anions of the type [Y  $(HX)_n$ ]<sup>-</sup>. Most of these compounds were studied using IR,

[Ph <sub>4</sub> As][HCl <sub>2</sub> ] + 2 K <mark>NCS</mark>	SO <sub>2</sub>	[Ph <sub>4</sub> As][H( <mark>NCS</mark> ) <sub>2</sub> ] + 2 KCI
[Ph <sub>4</sub> P] <mark>N<sub>3</sub> + Me<sub>3</sub>Si–N<sub>3</sub> + EtOH</mark>		[Ph <sub>4</sub> P][H(N <sub>3</sub> ) <sub>2</sub> ] + Me <sub>3</sub> Si–OEt
[WCC] <mark>CN</mark> + n HCN	HCN <sub>ex.</sub>	[WCC][ <mark>CN(HCN</mark> ) <sub>n</sub> ]

**Scheme 1** Synthesis of  $[Ph_4As][H(NCS)_2]$ ,<sup>26</sup>  $[Ph_4P][H(N_3)_2]^{29}$  and  $[WCC][CN(HCN)_n]^{31}$  ([WCC] = weakly coordinating cation =  $[Ph_4P]$  for n = 2 and [PPN] for n = 3).

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NMR or MS techniques, which gave information on the bond strengths of the hydrogen bridges.<sup>30,32–38</sup> Recently, the group of Hasenstab-Riedel reported on the crystal structures of  $[Ph_4P]$ - and [PPN]-salts, containing solvate anions with different halides, such as  $[X(HCl)_4]^-$  (X = Br, I),  $[I(HCl)_3]^-$ ,  $[I (HBr)_2]^-$  and  $[X(HF)_2(HX)]^-$  (X = Br, I), as well as the first structures of  $[ClO_4(HF)_2]^-$  and  $[Br(HCN)]^-$ , which contain both, a halide and pseudohalide.<sup>23</sup>

Just recently, we reported on the synthesis of HCN aggregates of the type  $[CN(HCN)_n]^-$  (n = 2, 3), starting from [WCC]CN ([WCC] = weakly coordinating cation<sup>39,40</sup> = [PPN],  $[Ph_4P]$ ) and liquid HCN at low temperatures.<sup>31</sup> This work prompted us to investigate the HCN solvation of other pseudohalides, such as N<sub>3</sub><sup>-</sup>, OCN<sup>-</sup>, SCN<sup>-</sup> and OCP<sup>-</sup>. Here, we present the synthesis of low-temperature stable  $[PPN]^+$ -salts with  $[X(HCN)_3]^-$  (X = N<sub>3</sub>, OCN),  $[SCN(HCN)_2]^-$  and  $[P(CN \cdot HCN)_2]^-$  as HCN-solvate counter anions, which were investigated by X-ray crystallography and low-temperature Raman spectroscopy.

### **Results and discussion**

#### Synthesis

We started this project with the synthesis of pseudohalide salts of the type [PPN]X (X = N<sub>3</sub>, OCN, SCN, OCP), which were produced using a modified literature reaction.<sup>27</sup> Gaseous HCN was synthesized from NaCN and stearic acid at 80-100 °C under vacuum.41-44 The [PPN]X salts were cooled to 0 °C and an excess (approx. 16-19 eq.) of cooled liquid HCN was transferred onto the salts. This led to dissolution of the pseudohalides when the mixtures were shaken gently, except for the OCP salt, where formation of a suspension was observed. Furthermore, in case of the [PPN]OCN and [PPN]OCP, fast progressing polymerization/oligomerization of the liquid layer was observed, which led to a darkening and an increase in the viscosity of the phase. In contrast, the HCN mixtures of the [PPN] N<sub>3</sub> and [PPN]SCN remained nearly colorless. Since all these reactions were carried out without further solvent, the highly concentrated reaction medium can be considered as a mixture with the properties of an ionic liquid.<sup>6,31</sup> Since we were not able to obtain crystals from any slowly cooled reaction mixture in HCN due to the formation of different solvate anions, a rather unconventional crystallization method was established as we noticed fast crystallization of the reaction mixture upon addition of non-polar perfluoropolyether. To this end, Fomblin YR-1800 perfluoropolyether was placed in a self-built low-temperature device for crystal picking, cooled with liquid nitrogen to -60 °C. Subsequently, the HCN mixtures were cooled until they solidified (for specifications see ESI<sup>†</sup>) and then transferred into the ether. Interestingly, in all cases, even at those low temperatures, release of gaseous HCN was observed within one minute, accompanied with the formation of X-ray suitable crystals. Structure elucidation unequivocally revealed the formation of [PPN]<sup>+</sup>-salts containing the pseudohalide HCN-aggregate anions [PPN][N<sub>3</sub>(HCN)<sub>3</sub>] (1, Fig. 1),



**Fig. 1** Ball-and-stick representation of the  $[N_3(HCN)_3]^-$  ion in a crystal of  $[PPN][N_3(HCN)_3]$ . The distorted Y-shaped molecular anion is formed by three hydrogen bridges (**a**–**c**). When short contacts (**d** and **e**) are considered, a chain is formed along the *c*-axis. The cations are omitted for clarity. Selected distances are given in Å, heavy atom distances in the H-bridges: N1–C1 2.97(2), N3–C2 3.02(2), N3–C3 3.033(8); **a** = 2.12, **b** = 2.15, **c** = 2.03. Shortest interanionic distances: **d** = N4–C3' 3.391(6), **e** = C1–N6' 3.70(2).



**Fig. 2** Ball-and-stick representation of the  $[OCN(HCN)_3]^-$  ion in a crystal of  $[PPN][OCN(HCN)_3]$ . Due to disorder (a layer 52% and b layer 48%), two different distorted Y-shaped isomers, which are formed by three hydrogen bridges (a–c), can be considered. Top: O-bound dimer **20** (2 O–H-bridges and 1 N–H-bridge), bottom: N-bound dimer **2N** (2 N–H-bridges and 1 O–H-bridge). In each case a chain is formed when short contacts (d–e) are considered. The cations are omitted for clarity. Selected distances are given in Å, heavy atom distances in the H bridges: (top) O1a–C2 3.06(2), O1a–C3 2.95(2), N1a–C4 2.97(3). **a** = 2.13, **b** = 2.06, **c** = 2.02. (Bottom) N1b–C2 2.95(3), N1b–C3 3.16(3), O1b–C4 2.89 (3). **a** = 2.00, **b** = 2.24, **c** = 1.95. Shortest interionic distances: (both) **d** = N4–C3' 3.379(7), **e** = C4–N3' 3.68(1).

[PPN][OCN(HCN)<sub>3</sub>] (2, Fig. 2) and [PPN][SCN(HCN)<sub>2</sub>] (3, Fig. 3, Scheme 2).

In case of [PPN]OCP (see ESI Fig. S11<sup>†</sup> for X-ray structure elucidation), a reaction with the HCN was observed, which led to the degradation of the phosphaethynolate anion, finally affording [PPN][P(CN·HCN)<sub>2</sub>] (4, Fig. 4). This is an exergonic



**Fig. 3** Left: Ball-and-stick representation of a separated  $[SCN(HCN)_2]^$ ion in the crystal of  $[PPN][SCN(HCN)_2]$ , whereas the cations are omitted for clarity. The distorted L-shaped molecular anion is formed by two hydrogen bridges (**a** and **b**). Selected distances in the H-bridges in Å and selected bond angles in °: S1–C2 3.452(3), N1–C3 3.060(5). **a** = 2.18, **b** = 2.50. C1–S1–C2 95.83(9), C3–N1–S1–C2 78.2(3). Right: Ball-and-stick (anions) and wireframe (cations) representation of the molecular structure of  $[PPN][SCN(HCN)_2]$  in the crystal. View along the *a*-axis.

[PPN]X + n HCN	$\frac{\text{Fomblin YR-}}{T = -60^{\circ}}$	1800 C	[PPN]][ <mark>X</mark> (	HCN) <sub>n</sub> ]
<i>n</i> = 2: X =	SCN n=	= 3: X = N <sub>3</sub> ,	OCN	
Scheme 2 Synthesis of OCN for $n = 3$ ).	[PPN][X(HCN)	<sub>n</sub> ] (X = SC	N for <i>n</i> =	2; X = N <sub>3</sub>

process according to computations ( $\Delta_r G^\circ = -35.8$  kcal mol<sup>-1</sup>, see below, Table S12†). So far, the formation of a possible byproduct, such as formaldehyde (PCO<sup>-</sup> + 4 HCN  $\rightarrow$  [P (CN·HCN)<sub>2</sub>] + H<sub>2</sub>CO), could not be observed by NMR analysis. However, we want to emphasize that all above discussed reactions and crystallizations were carried out several times, always leading to the discussed products. According to Raman spectroscopy, all solvates **1–4** are very labile with respect to moisture and loss of HCN was observed when the compounds were warmed-up to room temperature. Since HCN is the weakest acid amongst all considered HX species, always only the [X (HCN)<sub>n</sub>]<sup>-</sup> ions, with the proton attached to the CN<sup>-</sup> ion, were observed in accord with computations (Table S12†).

#### Structure elucidation

All crystals were selected at -60 °C under inert conditions (N<sub>2</sub> stream). A point fume cupboard was used because highly toxic HCN is released from the reaction mixture. Since the exact position of the hydrogen atoms cannot be determined accu-



**Fig. 4** Left: Ball-and-stick representation of the  $[P(CN \cdot HCN)_2]^-$  ion in the crystal of  $[PPN][P(CN \cdot HCN)_2]$ . The bent molecular anion is formed by two hydrogen bridges (a and b). A centrosymmetric dimer (finally *a* layer) is formed when further contacts (c and d) are considered. Selected distances in Å and selected bond angles in °: P1–C1 1.764(4), P1–C2 1.768(3), C1–N1 1.158(5), C2–N2 1.157(5), N1–C3a 3.088(7), N2–C4 3.112(5). a = 2.29, b = 2.17. C1–P1–C2 94.3(2), P1–C1–N1 174.1(4). Shortest interionic distances: c = C2–N4' 3.906(5), d = N2–C4' 3.439(5). Right: Ball-and-stick (anions) and wireframe (cations) representation of the molecular structure of  $[PPN][P(CN \cdot HCN)_2]$  in the crystal along the *b*-axis. The  $[P(CN \cdot HCN)_2]^-$  ions form a layer in the *a*–*b*-plane. Disorder (4% probability) is not shown for clarity (see ESI Fig. S10†).

rately by X-ray diffraction, the distances of the heavier atoms (A, B) in the A···H–B-bridges will be discussed. All ORTEP representations can be found in the ESI.† 1 crystallized in the monoclinic space group C2/c with four formula units per cell (Fig. 1).

The unit cell contains well-separated cations and anions. Distorted Y-shaped, trisolvate anions are formed due to three C-H…N hydrogen bridges. Two solvate molecules coordinate to the N<sub>α</sub> of the central azide (H-bridges **a** and **b**) with heavy atom distances of 3.02(2) and 3.033(8) Å, whereas the third HCN is linked to the N<sub>γ</sub> atom (d(N1...C1) = 2.97(1) Å, H-bridge **c** in Fig. 1). Interestingly, there are head-to-tail arrangements between the HCN groups of two adjacent Y-shaped solvate anions but rather long distances of 3.391(6) (**d**) and 3.70(2) Å (**e**, *cf.*  $d_{vdW}(C...N) = 3.25$  Å)<sup>45</sup> are observed. Hence, the formed anionic strands along the *c*-axis, might be better explained due to packing effects in the crystal. Due to the HCN-solvation, the N<sub>3</sub> anion is slightly bent ( $\Delta$ (N–N–N) = 177.5(6)°) and two slightly different N–N distances (1.173(6) and 1.136(10) Å) were found.

2 crystallizes isostructural to 1 (*C*2/*c*) and again well-separated cations and distorted Y-shaped anions are formed. Due to the disorder of the central OCN<sup>-</sup> ion, two isomers have to be considered. An *O*-linked isomer **2O** (Fig. 2, top) and a *N*-connected isomer **2N** (Fig. 2, bottom) with an occupation probability of 52(1)% and 48(1)%, respectively, which are the same considering the esd. In **2O**, two C–H···O hydrogen bridges are formed from two HCN groups, which are attached to the oxygen of the cyanate ion (**a**: d(O1a···C2) = 3.06(2) and **b**: d(O1a···C3) = 2.95(2) Å) and only one HCN, which is bound to the terminal N atom, forming a C–H…N hydrogen bridge (c: d(N1a...C4) = 2.97(3) Å, Fig. 2). In **2N**, it is exactly the other way around: there are two C–H…N (**a**: d(N1b...C2) = 2.95(3) and **b**: d(N1b...C3) = 3.16(3) Å) and one C–H…O hydrogen bridges (**c**: d(O1b...C4) = 2.89(3) Å, Fig. 2). Again, both isomers form anionic strands along the *c*-axis due to head-to-tail arrangements, attributed to packing effects in the crystal (**d**: d(C4...N3') = 3.379(7) and **e**: d(N4...C3') = 3.68(1) Å, Fig. 2), of two hydrogen cyanides with adjacent [OCN(HCN)<sub>3</sub>]<sup>–</sup> anions.

3 crystallizes in the monoclinic space group  $P2_1$  with two formula units per cell (Fig. 3, right). The  $[SCN(HCN)_2]^-$  anion is formed by one C-H…N hydrogen bridge (**a**: d(N1...C2) =3.060(5) Å) and one C-H…S hydrogen bridge (**b**: d(S1...C3) =3.452(3) Å, Fig. 3, left). The HCN, attached to the sulphur of the thiocyanate anion, is linked nearly orthogonal with  $\measuredangle$ (C2...S1-C1) = 95.83(9)°, thus leading to formation of a distorted L-shaped disolvate anion. In contrast to the crystal structures of **1** and **2**, no larger voids are formed by the bulky [PPN]<sup>+</sup> cation. Hence, only separated [SCN(HCN)<sub>2</sub>]<sup>-</sup> ions are found, which are located in a pocket, formed by the surrounding [PPN]<sup>+</sup> cations (Fig. 3, right).

 $[PPN][P(CN \cdot HCN)_2]$  4 crystallizes in the monoclinic space group  $P2_1/c$ . Layers of cations and anions are formed in the crystal (Fig. 4, right). Structural parameter of the bent, but planar  $[P(CN \cdot HCN)_2]^-$  in comparison with crystallographic data of the salts, bearing the unsolvated  $[P(CN)_2]^-$  ion, are listed in Table 1, indicating that solvation does not significantly change these structural parameters. However, as discussed before, interionic interactions, which arise from hydrogen bonding as well as CN head-to-tail arrangements (Fig. 4), lead to the formation of a layer type anion structure in contrast to the structural motifs found in unsolvated [Cat][P(CN)<sub>2</sub>]  $([Cat] = Na/K[18]crown-6, {}^{46,47} [Ph_4P]^{48})$ . Due to disorder, two different anion layers are found. In the main layer (a layer with 96%), each nitrogen of the dicyanophosphide anion is attached to one HCN molecule by one C-H ··· N hydrogen bridge, which results in the formation of the disolvate anion  $[P(CN \cdot HCN)_2]^-$  (a:  $d(N1 \cdots C3a) = 3.088(7)$  and b:  $d(N2 \cdots C4) =$ 3.112(5) Å, Fig. 4, left). The  $[P(CN \cdot HCN)_2]^-$  ions are further linked by very weak van der Waals interactions between two adjacent anions (c:  $d(C2\cdots N4') = 3.906(5)$  and d:  $d(N2\cdots C4') =$ 3.439(5) Å. Considering the b layer (4(1)%), with one disordered HCN moiety, a monosolvate anion [P(CN·HCN)(CN)] is formed, whereby the second HCN remains uncoordinated in the cavity (see ESI Fig. S10<sup>†</sup>).

## Table 1 Selected structural data (distance in Å, bond angle in °) of salts, containing the $[P(CN)_2]^-$ anion

Cation	<i>d</i> (P–C)	d(C-N)	∡(C-P-C)
$Na^{a,46} K^{a,47} [Ph_4P]^{48} [PPN]^{b}$	$\begin{array}{c} 1.76(2) - 1.72(2) \\ 1.67(1) - 1.69(1) \\ 1.80(1) - 1.755(6) \\ 1.764(4) - 1.766(3) \end{array}$	$\begin{array}{c} 1.155\\ 1.15(2) - 1.14(2)\\ 1.20(1) - 1.108(8)\\ 1.157(5) - 1.158(5) \end{array}$	95(1) 95.2(6) 92.7(3) 94.3(2)

<sup>*a*</sup> [18]crown-6 salt. <sup>*b*</sup> As HCN disolvate.

#### Raman spectroscopy

The Raman data of all compounds were obtained from cooled single crystals, which were used for the X-ray structure elucidation. It was very difficult to obtain reasonable spectra. In all cases, no bands for  $\nu_{\rm C-H,HCN}$  vibration of the molecular anions of 1–4 were observed due to the highly dynamic nature of the hydrogen-bridged systems, which leads to a broadening of the bands. Moreover, C–H vibrational bands of the cation were also found in the relevant area.

For the trisolvate species, 1 and 2, broad bands for the  $\nu_{\rm CN}$ stretching modes were found in the expected region for all three coordinated HCN molecules (1: 2056(br)/2067, 2: 2060/ 2073 cm<sup>-1</sup>, Table 2; cf. 2097 for pure HCN at 233 K; 2057(br)/ 2081 and 2055(br)/2071 cm<sup>-1</sup> for [CN(HCN)<sub>2</sub>]<sup>-</sup> and [CN  $(HCN)_3$ <sup>-</sup>, respectively),<sup>31</sup> however, no splitting for the in-phase (symmetric) and out-of-phase (antisymmetric) vibrations could observed. Furthermore, the antisymmetric stretching vibration of the  $N_3^-$  ion in 1 was detected at 2077 cm<sup>-1</sup>, while the symmetric mode was found at 1332 cm<sup>-1</sup> with the largest intensity (cf. [PPN]N<sub>3</sub> 1323 cm<sup>-1</sup>). The cyanide mode,  $\nu_{CN,OCN}$ , was observed at 2164 and for the SCN<sup>-</sup> ion at 2073 cm<sup>-1</sup>. For dicyanophosphide 4, the symmetric  $\nu_{PC-N,s}$  (antisymmetric  $\nu_{PC-N,as}$ ) stretching vibration of the phosphorus bound cyanide groups could be observed at 2105 (2084)  $\text{cm}^{-1}$  (cf.  $[\text{PPh}_4][P(\text{CN})_2]$ : 2111, 2089 cm<sup>-1</sup>).<sup>48</sup> Additionally, two bands arising from the coupled CN-vibrations of the two solvated HCN molecules were assigned to the bands at 2022 (in-phase) and 2025 (outof-phase) cm<sup>-1</sup>, respectively.

#### **Computational results**

DFT calculations (pbe0/aug-cc-pVTZ + dispersion corrections) were performed (see ESI Tables S2–S13†), to obtain additional structural und thermodynamic data for the isolated pseudoha-lide-HCN solvates of **1–3** and for the dicyanophosphide HCN-solvate **4**. The calculated bond lengths for the isolated anions in the gas phase are in good agreement with the observed bond lengths in all crystallized compounds (*cf.* ESI Table S13†). However, the geometry (angles and dihedral angles) of the solid state structures **1–4** slightly deviates, which can be attributed to very weak energy potentials, a problem that was already found for other mixed aggregates of the type [XHY]<sup>–</sup> (X, Y = F, Cl, Br, CN).<sup>49,50</sup> In agreement with our experi-

Table 2 Selected Raman data obtained from single crystals of 1–4. Frequencies in  $cm^{-1a}$ 

Compound	$ u_{ m CN,2HCN-solvate} $ (sym/anti)	$\nu_{ m CN,HCN}$ -solvate	$ u_{ m xyz}, $ pseudohalide <sup>g</sup>
1	2056 <sup>b</sup>	2067	$2077(anti)/1332(sym)^{c}$
2	$2060^{b}$	2073	2164
3	_	$2051^{d}/2059^{e}$	2073
4	2022/2025	—	2105(sym)/2084(anti) <sup>f</sup>

<sup>*a*</sup> Tentative assignment based on comparison with computed data. <sup>*b*</sup> Broad signal. <sup>*c*</sup> Only most intense band given. <sup>*d*</sup> Connected to N. <sup>*e*</sup> Connected to S. <sup>*f*</sup> P-bounded cyanide. <sup>*g*</sup> XYZ for 1: NNN, 2: NCO, 3: NCS, and 4: PCN. mental data and in accord with the gas phase acidities, HCN represents the weakest acid. That is, protonation of  $X^-$  (N<sub>3</sub>, NCO, NCS and PCO) is endergonic with 6.7–24.1 kcal mol<sup>-1</sup> (Table S11†). This means that those isomers are always the most stable in which Z···HCN hydrogen bonds are found (Z = terminal atoms of  $X^-$  ion).

Due to the flat potentials as well as many possible connectivities, often a large series of computations, including a variety of isomers, had to be considered, which will not be discussed in detail here (see ESI, Tables S2-S10<sup>†</sup>). For example, 22 different isomers for the  $[N_3(HCN)_3]^-$  ion were found. Of these, the Y-shaped solvate  $Y_T1$  with three C-H…N H-bridges is the energetically favoured isomer (Fig. 5), which agrees well with the experimental results (cf. Fig. 1). Already the isomerization of only one HCN moiety to HNC  $(Y_T 2)$  leads to a rise in energy of 8.24 kcal mol<sup>-1</sup>. Furthermore, two additional bent chain-like isomers  $B_T 1$  and  $B_T 2$  were found, which are only 2.97 and 6.26 kcal  $mol^{-1}$  less favoured, respectively. Interestingly, proton migration during the optimization was observed ( $B_T 2$ , for further isomers see ESI Table S2<sup>†</sup>), when the azide anion is located at the end of the chain. This leads to formation of hydrogen azide (HN<sub>3</sub>) and a cyanide ion (CN<sup>-</sup>), which is linked by one N-H···C and one C-H···N hydrogen bridge. The stepwise formation of the HCN solvate  $[N_3(HCN)_n]^-$  for n = 1-3 (see ESI, Table S3<sup>†</sup>) were computed to be exothermic and exergonic, but with less negative values  $(\Delta_n H_{298}^\circ: -22.7, -17.4, -13.4; \Delta_n G_{298}^\circ: -16.0, -10.1, -7.1$  kcal  $mol^{-1}$ ) when the degree of HCN-aggregation increases (*n* = 1 - 3).

42 isomers were found for the  $[OCN(HCN)_3]^-$  trisolvate ion (Table S4<sup>†</sup>). As mentioned before, two isomers have to be considered according to the results from X-ray diffraction. The energetically preferred isomers (**Y**<sub>T</sub>**1**, Fig. 6) exhibits a nonplanar structure and is built by two C-H···N and one C-H···O hydrogen bridges, as found for the observed isomer **2N** (*cf.* Fig. 2). The planar Y-shaped isomer **Y**<sub>T</sub>**2**, which shows the same connectivity as observed for isomer **2O**, was found to be only 2.08 kcal mol<sup>-1</sup> less favoured in the gas phase. This might explain the observation of both isomers in the solid state (52(1)% for **2O** and 48(1)% for **2N** according to X-ray crystallography). In addition, further bent chain-like structures were found, in which the OCN anion either shows a 1,3-*O*,*N*-coordination mode (**B**<sub>T</sub>**1** and **B**<sub>T</sub>**2**) or is only linked at one terminal atom of the OCN<sup>-</sup> ion (O: **B**<sub>T</sub>**3** and N: **B**<sub>T</sub>**4**). Again, proton

Fig. 5 Selected computed isomers of the trisolvate ion  $[N_3(\text{HCN})_3]^-$  with the relative total energies (pbe0/aug-cc-pVTZ, in italics) in kcal mol^{-1}.

8.24

B<sub>T</sub>1

B<sub>T</sub>2

2.97

6.26

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Fig. 6 Selected computed isomers of the trisolvate ion  $[OCN(HCN)_3]^-$  with the relative total energies (pbe0/aug-cc-pVTZ, in italics) in kcal mol<sup>-1</sup>.

migration (**B**<sub>T</sub>**4**, for further isomers see ESI Table S4<sup>†</sup>) was observed during the optimization process, forming a hydrogen cyanate and a cyanide ion, which is linked *via* one N–H···C and one C–H···N hydrogen bridge. All reaction energies for the stepwise formation of both trisolvates **Y**<sub>T</sub>**1** and **Y**<sub>T</sub>**2** were found to be exothermic and exergonic for n = 1-3 (**Y**<sub>T</sub>**1**:  $\Delta_n H_{298}^{\circ}$  :  $-24.6, -17.8, -12.7; \Delta_n G_{298}^{\circ} = -17.6, -9.8, -6.7$  kcal mol<sup>-1</sup>; **Y**<sub>T</sub>**2**:  $\Delta_n H_{298}^{\circ}$  :  $-24.6, -15.8, -12.5; \Delta_n G_{298}^{\circ} = -17.6, -9.0,$ -4.7 kcal mol<sup>-1</sup>, Tables S5 and S6<sup>†</sup>).

18 isomers were found for the disolvate of [SCN(HCN)<sub>2</sub>]<sup>-</sup>, (Table S7<sup>†</sup>). In contrast to the experimental results, the calculated isomer with the lowest energy  $(Y_D1, Fig. 7)$  features a Y-shaped structure, however the experimentally observed bent L-shaped isomer **B**<sub>D</sub>2 is only 0.58 kcal mol<sup>-1</sup> higher in energy, which might be compensated due to crystal packing (cf. Fig. 3).  $B_D 2$  exhibits a similar shape as the observed [SCN  $(HCN)_2$ <sup>-</sup> ion in 3, however, the gas phase structure deviates slightly from the experimental geometry, especially the C2-S1-N1–C3 dihedral angle with 179.9° (cf.  $[SCN(HCN)_2]^-$  in 3 with 78.2(3)°). When the SCN<sup>-</sup> anion is located at the end of the disolvate HCN...HCN, two additional types of structures are found, depending on whether the hydrogen cyanide is connected by a C-H…N ( $L_D$ 1, linear) or C-H…S ( $B_D$ 1, L-shaped) H-bridge. Beside these structures, a C1-symmetric, distorted trigonal pyramidal-shaped isomer P<sub>D</sub>1 with two C-H···S hydrogen bridges was found, which is 4.47 kcal  $mol^{-1}$  less favoured.



Fig. 7 Selected computed isomers of the disolvate ion  $[SCN(HCN)_2]^-$  with the relative total energies (pbe0/aug-cc-pVTZ, in italics) in kcal mol<sup>-1</sup>.

Y<sub>T</sub>2

0.00

Y<sub>⊤</sub>1



Fig. 8 Selected computed isomers of the disolvate ion  $[P(CN\cdot HCN)_2]^-$  with the relative total energies (pbe0/aug-cc-pVTZ, in italics) in kcal mol^{-1}.

The stepwise formation (n = 1-2) of the energetically favoured  $[SCN(HCN)_2]^-$  anion  $Y_D1$  ( $B_D2$ ) was again calculated to be exothermic and exergonic for all steps ( $\Delta_n H_{298}^\circ = -19.4$  (-19.4), -14.0 (-13.5);  $\Delta_n G_{298}^\circ : -12.0$  (-12.0), -7.5 (-7.2) kcal mol<sup>-1</sup>) and even a possible but not observed aggregation of a third HCN was found to be energetically favoured ( $\Delta_3 H_{298}^\circ = -11.1$ ,  $\Delta_3 G_{298}^\circ = -4.9$  kcal mol<sup>-1</sup>, Table S8†).

As depicted in Fig. 8, the  $C_{2v}$ -symmetric HCN disolvate [P (CN·HCN)<sub>2</sub>]<sup>-</sup>, **B**<sub>D</sub>**1**, was found to be the energetically preferred isomer. Like the solid-state structure for the anion in **4** (*cf.* Fig. 4), the computed species exhibits a planar, bent geometry and is associated to two HCN molecules by two C-H…N hydrogen bridges. Two further isomers were found, one bent structure with  $C_s$ -symmetry, **B**<sub>D</sub>**2** ( $\Delta E_{rel.} = +3.6$  kcal mol<sup>-1</sup>), exhibiting an almost linear HCN…HCN chain, and a  $C_s$ -symmetric, bisphenoidal isomer, **D**<sub>D</sub>**1** ( $\Delta E_{rel} = +6.27$  kcal mol<sup>-1</sup>), with two C-H…P H-bridges, which form the axis of the pseudo-trigonal bipyramid with the P-atom in the centre (Fig. 8, Table S10<sup>†</sup>).

From the computational study, some features can be generalized: (i) the energetically favoured isomer, is the one with the maximum number of covalent NC-H bonds (of the HCN solvate molecule) and the largest number of C-H...N H-bridges. (ii) If isonitrile groups are present in the structure, the energy of the isomer increases significantly. (iii) All anion structures observed in the X-ray structure elucidations represent the energetically most favoured isomers from gas phase calculations, except for the [SCN(HCN)<sub>2</sub>]<sup>-</sup> solvate ion, which possesses two more or less energetically equal isomers  $Y_D1$  and  $B_D2$ , with  $B_D2$ , the experimental structure, being slightly less favoured ( $\Delta E_{\rm rel.} = 0.58$  kcal  $mol^{-1}$ ) at the theoretical method applied. (iv) The theoretically determined distances of the heavier atoms in the hydrogen bridges C-H···O (d(C···O) = 2.66–2.95 Å) are usually shorter than the C-H···N hydrogen bonds ( $d(C \cdot \cdot \cdot N) = 2.77 - 3.11$  Å), while the C-H···S distances  $(d(C \cdots S) = 3.29 - 3.41 \text{ Å})$  are the longest (only isomers with covalent NC-H bonds and isomers without proton migration considered), in accord with the experimentally determined distances.

### Conclusions

A low temperature crystallization technique in a rather unconventional crystallization medium (Fomblin YR-1800) was used to generate and isolate single crystals of [PPN][N<sub>3</sub>(HCN)<sub>3</sub>], [PPN][OCN(HCN)<sub>3</sub>], [PPN][SCN(HCN)<sub>2</sub>] and [PPN][P  $(CN \cdot HCN)_2$ ], starting from [PPN]X (X = N<sub>3</sub>, OCN, SCN, OCP) and HCN. The molecular anions in 1-3 represent the first members of solvate anions of the type  $[X(HY)_n]^-$ , in which X and Y are different pseudohalides. In all cases, the HCN solvates were formed since HCN is the weakest acid amongst the considered pseudohalide acids HX; therefore, no protonation of the pseudohalide X<sup>-</sup> was found. These temperature labile compounds were characterized by X-ray diffraction, Raman spectroscopy and quantum chemical calculations. Experimentally, it was shown that the trisolvates,  $[N_3(HCN)_3]^$ and [OCN(HCN)3], form distorted Y-shaped molecular anions, while the HCN disolvate [SCN(HCN)<sub>2</sub>]<sup>-</sup> shows a distorted L-shaped geometry. Moreover, it was observed that the central cyanate in the molecular anion in 2 is disordered, so two different isomers, 20 with two C-H-O H-bridges and 2N with two C-H ... N H-bridges, have to be considered. The phosphaethynolate anion, OCP<sup>-</sup>, was found to react with HCN, leading to formation of the dicyanophosphide anion in a hitherto unknown decomposition process. Its [PPN]<sup>+</sup>-salt 4 crystallized in form of a HCN disolvate, forming a bent [P  $(CN \cdot HCN)_2$  anion. In accord with experimental structural data, the computational results show that a Y-shaped structure of the [N<sub>3</sub>(HCN)<sub>3</sub>]<sup>-</sup>, [OCN(HCN)<sub>3</sub>]<sup>-</sup>, and [SCN(HCN)<sub>2</sub>]<sup>-</sup> anion is always the energetically slightly preferred isomer. However, due to very flat potentials, distortions from the ideal structure were found in the solid state, which can be attributed to small solid state effects (especially for the [SCN(HCN)<sub>2</sub>]<sup>-</sup> anion with an energy difference of  $\Delta E_{\rm rel.} = 0.6$  kcal mol<sup>-1</sup> between the two energetically lowest lying isomers).

### Conflicts of interest

There are no conflicts to declare.

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### Notes and references

- 1 L. Birckenbach and K. Kellermann, *Ber. Dtsch. Chem. Ges.*, 1925, **58**, 786–794.
- 2 L. Birckenbach and K. Kellermann, *Ber. Dtsch. Chem. Ges.*, 1925, **58**, 2377–2386.
- 3 L. Birckenbach and K. Huttner, *Ber. Dtsch. Chem. Ges.*, 1929, **62**, 153–163.
- 4 L. Birckenbach and M. Linhard, Ber. Dtsch. Chem. Ges., 1929, 62, 2261–2277.

- 5 L. Birckenbach and K. Huttner, Z. Anorg. Allg. Chem., 1930, 190, 38–47.
- 6 J. Harloff, D. Michalik, S. Nier, A. Schulz, P. Stoer and A. Villinger, *Angew. Chem., Int. Ed.*, 2019, **58**, 5452–5456.
- 7 V. V. Stopenko, A. M. Golub and H. Köhler, *Chemistry of Pseudohalides*, Elsevier, Amsterdam, 1986.
- 8 Z. M. Smallwood, M. F. Davis, J. G. Hill, L. J. R. James and P. Portius, *Inorg. Chem.*, 2019, **58**, 4583–4591.
- 9 E. M. Frémy, Ann. Chim. Phys., 1856, 3, 5-50.
- 10 R. M. Bozorth, J. Am. Chem. Soc., 1923, 45, 2128-2132.
- 11 R. Kruh, K. Fuwa and T. E. McEver, *J. Am. Chem. Soc.*, 1956, 78, 4256–4258.
- 12 S. I. Troyanov, I. V. Morozov and E. Kemnitz, Z. Anorg. Allg. Chem., 2005, 631, 1651–1654.
- 13 S. I. Ivlev, T. Soltner, A. J. Karttunen, M. J. Mühlbauer, A. J. Kornath and F. Kraus, *Z. Anorg. Allg. Chem.*, 2017, 643, 1436–1443.
- 14 D. Mootz, U. Ohms and W. Poll, Z. Anorg. Allg. Chem., 1981, 479, 75–83.
- 15 D. Mootz and W. Poll, Z. Anorg. Allg. Chem., 1982, **484**, 158– 164.
- 16 D. Mootz and W. Poll, Z. Naturforsch., 1984, 39, 290-297.
- 17 D. Mootz and D. Boenigk, J. Am. Chem. Soc., 1986, 108, 6634-6636.
- 18 D. Mootz and D. Boenigk, Z. Anorg. Allg. Chem., 1987, 544, 159–166.
- 19 R. Rathore, S. V. Lindeman, C. J. Zhu, T. Mori, P. V. R. Schleyer and J. K. Kochi, *J. Org. Chem.*, 2002, 67, 5106–5116.
- 20 D. Mootz and A. Deeg, Z. Anorg. Allg. Chem., 1992, 615, 109–113.
- 21 J. L. Atwood, S. G. Bott, C. M. Means, A. W. Coleman, H. Zhang and M. T. May, *Inorg. Chem.*, 1990, 29, 467– 470.
- 22 D. Mootz and J. Hocken, Z. Naturforsch., 1989, 44, 1239– 1246.
- 23 S. Hasenstab-Riedel, P. Voßnacker, S. Steinhauer and J. Bader, *Chem. Eur. J.*, 2020, DOI: 10.1002/ chem.202001864.
- 24 L. W. Schroeder and J. A. Ibers, *Inorg. Chem.*, 1968, 7, 594–599.
- 25 G. W. Driver and I. Mutikainen, *Dalton Trans.*, 2011, 40, 10801–10803.
- 26 M. F. A. Dove, Chem. Commun., 1965, 23-24.
- 27 S. Arlt, J. Harloff, A. Schulz, A. Stoffers and A. Villinger, *Inorg. Chem.*, 2019, 58, 5305–5313.

- 28 S. Nuzzo, B. Twamley, J. A. Platts and R. J. Baker, *Chem. Commun.*, 2016, **52**, 13296–13298.
- 29 B. Neumüller, F. Schmock and K. Dehnicke, Z. Anorg. Allg. Chem., 1999, 625, 1243–1245.
- 30 J. A. Salthouse and T. C. Waddington, J. Inorg. Nucl. Chem., 1978, 40, 1696–1698.
- 31 K. Bläsing, J. Harloff, A. Schulz, A. Stoffers, P. Stoer and A. Villinger, *Angew. Chem., Int. Ed.*, 2020, **59**, 10508–10513.
- 32 J. W. Nibler and G. C. Pimentel, *J. Chem. Phys.*, 1967, 47, 710–717.
- 33 M. Meot-Ner, S. M. Cybulski, S. Scheiner and J. F. Liebman, *J. Phys. Chem.*, 1988, 92, 2738–2745.
- 34 D. H. McDaniel and R. E. Valleé, *Inorg. Chem.*, 1963, 2, 996–1001.
- 35 F. Y. Fujiwara and J. S. Martin, J. Am. Chem. Soc., 1974, 96, 7625–7631.
- 36 J. C. Evans and G. Y. S. Lo, J. Phys. Chem., 1966, 70, 20-25.
- 37 S. A. Chacko, I. H. Krouse, L. A. Hammad and P. G. Wenthold, J. Am. Soc. Mass Spectrom., 2006, 17, 51–55.
- 38 J. A. Salthouse and T. C. Waddington, J. Chem. Soc., 1964, 1, 4664–4666.
- 39 C. J. Price, H.-Y. Chen, L. M. Launer and S. A. Miller, Angew. Chem., Int. Ed., 2009, 48, 956–959.
- 40 L. Mann, E. Hornberger, S. Steinhauer and S. Riedel, *Chem.* – *Eur. J.*, 2018, **24**, 3902–3908.
- 41 K. Bläsing, J. Bresien, R. Labbow, A. Schulz and A. Villinger, *Angew. Chem., Int. Ed.*, 2018, **57**, 9170–9175.
- 42 R. Labbow, D. Michalik, F. Reiß, A. Schulz and A. Villinger, *Angew. Chem., Int. Ed.*, 2016, 55, 7680–7684.
- 43 A. Hinz, R. Labbow, C. Rennick, A. Schulz and J. M. Goicoechea, *Angew. Chem., Int. Ed.*, 2017, 56, 3911– 3915.
- 44 P. Günther, R. Mexer and F. Muller-Skjord, *Z. Phys. Chem.*, 1935, **175**, 154–169.
- 45 M. Mantina, A. C. Chamberlin, R. Valero, C. J. Cramer and D. G. Truhlar, *J. Phys. Chem.*, 2009, **113**, 5806–5812.
- 46 W. S. Sheldrick, J. Kroner, F. Zwaschka and A. Schmidpeter, Angew. Chem., Int. Ed. Engl., 1979, 18, 934–935.
- 47 A. Schmidpeter, G. Burget, F. Zwaschka and W. S. Sheldrick, *Z. Anorg. Allg. Chem.*, 1985, 527, 17–32.
- 48 J. F. Binder, S. C. Kosnik, P. B. J. St Onge and C. L. B. Macdonald, *Chem. – Eur. J.*, 2018, 24, 14644–14648.
- 49 J. W. Larson and T. B. Mcmahon, *Inorg. Chem.*, 1984, 23, 2029–2033.
- 50 M. Meot-Ner, S. M. Cybulski, S. Scheiner and J. F. Liebman, J. Phys. Chem., 1988, 92, 2738–2745.