1,3,5-Triazine Adducts with AsF_5. Crystal Structure of $(HCN)_3{\cdot}AsF_5$†

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1,3,5-Triazine was treated with AsF_5 in different stoichiometries to yield the adduct complexes $(HCN)_3{\cdot}nAsF_5$ **1–3** (n = 1–3), the latter of which (**3**) is stable in solution only. The monoadduct $(HCN)_3{\cdot}AsF_5$ crystallizes in the orthorhombic space group *Pcab* with cell parameters a = 10.584(13), b =12.965(11) and c = 10.369(5) Å. The crystal data were collected at 100 K and the final refinement values are R = 0.051 and R' = 0.071. All compounds have been characterized by chemical analyses, vibrational spectrometry (IR and Raman) and ^1H, ^{13}C and ^{14}N NMR spectroscopy. The thermodynamics of the adduct formation between $(HCN)_3$ and AsF_5 are discussed on the basis of the extended hard-soft acid-base principle.

In our research group recently we have been interested in the preparation of Lewis-acid–Lewis-base adduct complexes between nitrile bases and the pentafluorides of the Group 15 elements.[1–3] One of our goals is to explore the thin borderline between stability and instability of these weakly bonded co-ordination compounds. In this context we studied the reaction behaviour of AsF_5 towards the nitrile species R–CN [equation (1), R = CH_3, I, Br, Cl, F, H or CN] and investigated the

$$R{-}CN + AsF_5 \longrightarrow [R{-}CN{\cdot}AsF_5] \qquad (1)$$

influence of the substituent's (R) electronegativity towards the stability of the adducts formed.

By this we have been able to demonstrate that not only the electronegativity of the bases being co-ordinated but also their hardness parameters clearly determine the stability of the complexes formed. These results are nicely in agreement with the hard-soft acid-base principle (HSAB), and quantitative calculations of the number of electrons transferred fit all the experimental results.[2,3] The existence and stability of the known but poorly characterized 1,3,5-triazine (trimeric HCN) adducts with metal chlorides[4] [*e.g.* $(HCN)_3{\cdot}nSbCl_5$, $n(HCN)_3{\cdot}AlCl_3$, $n(HCN)_3{\cdot}TiCl_4$ and $2(HCN)_3{\cdot}SnCl_4$: n = 1 or 2] led naturally to the attempted preparation of the hitherto unknown triazine–AsF_5 adducts in different stoichiometries $(HCN)_3{\cdot}nAsF_5$ (n = 1, 2 or 3). In terms of stability these species should be of interest since now the electronegativity of the N-base and the local hardness at the nitrogen atoms should be dependent on the number of acids co-ordinated. Herein we report on the co-ordination chemistry of 1,3,5-triazine towards AsF_5 in general and on the molecular structure of the most stable 1:1 adduct $(HCN)_3{\cdot}AsF_5$ **1**.

Table 1 Analytical and melting-point data for adducts 1 and 2

Compound	Analysis[a] (%) C	H	N	M.p.[b] (°C)
1 $(HCN)_3{\cdot}AsF_5$	14.5 (14.4)	1.2 (1.2)	17.3 (16.7)	170 (decomp.)
2 $(HCN)_3{\cdot}2AsF_5$	8.8 (8.6)	0.8 (0.7)	10.2 (10.0)	147–150 (decomp.)

[a] Required values given in parentheses. [b] The m.p. of $(HCN)_3$ is 81–83 °C.

Results and Discussion

1,3,5-Triazine was treated with stoichiometric amounts of AsF_5 in SO_2 solution at room temperature to yield $(HCN)_3{\cdot}AsF_5$ **1** and $(HCN)_3{\cdot}2AsF_5$ **2** as white solids, which are stable in SO_2 solution and in the solid state at room temperature. $(HCN)_3{\cdot}3AsF_5$ **3** also has been formed [equation (2)]. However, in the

$$(HCN)_3 + nAsF_5 \longrightarrow (HCN)_3{\cdot}nAsF_5 \qquad (2)$$

$$\mathbf{3} \longrightarrow \mathbf{2} + AsF_5 \qquad (3)$$

solid state **3** is a metastable white powder which tends to decompose spontaneously to give **2** and AsF_5 in quantitative yield [equation (3)].

Compounds **1** and **2** have been characterized by chemical analyses, IR and Raman spectroscopy (Tables 1 and 2). The IR spectra of **1** and **2** were measured between KBr plates on suspensions either in Nujol or Fluorolube. The Raman spectra were recorded on the pure solids. Besides the bands of the $(HCN)_3$-ring moiety[5] the vibrational spectra of **1** and **2** in addition show bands which can be assigned to the co-ordinated AsF_5 unit.[6] Fig. 1 shows the IR spectrum of $(HCN)_3{\cdot}AsF_5$ **1**.

All compounds have been characterized by solution NMR spectroscopy (Table 3). In the ^1H NMR spectra (SO_2 solution) compounds **1** (δ 9.66), **2** (δ 10.20) and **3** (δ 10.50) show a singlet resonance which is shifted to lower field (high frequency) compared with unco-ordinated $(HCN)_3$ (δ 9.10) depending on the number of AsF_5 molecules co-ordinated. Whereas **1** shows two signals (δ 9.37 and 9.24) in the relative intensity ratio of 1:2 in a toluene–SO_2 mixture (1:5) compounds **2** and **3** decompose in the presence of toluene.

For compound **1** two signals (δ 172.1 and 162.3) in the ratio

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† *Supplementary data available:* Further details concerning the crystal structure determination may be obtained from Fachinformationszentrum Karlsruhe Gesellschaft für wissenschaftlich-technische Information mbH, D-W-7514 Eggenstein-Leopoldshafen 2, Germany, by quoting reference CSD 55825.

Non-SI unit employed: eV ≈ 1.60×10^{-19} J.

Table 2 Vibrational data (cm^{-1})

$(HCN)_3$	$(HCN)_3\cdot AsF_5$ **1**		$(HCN)_3\cdot 2AsF_5$ **2**		
IR[a]	IR[a]	Raman[b]	IR[a]	Raman[c]	Assignment
	3150vw		3138m[d]		ν(CH)
	3107m	3125(2)	3120s[d]		
3060m	3060w		3090s[d]		
			3022m[d]		
			2982m[d]		
2535w					
2395w					
2265w					
2060vw					
1967w					
1845vw					
1778w	1785vw				
1668w	1605s		1621vs		$\nu(C_3N_3)$
1552vs	1545s	1540(1)	1560vs	1610(8)	
	1525vw(sh)[d]		1492vw[d]	1576–1582(3)	
	1440m[d]		1440vs[d]	1559–1562(2)	
				1482–1485(4)	
	1425s[d]		1425s[d]	1465(2)	
1407vs	1378m[d]		1372vw[d]		
	1218m				δ(CH)
	1212w		1214s		
1176w	1182vw	1173(1)	1185m		
	1170w				
	1120w			1118(7)	$\nu(C_3N_3)$
	1110s	1105(6)		1076(2)	
1032w	1047s	1048(3)		1062–	$\delta(C_3N_3)$
	942vw			1068(2)	$\nu(C_3N_3)$
			760s		$\nu(AsF_5)$
	740s		750vs		
735s	732s	736(1)	735vs		γ(CH)
725s	720vs	720(2)	725vs	726(6)	
	708ms	704(5)	718vs	715(4)	$\delta(C_3N_3)$
	698s	696(3)	687vs	685(5)	
676s	668ms	665(2)	668s	663(10)	
	645ms	647(10)	662ms(sh)		
		621(2)	608m	627(2)	
		613(1)		606(2)	
		594(1)			
	482vw				
	440w				
	385ms	376(2)	380s	386(4)	$\delta(AsF_5)$
	370ms	361(1)	360s	322(2)	
		333(1)	340m	260(2)	
		240(6)		248(2)	
		218(4)		211(4)	
		109(7)		158(2)	
				139(4)	
				118(5)	

[a] Nujol suspension between KBr plates. [b] 30 mW, room temperature, 1 s per point, relative intensities in parentheses. [c] 30 mW, room temperature, 2 s per point, relative intensities in parentheses. [d] Fluorolube suspensions between KBr plates.

Table 3 Proton, ^{13}C and ^{14}N NMR data for $(HCN)_3$ and its adducts with AsF_5[a]

Compound	^1H (δ_H)	^{13}C (δ_H)	^{14}N (δ_N)
$(HCN)_3$	9.10 (s)	166.0 (s)	−97 (s)
	9.37 (s, 2)[b,c]		
	9.24 (s, 1)[b,c]		
1 $(HCN)_3\cdot AsF_5$	9.66 (s)	162.3 (s, 2)[c]	−143 (s)
		172.1 (s, 1)[c]	
2 $(HCN)_3\cdot 2AsF_5$	10.20 (s)	165.5 (s br)	−120 (s)
3 $(HCN)_3\cdot 3AsF_5$	10.50 (s)	165.7 (s)	−124 (s)

[a] In SO_2 solution unless otherwise stated (^1H and ^{13}C NMR referenced to $SiMe_4$; ^{14}N NMR referenced to $MeNO_2$). [b] In SO_2–toluene (5:1). [c] Relative intensities in parentheses.

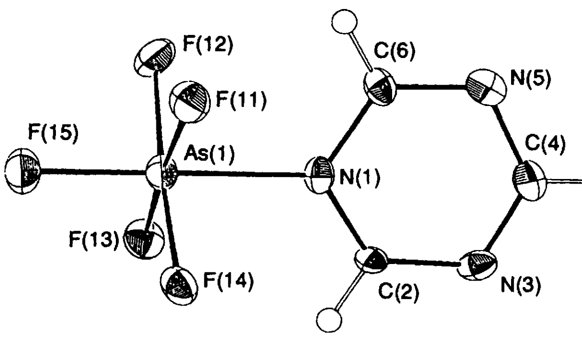

Fig. 2 Molecular structure of $(HCN)_3\cdot AsF_5$ **1**

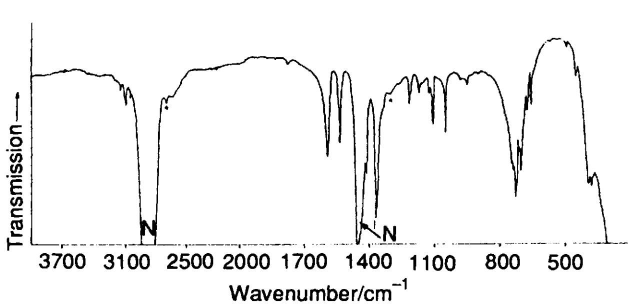

Fig. 1 IR spectrum of $(HCN)_3\cdot AsF_5$ **1**. N = Nujol. * Impurity in the Nujol

1:2 have been observed in the ^{13}C NMR spectrum, which are substantially different from that of unco-ordinated 1,3,5-triazine (δ 166.0). Adducts **2** and **3** only show one signal each identical with that of 1,3,5-triazine which can be explained by the weaker co-ordination of AsF_5 to $(HCN)_3$ in **2** and **3** due to the lower basicity of the nitrogen atoms (see below) and to fast exchange processes in solution. In an attempt to investigate the exchange processes in solution and to understand the nature of compound **2** and **3** we recorded the low-temperature ^1H NMR spectra (−50 °C). However, no change compared with the room-temperature spectra could be observed at this temperature.

The ^{14}N NMR spectra of compounds **1** (δ −143), **2** (δ −120) and **3** (δ −124) only show one signal which is shifted to higher field compared with unco-ordinated $(HCN)_3$ (δ −97). The smaller shift of **2** and **3** is in good agreement with the assumption of weaker co-ordination of AsF_5 in **2** and **3** relative to **1**.

For the formation of the 1:1 adduct [equation (4)] we

$$(HCN)_3 + AsF_5 \longrightarrow \mathbf{1} \qquad (4)$$

calculated the gain in energy due to electron transfer (Δ*E*) according to the Pearson–Parr principle. Using the ionization potential (I_P = 10.37 eV)[7] and the electron affinity (E_A = 0.45 eV)[7] of $(HCN)_3$ we estimated[8] the absolute electronegativity (χ) of triazine to be equal to 5.14 eV and the absolute hardness (η) to be equal to 4.96 eV. This gives a Δ*E* value of −69.4 kJ mol^{-1} (AsF_5: χ = 10.44 eV, η = 5.14 eV).[2] Compared with the

Table 4 Atomic parameters with estimated standard deviations (e.s.d.s) in parentheses for $(HCN)_3{\cdot}AsF_5$ **1**

Atom	*x*	*y*	*z*
As(1)	0.443 90(7)	0.691 49(6)	0.006 23(6)
N(1)	0.508 4(6)	0.615 8(4)	0.156 7(5)
C(2)	0.628 7(7)	0.582 8(6)	0.163 8(6)
N(3)	0.671 2(6)	0.523 7(5)	0.257 9(5)
C(4)	0.586 3(8)	0.499 8(6)	0.346 8(7)
N(5)	0.466 1(7)	0.530 2(5)	0.350 5(6)
C(6)	0.429 9(7)	0.588 9(6)	0.254 0(6)
F(11)	0.318 7(4)	0.607 9(4)	0.005 3(3)
F(12)	0.363 5(4)	0.770 4(3)	0.110 3(4)
F(13)	0.574 3(4)	0.770 0(4)	0.016 3(4)
F(14)	0.527 9(4)	0.607 3(3)	−0.088 2(4)
F(15)	0.387 0(5)	0.755 6(4)	−0.125 5(4)
H(2)	0.685	0.603	0.096
H(4)	0.613	0.456	0.417
H(6)	0.344	0.613	0.252

Table 5 Interatomic distances (Å) and bond angles (°) with e.s.d.s in parentheses

As(1)–N(1)	1.966(6)	C(2)–N(3)	1.320(9)
As(1)–F(11)	1.712(5)	C(2)–H(2)	0.960(7)
As(1)–F(12)	1.713(4)	N(3)–C(4)	1.324(10)
As(1)–F(13)	1.719(5)	C(4)–N(5)	1.332(11)
As(1)–F(14)	1.715(4)	C(4)–H(4)	0.960(7)
As(1)–F(15)	1.709(4)	N(5)–C(6)	1.314(9)
N(1)–C(2)	1.346(10)	C(6)–H(6)	0.960(8)
N(1)–C(6)	1.352(9)		
N(1)–As(1)–F(11)	87.5(2)	As(1)–N(1)–C(2)	122.1(5)
N(1)–As(1)–F(12)	88.3(2)	As(1)–N(1)–C(6)	120.5(5)
N(1)–As(1)–F(13)	88.2(2)	C(2)–N(1)–C(6)	117.3(6)
N(1)–As(1)–F(14)	87.4(2)	N(1)–C(2)–N(3)	123.2(6)
N(1)–As(1)–F(15)	179.1(2)	N(1)–C(2)–H(2)	117.5(7)
F(11)–As(1)–F(12)	89.9(2)	N(3)–C(2)–H(2)	119.3(7)
F(11)–As(1)–F(13)	175.7(2)	C(2)–N(3)–C(4)	114.8(6)
F(11)–As(1)–F(14)	89.7(2)	N(3)–C(4)–N(5)	126.8(7)
F(11)–As(1)–F(15)	91.7(2)	N(3)–C(4)–H(4)	117.6(8)
F(12)–As(1)–F(13)	90.4(2)	N(5)–C(4)–H(4)	115.6(7)
F(12)–As(1)–F(14)	175.8(2)	C(4)–N(5)–C(6)	115.3(6)
F(12)–As(1)–F(15)	92.2(2)	N(1)–C(6)–N(5)	122.5(7)
F(13)–As(1)–F(14)	89.7(2)	N(1)–C(6)–H(6)	118.9(7)
F(13)–As(1)–F(15)	92.5(2)	N(5)–C(6)–H(6)	118.6(7)
F(14)–As(1)–F(15)	92.1(2)		

ΔE value of the reaction of HCN with AsF_5 ($\Delta E = -42.3$ kJ mol^{-1})[2] the triazine–AsF_5 adduct is expected to be more stable than $HCN{\cdot}AsF_5$ due to the higher basicity of the N atom. This agrees well with the change of hybridisation from sp (HCN) to sp^2 [$(HCN)_3$] and therefore decreased orbital s character.[9] Unfortunately, we have not been able so far to determine the I_P and E_A values of **1** and **2**, therefore we cannot estimate the thermodynamics of the adduct formation of **2** and **3**. However, as one would expect, the basicity decreases with the number of co-ordinated AsF_5 units, and therefore the stability decreases from **1** to **3** (*cf.* **3** is stable in solution only, see above).

Crystal Structure of $(HCN)_3{\cdot}AsF_5$ **1**.—Atomic parameters are given in Table 4. Interatomic distances and bond angles are given in Table 5. Fig. 2 shows a view of the molecule. There are no significant intermolecular interactions.

In contrast to unco-ordinated triazine, which exists in D_{3h} symmetry (low-temperature X-ray structure)[10] the low-temperature single-crystal X-ray diffraction study of **1** reveals the co-ordinated six-membered $(HCN)_3$ ring to exist in a distorted-hexagonal geometry. The As atom in **1** possesses a distorted octahedral geometry surrounded by the five F atoms and one N of the co-ordinated triazine base. The CN bond distances lie between 1.314 and 1.352 Å and therefore are of the same order of magnitude as those of the highly symmetrical unco-ordinated $(HCN)_3$ molecule (1.338 Å).[10] However, they are slightly longer than the reported distances found in the structure of $(FCN)_3{\cdot}AsF_5$.[11] The CNC angles (114.8–117.3°) and the NCN angles (122.5–126.8°) in **1** are similar to the CNC (114.8°) and the NCN (125.2°) angles of $(HCN)_3$, but differ from the angles reported for the $(FCN)_3{\cdot}AsF_5$ complex (CNC: 112.6, NCN: 127.3°).[11] A significant difference between the $(HCN)_3{\cdot}AsF_5$ **1** and $(FCN)_3{\cdot}AsF_5$ adducts is the As–N bond length. In **1** the As–N bond distance is 1.966 Å which is very similar to that in $MeSCN{\cdot}AsF_5$ [*d*(As–N) = 1.995 Å][12] but is substantially shorter (by 0.146 Å) than the As–N distance in $(FCN)_3{\cdot}AsF_5$ (2.112 Å) and 0.166 Å longer than the As–N distance reported for $S_4N_4{\cdot}AsF_5$ (1.80 Å).[13] The shorter As–N distance in **1** compared with $(FCN)_3{\cdot}AsF_5$ agrees well with the lower basicity (and therefore weaker As–N bond) of $(FCN)_3$ compared with $(HCN)_3$.

Experimental

The reactions were carried out in glass vessels fitted with poly(tetrafluoroethylene) valves. All manipulations were carried out in an inert-gas atmosphere (N_2, dry-box). Gaseous compounds were added volumetrically using a calibrated vacuum line.

Arsenic pentafluoride was prepared from the elements,[14] $(HCN)_3$ (Aldrich) was used after drying over P_4O_{10}, SO_2 (Messer Griesheim, stored over CaH_2) and $CFCl_3$ (Merck, stored over P_4O_{10}) were used after distillation. IR spectra were obtained using a Perkin-Elmer 580 B instrument, Raman spectra were obtained using a Jobin Yvon Ramanor U 1000 spectrometer equipped with a Spectra Physics krypton laser (647.09 nm). Proton NMR spectra were recorded in SO_2 or SO_2–toluene (5:1) solution at 23 °C using a Varian EM 360 (60 MHz) or a Bruker WP 80 spectrometer operating at 80 MHz and are referenced to external $SiMe_4$ (in $CDCl_3$; internal lock [$^2H_8$]toluene). Carbon-13 NMR spectra were recorded in SO_2 solution at room temperature (23 °C) without lock using a Bruker WH 270 spectrometer operating at 67.9 MHz and referenced to external $SiMe_4$ (^{13}C NMR acquisition parameters: pulse width, 2.0 μs per 30°; spectral width, 15 151 Hz; relaxation delay, 1 s; data point resolution, 0.925 Hz per point; number of scans, 600–800). Nitrogen-14 spectra were recorded in SO_2 solution at 24 °C using a Bruker AM 250 (18.075 MHz) and referenced to neat external $MeNO_2$; C_6D_6 was used as an external lock [^{14}N NMR acquisition parameters: pulse width, 20.0 μs per 70°; spectral width, 10 000 Hz; acquisition time, 1.638 s; no relaxation delay; number of scans, $(HCN)_3$ 408, **1** 1919, **2** 5184, **3** 876].

Microanalyses were performed by the Technische Universität Berlin service.

Synthesis of $(HCN)_3{\cdot}AsF_5$ **1**.—At −196 °C AsF_5 (0.680 g, 4.00 mmol) was condensed onto a frozen solution (10 cm^3) of $(HCN)_3$ (0.323 g, 4.00 mmol) in SO_2. The reaction mixture was warmed to room temperature and stirred for 15 min. Sulfur dioxide was removed yielding **1** as a white solid (0.84 g, 88%). Cooling a solution of **1** in SO_2–$CFCl_3$ (1:1) from room temperature to 0 °C over a period of 2 d yielded **1** as colourless crystals, which were suitable for an X-ray diffraction study.

Synthesis of $(HCN)_3{\cdot}2AsF_5$ **2**.—Arsenic pentafluoride (0.782 g, 4.60 mmol) and $(HCN)_3$ (0.187 g, 2.30 mmol) were treated as described above. Adduct **2** was isolated as a white solid (0.87 g, 90%).

Synthesis of $(HCN)_3{\cdot}3AsF_5$ **3**.—1,3,5-Triazine (0.058 g, 0.70 mmol) and AsF_5 (0.365 g, 2.1 mmol) were allowed to react in a NMR tube in SO_2 to give a colourless solution of **3**.

X-Ray Crystal Structure Determination of $(HCN)_3{\cdot}AsF_5$ **1**.—

Colourless crystals were obtained by cooling a solution of **1** in SO_2–$CFCl_3$ (1:1) from room temperature to 0 °C.

Crystal data. $C_3H_3AsF_5N_3$, $M = 250.99$, orthorhombic, space group *Pcab* (no. 61), $a = 10.584(13)$, $b = 12.965(11)$, $c = 10.369(5)$ Å, $U = 1422.9(2)$ Å^3, $Z = 8$, $D_c = 2.343$ g cm^{-3}, $F(000) = 961$. Colourless crystals. Crystal dimensions 0.40 × 0.30 × 0.20 mm (put into Kel-F grease), μ(Mo-Kα) = 0.709 30 Å.

Data collection and processing. Rigaku diffractometer, ω–2θ scan mode ($2\theta_{max} = 55°$), $T = 100$ K, graphite monochromated Mo-Kα radiation; 1636 unique reflections up to $2\theta = 55°$ measured, 957 with $I_{net} \geqslant 2.5\sigma(I_{net})$ used for calculations (max., min. transmission factors = 0.3683, 0.2157).

Structure analysis and refinement. Direct methods (NRCVAX).[15] All non-hydrogen atoms in the molecule were given anisotropic thermal parameters. Hydrogen atoms bonded to carbon were included in calculated positions (hydrogen bond classification [16,17]). An absorption correction was applied.[18] Final R and R' values are 0.051, 0.071 where $w = 1/\sigma^2(F)$. The maximum shift/error ratio was 0.055; maximum residual electron density was −0.860 e Å^{-3} at the deepest hole and +1.000 e Å^{-3} at the highest peak. An ORTEP diagram [19] of the molecular structure of **1** is shown in Fig. 2.

Additional material available from the Cambridge Crystallographic Data Centre comprises thermal parameters.

Acknowledgements

We thank the Fonds der Chemischen Industrie and the Deutsche Forschungsgemeinschaft (Kl 636/2-1) for financial support, Mr. M. Dettlaff for recording the ^{1}H NMR, Mr. K. Siems for the ^{13}C NMR and Dr. Elter for the ^{14}N NMR spectra and Mrs. D. Bernhardt for carrying out the elemental analyses.

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Received 3rd *December* 1991; *Paper* 1/06110K