Inorganica Chimica Acta, 205 (1993) 167–173

Synthesis and characterization of novel halogeno(+I) adduct complexes containing malononitrile and 1,3,5-triazine

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(Received June 19, 1992; revised October 29, 1992)

Abstract

The 1-halogeno-1,3,5-triazinium hexafluoroarsenate and hexafluoroantimonate compounds of the type $[(\mathrm{HCN})_3\mathrm{X}][\mathrm{MF}_6]$ (M = As; X = F, (**1**), Cl (**2**) and M = Sb; X = Br (**3**)) have been synthesized by direct reaction of 1,3,5-triazine, $(\mathrm{HCN})_3$, with halogenomonofluorides, XF, in the presence of AsF_5 or SbF_5, respectively. The reactions of $(\mathrm{HCN})_3$ and malonitrile, $\mathrm{CH_2(CN)_2}$, with $[\mathrm{I_3}][\mathrm{AsF_6}]$ afforded the iodonium adduct species $[\{(\mathrm{HCN})_3\}_n\mathrm{I}][\mathrm{AsF_6}]$ ($n = 1$ (**4**), 2 (**5**)) and $[\{\mathrm{CH_2(CN)_2}\}_n\mathrm{I}][\mathrm{AsF_6}]$ ($n = 1$ (**6**), 2 (**7**)). All compounds have been characterized by chemical analyses, proton NMR spectroscopy and vibrational spectral data (IR, Raman). Temperature dependent ^{1}H NMR spectroscopy on $\mathrm{SO_2}$ solutions of **1**–**3** revealed fluctional behaviour at room temperature which was frozen down at −60 °C (two resonances, ratio 1:2). According to the NMR time scale the cations in **4** and **5** exist already in the slow exchange region at room temperature. Solution behaviour, IR and UV data of **6** (naples yellow reddish) and **7** (black) suggest **7** to be polymeric and **6** to be monomeric with strong intermolecular I···I interactions.

Introduction

Exploring the applicability of the extended hard–soft acid–base principle [1] in inorganic main group chemistry we have extensively studied the coordination behaviour of nitriles towards the Lewis acids $\mathrm{AsF_5}$, $\mathrm{SbF_5}$ and $[\mathrm{I_3}]^+$ [2–7]. For example, the linear 22-valence-electron cation $[\mathrm{ICNI}]^+$ was prepared according to eqn. (1).

$$\mathrm{ICN} + [\mathrm{I_3}][\mathrm{AsF_6}] \longrightarrow [\mathrm{ICNI}][\mathrm{AsF_6}] + \mathrm{I_2} \tag{1}$$

Systematic attempts to prepare further $[\mathrm{XCNY}]^+$ cations according to eqn. (2) were unsuccessful. All reactions led to the formation of the neutral Lewis base adduct species (eqn. (3)) [2, 8].

$$\mathrm{XCN} + \mathrm{YF} + \mathrm{AsF_5} \not\longrightarrow [\mathrm{XCNY}][\mathrm{AsF_6}] \tag{2}$$

$$\mathrm{XCN} + \mathrm{AsF_5} \longrightarrow \mathrm{XCN\cdot AsF_5} \overset{\mathrm{YF}}{\not\longrightarrow} \tag{3}$$

X = Cl, Br; Y = F, Cl, Br

However, we have been able to prepare $[\mathrm{FCNF}][\mathrm{AsF_6}]$ from $[\mathrm{HCNH}][\mathrm{AsF_6}]$ and elemental fluorine [9].

The synthesis of 1,3,5-triazinium cations according to eqns. (4) and(5) has been reported in the literature [10].

$$(\mathrm{HCN})_3 + \mathrm{HX} \longrightarrow [(\mathrm{HCN})_3\mathrm{H}]\mathrm{X} \tag{4}$$

X = Cl, Br

$$[(\mathrm{HCN})_3\mathrm{H}]\mathrm{Cl} + \mathrm{SbCl_5} \longrightarrow [(\mathrm{HCN})_3\mathrm{H}][\mathrm{SbCl_6}] \tag{5}$$

We therefore attempted analogous reactions of 1,3,5-triazine and halogeno(+I) fluorides, XF (X = F, Cl, Br). We also studied the reaction of $[\mathrm{I_3}][\mathrm{AsF_6}]$ towards 1,3,5-triazine and malononitrile. An account of this work is given below.

Experimental

Reagents and general procedures

Except where stated, the apparatus and chemicals were as previously described [2–6]. The solvents $\mathrm{CFCl_3}$ (Merck, $\mathrm{P_4O_{10}}$), $\mathrm{SO_2}$ (Messer Griesheim, $\mathrm{CaH_2}$) and $\mathrm{SO_2F_2}$ (Solvay, $\mathrm{CaH_2}$) were dried before use. $\mathrm{F_2}$ (Solvay) was stored over KF, $\mathrm{Cl_2}$ (Messer Griesheim), $\mathrm{Br_2}$ (Merck), $\mathrm{SbF_5}$ (Alfa) and $\mathrm{I_2}$ (Ferak) and $\mathrm{CH_2(CN)_2}$ (Aldrich) were purified by two-fold distillation or sublimation, respectively. $(\mathrm{HCN})_3$ (Aldrich) was vacuum dried over $\mathrm{P_4O_{10}}$ before use. $\mathrm{AsF_5}$ [11] and $[\mathrm{I_3}][\mathrm{AsF_6}]$ [12] were prepared as described in the literature.

IR spectra of Nujol or Fluorolube mulls between KBr, CsI or Si plates were obtained on a Perkin-Elmer

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0020-1693/93/$6.00

model 580 B grating spectrometer. Raman spectra were obtained at room temperature on a Jobin Yvon Ramanor U 1000 spectrometer (excitation line 647.09 nm). ^1H NMR spectra were recorded at 60 MHz on a Varian EM 360 or at 80 MHz on a Bruker WP 80 spectrometer. Chemical shift values are reported on the scale with tetramethylsilane (in the solvent used) at 23 °C as an external reference.

Preparation of $[(HCN)_3F][AsF_6]$ *(1)*

Arsenic pentafluoride (0.503 g, 2.96 mmol) and F_2 (0.112 g, 2.96 mmol) were condensed at -196 °C onto a frozen solution of $(HCN)_3$ (0.240 g, 2.96 mmol) in $CFCl_3$ (5 ml). The reaction mixture was warmed to -100 °C and then slowly (within 12 h) to room temperature. Removal of the volatile material gave compound **1** in 96% yield (0.825 g).

Dec. 120 °C. ^1H NMR ($SO_2/CDCl_3$): $\delta = 9.67$s ppm.

Anal. Calc.: C, 12.47; H, 1.04; N, 14.54. Found: C, 12.34; H, 1.04; N, 14.10%.

Preparation of $[(HCN)_3Cl][AsF_6]$ *(2)*

$(HCN)_3$ (0.141 g, 1.74 mmol), ClF (0.095 g, 1.74 mmol) and AsF_5 (0.296 g, 1.74 mmol) were reacted as described for the preparation of **1** (see above). Compound **2** was obtained in 94% yield (0.501 g).

Dec. 187 °C. ^1H NMR ($SO_2/CDCl_3$, 23 °C): $\delta = 9.73$s ppm.

Anal. Calc.: C, 11.79; H, 0.99; N, 13.76. Found: C, 11.80; H, 1.09; N, 13.71%.

Preparation of $[(HCN)_3Br][SbF_6]$ *(3)*

For this reaction a glass reaction vessel which consisted of two bulbs equipped with two Teflon-in-glass J. Young valves was used. In one bulb BrF was prepared from the elements in SO_2F_2 (5 ml) solution reacting Br_2 (0.396 g, 2.48 mmol) and F_2 (0.094 g, 2.48 mmol). The reaction mixture was allowed to warm to -10 °C followed by slow removal of SO_2F_2 with the vessel held at -30 °C. BrF (4.96 mmol) and SbF_5 (0.428 g, 4.91 mmol) were now condensed at -196 °C onto a frozen solution of $(HCN)_3$ (0.398 g, 4.90 mmol) in SO_2 (5 ml). The reaction mixture was warmed to room temperature and reacted for 1 day with stirring. Removal of the volatile material to constant weight and recrystallization from SO_2 (5 ml) afforded **3** in 15% yield (0.292 g).

Dec. 184 °C. ^1H NMR (SO_2, 23 °C): $\delta = 9.67$s ppm.

Anal. Calc.: C, 9.08; H, 0.76; N, 10.56. Found: C, 8.79; H, 0.94; N, 10.48%.

Preparation of $[(HCN)_3I][AsF_6]$ *(4)*

A solution of $(HCN)_3$ (0.136 g, 1.70 mmol) in SO_2 (5 ml) was reacted with a solution of $[I_3][AsF_6]$ (0.968 g, 1.70 mmol) in SO_2 (5 ml) at -30 °C and warmed to room temperature. The solvent was then removed. The crude product was extracted with $CFCl_3$ (10 ml) to remove the iodine. The insoluble product was separated by filtration and vacuum dried to give **4** in 60% yield (0.399 g).

^1H NMR (SO_2, 23 °C): $\delta = 9.83$s (1H), 9.53s (2H) ppm.

Anal. Calc.: C, 9.08; H, 0.76; N, 10.59. Found: C, 10.34; H, 1.00; N, 12.19%.

Preparation of $[\{(HCN)_3\}_2I][AsF_6]$ *(5)*

$(HCN)_3$ (0.285 g; 3.51 mmol) and $[I_3][AsF_6]$ (1.000 g, 1.76 mmol) were reacted as described for the preparation of **4** (see above). Compound **5** was obtained in 61% yield (0.510 g).

^1H NMR (SO_2, 23 °C): $\delta = 9.71$s (1H), 9.43s (2H) ppm.

Anal. Calc.: C, 15.08; H, 1.27; N, 17.58. Found: C, 15.10; H, 1.33; N, 18.40%.

Preparation of $[CH_2(CN)_2I][AsF_6]$ *(6)*

$CH_2(CN)_2$ (0.138 g, 2.10 mmol) and $[I_3][AsF_6]$ (1.186 g, 2.10 mmol) were reacted as described for the preparation of **4** (see above). Compound **6** was isolated as a yellowish solid in 85% yield (0.682 g).

Dec. 85 °C. ^1H NMR (AsF_3, 23 °C): $\delta = 3.84$s ppm.

Anal. Calc.: C, 9.44; H, 0.53; N, 7.34. Found: C, 9.47; H, 0.58; N, 7.39%.

Preparation of $[\{CH_2(CN)_2\}_2I][AsF_6]$ *(7)*

$CH_2(CN)_2$ (0.298 g, 4.50 mmol) and $[I_3][AsF_6]$ (1.283 g, 2.25 mmol) were reacted as described for the preparation of **4** (see above). The black solid product was isolated in 56% yield (0.565 g).

Dec. 110 °C. ^1H NMR (AsF_3, 23 °C): $\delta = 3.75$s ppm; (SO_2, 23 °C): $\delta = 3.67$s ppm. UV ($POCl_3$, 23 °C): $\lambda_{max} < 365$ nm.

Anal. Calc.: C, 16.09; H, 0.90; N, 12.51. Found: C, 15.18; H, 0.79; N, 11.99%.

Results and discussion

The reaction of a 1:1 mixture of 1,3,5-triazine and halogen(+I) fluorides in the presence of either AsF_5 or SbF_5 led to the formation of three hitherto unknown 1-halogeno-1,3,5-triazinium hexafluoroarsenates or hexafluoroantimonates, respectively (eqns. (6) and (7)).

$$(HCN)_3 + XF + AsF_5 \xrightarrow{\text{Freon-11}} [(HCN)_3X][AsF_6] \qquad (6)$$

X = F (**1**), Cl (**2**)

$$(HCN)_3 + BrF + SbF_5 \xrightarrow{\text{sulfur dioxide}} \underset{\mathbf{3}}{[(HCN)_3Br][SbF_6]} \qquad (7)$$

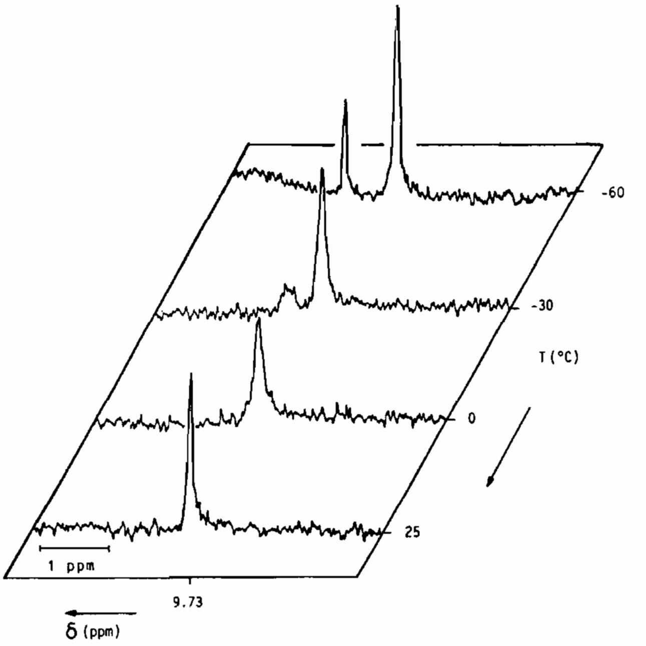

Fig. 1. Temperature dependent ^{1}H NMR spectrum of $[(HCN)_3Cl][AsF_6]$ (**2**) (SO_2 solution).

TABLE 1. ^{1}H NMR data for **1–7**[a]

Compound	Solvent	δ (ppm) (rel. int.)
1	$SO_2/CDCl_3$	9.67s
2	$SO_2/CDCl_3$	9.73s
3	SO_2	9.67s
4	SO_2	9.83s
5	SO_2	9.71s (1)
		9.43s (2)
6	AsF_3	3.84s
7	SO_2	3.67s
	AsF_3	3.75s

[a] 23 °C, referenced to internal TMS.

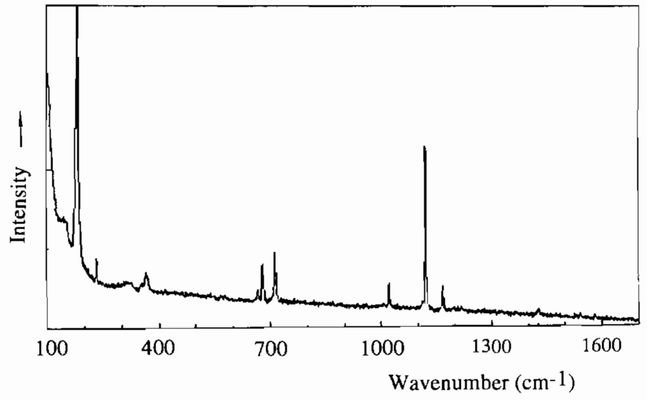

Fig. 2. Raman spectrum of $[\{(HCN)_3\}_2I][AsF_6]$ (**5**) (647 nm, 25 °C, 50 mW, 1 s/point).

Whereas compounds **1** and **2** have been isolated essentially quantitatively, the yield of complex **3** was only 15% due to the formation of the neutral adduct $(HCN)_3 \cdot SbF_5$ as a side product. The latter one is readily soluble in SO_2 and compound **3** was separated by recrystallization from a SO_2 solution. The iodonium analogue **4** as well as the 1:2 adduct species **5** have been prepared according to eqn. (8).

$$n(HCN)_3 + [I_3][AsF_6] \xrightarrow{\text{sulfur dioxide}} [\{(HCN)_3\}_n I][AsF_6] + I_2 \qquad (8)$$

$n = 1$, **4**; 2, **5**

The reaction of a 1:1 or a 1:2 mixture of $[I_3][AsF_6]$ and malononitrile in SO_2 led to the formation of the naples yellow reddish **6** and the black compound **7** (eqn. (9)).

$$nCH_2(CN)_2 + [I_3][AsF_6] \xrightarrow{\text{sulfur dioxide}} [\{CH_2(CN)_2\}_n I][AsF_6] + I_2 \qquad (9)$$

$n = 1$ (**6**), 2 (**7**)

All new compounds **1–7** are stable at room temperature and are sensitive towards air and moisture. Whereas the complexes **1–6** are pale white to yellow ochre solids the malononitrile derivative **7** is black. The compounds **1–5** and **7** are moderately soluble in liquid sulfur dioxide at room temperature. Complex **6**, however, is almost insoluble in SO_2 (cf. ^{1}H NMR in AsF_3 solution, see below and 'Experimental').

The presence of protons in all compounds investigated allows the possibility of applying ^{1}H NMR spectroscopy in order to identify and characterize the species in solution. At room temperature the triazinium complexes **1–3** only show one singlet resonance in SO_2 solution (**1**, 9.67; **2**, 9.73; **3**, 9.67 ppm). This can very well be explained by fast intermolecular halogeno exchange processes. This means that at room temperature (in the NMR time scale) the nitrogen atoms are equivalent and therefore only one proton resonance can be observed. At low temperature (−60 °C) all three species show two peaks due to the slow exchange rate in a ratio of 1:2. The temperature dependent ^{1}H NMR spectrum of compound **2** is illustrated in Fig. 1. Compounds **4** and **5** are at room temperature already in the slow exchange region and show two singlet resonances in a ratio of 1:2 (**4**, 9.83 (1H), 9.53 (2H); **5**, 9.71 (1H), 9.43 (2H) ppm). The high frequency (downfield) shift relative to the neutral $(HCN)_3$ (9.10 ppm) can be explained by the presence of a tricoordinate positively charged nitrogen atom.

Due to the insolubility of complex **6** in SO_2 solution the NMR spectra of **6** and **7** were recorded in saturated AsF_3 solutions (N.B. there is no significant difference in the chemical shifts using SO_2 or AsF_3 as the solvent;

TABLE 2. IR and Raman data for compounds **1**–**5**[a]

$[(HCN)_3F][AsF_6]$ (**1**)		$[(HCN)_3Cl][AsF_6]$ (**2**)		Tentative assignment
IR	Raman	IR	Raman	
3125w, sh			3121 (<1)	
3105m		3107m		
		2960w		νCH
		2927m		
		2855w		
1725w				
1622m		1622m, sh		
1605ms		1605s		
1575w		1562w		νC_3N_3
1564m		1545ms		
1515vw		1442ms	1489 (<1)	
		1425s	1422 (<1)	
		1378w		
1217m		1217w	1219(1)	
1212m		1212w		
1170w			1173(2)	δCH
1120w	1119(1)		1119(2)	νC_3N_3
1108m	1106(5)	1108m	1106(6)	
1068w	1070(1)		1065(1)	δCH
1045m	1049(2)	1045m	1048(4)	
	1008(1)		1005(1)	δC_3N_3
975w	991(1)			
835w	836(5)			
		760w, sh		
	736(1)	735ms, sh	739(1)	γCH
720vs	718(2)	720vs	723(3)	
705s, sh	703(4)		702(6)	δC_3N_3
695s		697s		$\nu_3 AsF_6$
	684(3)		686(2)	$\nu_1 AsF_6$
667ms	663(4)	668w	663(4)	$\nu_1 SbF_6/\delta C_3N_3$
645m	647(8)	645w	647(10)	δC_3N_3
	624(1)			
	593(1)		591(2)	$\nu_2 AsF_6$
				$\nu_2 SbF_6$
			478(1)	
			428(2)	
385vs		380s		$\nu_4 AsF_6$
	376(3)		376(3)	$\nu_5 AsF_6$
365vs		360s		
	335(1)		332(2)	γC_3N_3
	240(5)		240(7)	
	219(3)		219(5)	
	144(1)			
	116(10)			

$[(HCN)_3Br][SbF_6]$ (**3**)		$[(HCN)_3I][AsF_6]$ (**4**)	$[((HCN)_3)_2)I][AsF_6]$ (**5**)		Tentative assignment
IR	Raman	IR	IR	Raman	
			3135w	3107(<1)	
3095m		3070m	3070m	3075(<1)	
2955w		2955w	2960w	3056(<1)	νCH
		2930w	2945w		
1735w					
1685w		1625w			
1600ms		1585s	1582m		
1543s		1548m	1542s		νC_3N_3
		1540m	1520w, sh		

(continued)

TABLE 2. (*continued*)

$[(HCN)_3Br][SbF_6]$ (**3**)		$[(HCN)_3I][AsF_6]$ (**4**)	$[((HCN)_3)_2)I][AsF_6]$ (**5**)		Tentative assignment
IR	Raman	IR	IR	Raman	
1448s		1432s	1432s	1427(<1)	
1422m		1415s	1418s		
1385w			1395m		
1338s			1378w		
1191m	1188(1)	1195m	1197m		
1168m		1163	1163m	1166(1)	δCH
1153m		1150m, sh		1121(7)	
1106ms	1114(10)	1108m	1113s	1112(1)	νC_3N_3
1038m	1055(5)	1035m			δCH
		1017m	1018m	1021(1)	δC_3N_3
		972w			
941w		947w			
		890w			
		845w			
	740(2)	765m, sh			
720s	725(1)	720vs	720s		γCH
690ms, sh			710s	714(2)	
					δC_3N_3
		690vs	695s		$\nu_3 AsF_6$
			680s	682(1)	$\nu_1 AsF_6$
			680s	682(1)	$\nu_1 AsF_6$
	676(3)	672s			$\nu_3 SbF_6$
653vs, br	658(1)		663	667(5)	$\nu_1 SbF_6/\delta C_3N_3$
640s, sh	646(3)				δC_3N_3
		570w			$\nu_2 AsF_6$
569m, sh	562(1)				$\nu_2 SbF_6$
520m					
			480w		
		395vs	395vs		$\nu_4 AsF_6$
					$\nu_5 AsF_6$
				366(1)	
					γC_3N_3
285s	278(1)			313(1)	
	188(3)			181(10)	
				146(1)	

[a]For details see 'Experimental'.

7: (SO_2) 3.67, (AsF_3) 3.75 ppm; see 'Experimental'). Both species show a singlet resonance and a downfield shift compared with free and uncoordinated malononitrile (AsF_3 solution: **6**, 3.84; **7**, 3.75; $CH_2(CN)_2$, 3.58 ppm; SO_2 solution: $CH_2(CN)_2$, 3.36 ppm). The downfield shift from $CH_2(CN)_2$ via **7** to **6** is nicely in agreement with the increase of the positive charge on the coordinated Lewis base (cf. ref. 13). ^1H NMR data for **1**–**7** are given in Table 1.

The IR spectra of Nujol or Fluorolube mulls were recorded between KBr or CsI plates. Due to its reactivity towards both KBr and CsI, Si plates were used to record the IR spectrum of compound **6**. Raman spectra were obtained only for compounds **1**–**3** and **5** (Fig. 2) because of fluorescence problems (**4**, **6**) and the black colour of compound **7**. Tables 2 and 3 summarize the vibrational spectral data of all new compounds and contain tentative assignments (AsF_6^-, SbF_6^- [14]; $(HCN)_3$ [15]; $CH_2(CN)_2$ [16]).

Whereas the IR spectrum of compound **6** (Fig. 3) consists of one strong absorption in the C≡N stretching region, compound **7** shows two bands in this region (Fig. 4) due to two differently coordinated CN unities. This can be discussed on the basis of a polymeric structure for compound **6** (N.B. insolubility in SO_2, see above) whereas complex **7** is apparently monomeric and contains both, free and coordinated CN unities (Fig. 5). The black colour of species **7**, however, indicates strong intermolecular I···I interactions. Therefore, a resonance structure for **7**(II) as given in Fig. 5 may be drawn (cf. existence of I_2^+, ref. 17) although the one indicated in **7**(I) (Fig. 5) still seems to be more likely. Moreover, the UV data of a $POCl_3$ solution of

TABLE 3. IR data for compounds **6** and **7**[a]

$[CH_2(CN)_2I][AsF_6]$ (**6**)	$[(CH_2(CN)_2)_2I][AsF_6]$ (**7**)	Tentative assignment
2942vs	2950m	νCH
2910vs	2915m	
2320vs	2322m	νCN, coord.
	2280w, sh	νCN, free
1372s	1372w	
1318ms	1317w	δCH_2
1162m		
970–1000ms	950m	νCC, δCH_2
905ms	905w	νCC
897s	895m	
	835w	
772w		
700–720vs	720vs	$\nu_3AsF_6/\gamma CH$
	698vs	ν_3AsF_6
593ms	592w	δCCC
395vs	392vs	ν_4AsF_6
370ms, sh		
220m		

[a] For details see 'Experimental'.

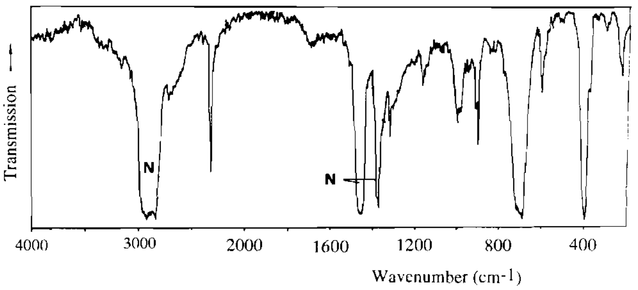

Fig. 3. IR spectrum of $[CH_2(CN)_2I][AsF_6]$ (**6**) (Nujol mull between Si plates).

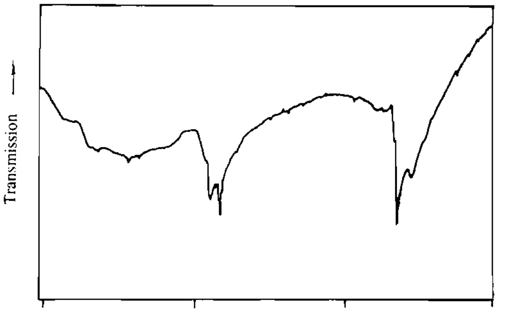

Fig. 4. IR spectrum (C–H and C≡N stretching region) of $[\{CH_2(CN)_2\}_2I][AsF_6]$ (**7**) (Fluorolube mull between KBr plates).

complex **7** (λ_{max}<365 nm) clearly indicate that the deep colour is due to the presence of species **7** rather than impurities of iodine (λ_{max}=470–490 nm). Unfortunately, despite several attempts, we have so far been unable to grow crystals of compound **6** or **7** in order to determine the solid state structure of both species.

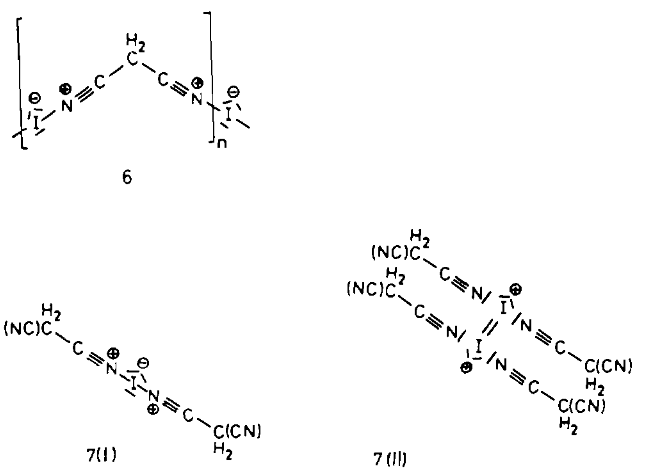

Fig. 5. Tentative resonance structures for $[CH_2(CN)_2I][AsF_6]$ (**6**) and $[\{CH_2(CN)_2\}_2I][AsF_6]$ (**7**).

Acknowledgements

We thank the Deutsche Forschungsgemeinschaft (KL 636/2-1) and the Fonds der Chemischen Industrie for financial support. We thank the Solvay Fluor und Derivate GmbH for SO_2F_2 and Freon gases and the Wacker Chemie, Burghausen for providing Si plates for IR spectroscopy.

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