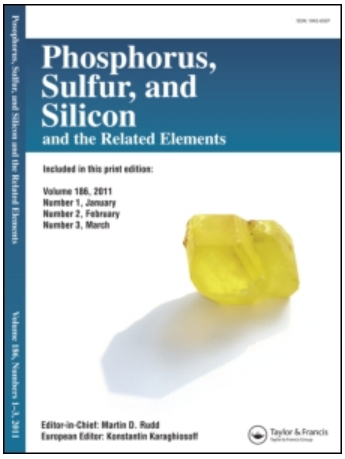

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PREPARATION, X-RAY STRUCTURE AND VIBRATIONAL SPECTRA OF $[S_4N_3]_3Cl[SbCl_6]_2$

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PREPARATION, X-RAY STRUCTURE AND VIBRATIONAL SPECTRA OF $[S_4N_3]_3Cl[SbCl_6]_2$

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The X-ray crystal structure of the title compound reveals that the planar $[S_4N_3]^+$ cations surround the Cl^- anion with an array of $S(\delta+)\cdots Cl^-$ interactions. The FT Raman spectrum shows a significant reduction of the ν(SS) frequency in the title compound cf. $[S_4N_3]Cl$.

Key words: Charge-transfer; solid state; X-ray; antimony.

INTRODUCTION

We are interested in the preparation and properties of solid state charge-transfer systems. Electron rich S—N compounds offer great potential in this regard as a consequence of, in part, the polarisability of their sulfur atoms. We have previously reported the stacking properties of $[Pt(S_2N_2H)(PR_3)_2]X$ (PR_3 = PMe_3, PMe_2Ph; X = Cl^-, PF_6^-, BF_4^-) and $[CoCp_2][S_3N_3]$.[1,2] Sulfur-nitrogen cations have also been shown to dimerise in the solid state.[3,4] Thus, we have embarked upon a study of the ability of $[S_4N_3]^+$ to form stacking structures with a range of anions. Here we report the preparation and single crystal X-ray structure of $[S_4N_3]_3Cl[SbCl_6]_2$.

RESULTS AND DISCUSSION

The X-ray structure shows the asymmetric unit in the crystal contains three $[S_4N_3]^+$ cations, two $[SbCl_6]^-$ anions and one chloride anion (Figure 1). Thus, despite the initial 1:1 stoichiometry of $[S_4N_3]Cl$ and $SbCl_5$ in the reaction which was performed in 98% formic acid, it does not go to completion. The two crystallographically independent $[SbCl_6]^-$ anions have essentially O_h symmetry, with maximum deviations from 90 and 180° at Sb of 2.1(1)° (Table I). There are however noticeable variations in the Sb—Cl bondlengths, which are in the range 2.339(2) to 2.396(2) A for Sb(1) and 2.341(2) to 2.391(3) A for Sb(2). These variations in bondlengths are of the order of 20σ. Librational analyses of both $[SbCl_6]^-$ anions shows that the bond length corrections are essentially isotropic (between 0.013 and 0.021 A) and thus we believe that the large variations observed in the Sb—Cl bondlengths are both real and significant. We cannot, however, relate these bond length variations to any intermolecular interactions in the crystal.

All three $[S_4N_3]^+$ rings have approximate C_{2v} symmetry with the S—S and S—N bondlengths (Table II) all within the ranges previously reported for this cation.[5,6] As observed previously, the angles at N(1) and N(2) are significantly enlarged at 147.7(5)–152.9(5)°; the remaining angles also compare well with those in the lit-

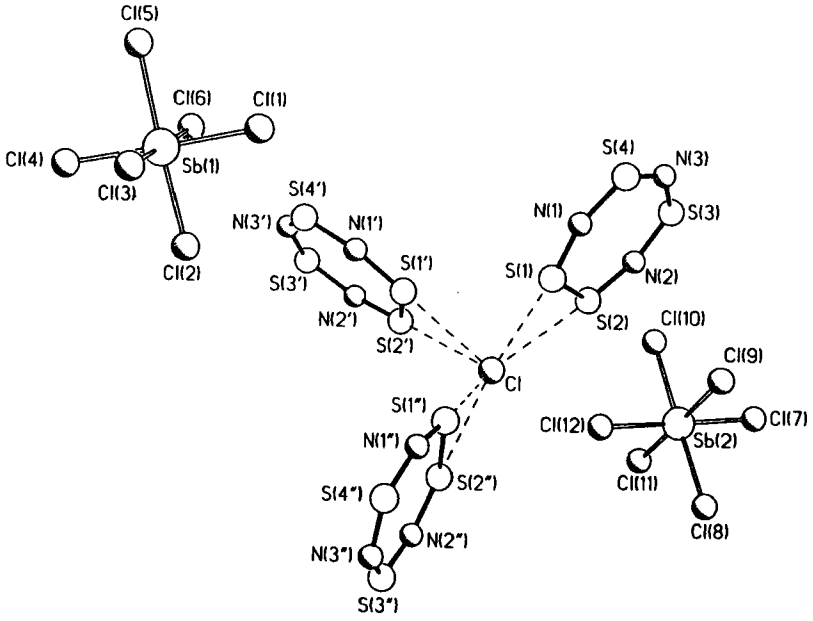

FIGURE 1 The asymmetric unit of the crystal structure of $[S_4N_3]_3Cl[SbCl_6]_2$.

TABLE I

Bondlengths (Å) and angles (°) for the $SbCl_6^-$ anions in the structure

Sb(1)-Cl(1)	2.389 (2)	Sb(1)-Cl(2)	2.339 (2)
Sb(1)-Cl(3)	2.354 (2)	Sb(1)-Cl(4)	2.396 (2)
Sb(1)-Cl(5)	2.347 (2)	Sb(1)-Cl(6)	2.362 (3)
Sb(2)-Cl(7)	2.348 (3)	Sb(2)-Cl(8)	2.366 (2)
Sb(2)-Cl(9)	2.367 (2)	Sb(2)-Cl(10)	2.353 (3)
Sb(2)-Cl(11)	2.341 (2)	Sb(2)-Cl(12)	2.391 (3)

Cl(1)-Sb(1)-Cl(2)	91.0(1)	Cl(1)-Sb(1)-Cl(3)	177.9(1)
Cl(2)-Sb(1)-Cl(3)	90.6(1)	Cl(1)-Sb(1)-Cl(4)	89.2(1)
Cl(2)-Sb(1)-Cl(4)	89.6(1)	Cl(3)-Sb(1)-Cl(4)	89.4(1)
Cl(1)-Sb(1)-Cl(5)	90.8(1)	Cl(2)-Sb(1)-Cl(5)	91.5(1)
Cl(3)-Sb(1)-Cl(5)	90.5(1)	Cl(4)-Sb(1)-Cl(5)	178.9(1)
Cl(1)-Sb(1)-Cl(6)	89.0(1)	Cl(2)-Sb(1)-Cl(6)	178.2(1)
Cl(3)-Sb(1)-Cl(6)	89.4(1)	Cl(4)-Sb(1)-Cl(6)	88.6(1)
Cl(5)-Sb(1)-Cl(6)	90.3(1)	Cl(7)-Sb(2)-Cl(8)	91.0(1)
Cl(7)-Sb(2)-Cl(9)	90.0(1)	Cl(8)-Sb(2)-Cl(9)	179.0(1)
Cl(7)-Sb(2)-Cl(10)	90.4(1)	Cl(8)-Sb(2)-Cl(10)	89.9(1)
Cl(9)-Sb(2)-Cl(10)	90.1(1)	Cl(7)-Sb(2)-Cl(11)	90.8(1)
Cl(8)-Sb(2)-Cl(11)	90.0(1)	Cl(9)-Sb(2)-Cl(11)	90.0(1)
Cl(10)-Sb(2)-Cl(11)	178.8(1)	Cl(7)-Sb(2)-Cl(12)	179.1(1)
Cl(8)-Sb(2)-Cl(12)	89.6(1)	Cl(9)-Sb(2)-Cl(12)	89.5(1)
Cl(10)-Sb(2)-Cl(12)	88.9(1)	Cl(11)-Sb(2)-Cl(12)	90.0(1)

erature. All three cations are planar with maximum deviations from their respective mean planes of 0.01 Å [S(1)], 0.014 Å[S(4')] and 0.02 Å [S(2")].

A study of the packing of the anions and the cations in the crystal (Figures 1 and 2) reveals a dominant interaction between the chloride ion and the three

TABLE II

Bondlengths (Å) and angles (°) for the three independent $[S_4N_3]^+$ cations in the structure

	$[S_4N_3]^+$	$[S'_4N'_3]^+$	$[S''_4N''_3]^+$	mean
S(1)-S(2)	2.081(3)	2.085(3)	2.093(3)	2.09
S(1)-N(1)	1.573(7)	1.564(8)	1.554(8)	1.56
S(2)-N(2)	1.560(7)	1.563(8)	1.570(7)	
S(3)-N(2)	1.542(7)	1.541(8)	1.531(7)	1.54
S(4)-N(1)	1.546(7)	1.531(8)	1.543(8)	
S(3)-N(3)	1.589(8)	1.571(7)	1.564(8)	1.56
S(4)-N(3)	1.539(7)	1.552(7)	1.561(8)	
S(1)-S(2)-N(2)	112.9(3)	111.2(3)	111.9(3)	112.1
S(2)-S(1)-N(1)	113.6(3)	111.4(3)	111.9(3)	
S(1)-N(1)-S(4)	147.7(5)	152.9(5)	151.5(5)	151.3
S(2)-N(2)-S(3)	150.6(5)	152.7(5)	152.4(5)	
N(1)-S(4)-N(3)	120.9(4)	117.7(4)	118.1(4)	118.2
N(2)-S(3)-N(3)	117.9(4)	117.4(4)	117.3(4)	
S(3)-N(3)-S(4)	136.5(4)	136.7(5)	137.3(5)	136.8

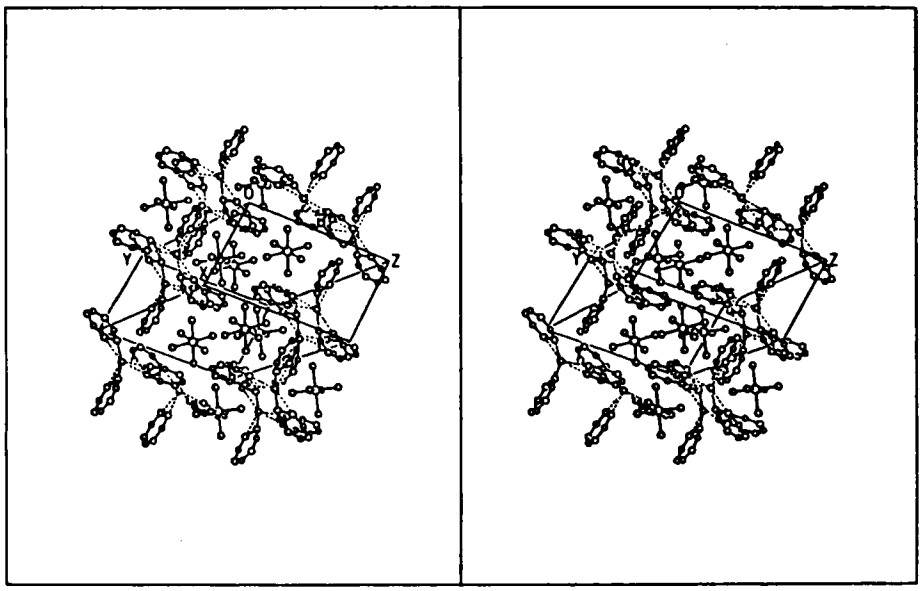

FIGURE 2 Packing of the anions and cations in the crystal of $[S_4N_3]_3Cl[SbCl_6]_2$.

independent $[S_4N_3]^+$ cations. The chloride ion is surrounded approximately equidistantly by three $[S_4N_3]^+$ cations. It is coplanar with two of the $[S_4N_3]^+$ cations but slightly out of the plane of the third ring [0.03 A]. The S$\cdots$Cl distances are short and in the range 2.96–3.01 A. This arrangement must reflect the cumulative

electrostatic interactions between $S(\delta+)$ and Cl^-. Similar electrostatic interactions have been noted in S_2N_2 complexes.[7,8]

The infrared and Raman spectra of $[S_4N_3]_3Cl[SbCl_6]_2$ reveals the expected peaks due to the anions and the cations. The most striking feature is the shift to lower frequency of the $\nu(SS)$ vibration which is observed at 419 cm^{-1} (FT Raman) here compared to 447 cm^- in $[S_4N_3]Cl$[9] indicating a slight weakening of the S—S bond as a consequence of the $S(\delta+)\cdots Cl^-$ interactions.

EXPERIMENTAL

Preparation of $[S_4N_3]_3Cl[SbCl_6]_2$: $SbCl_5$ (1.46 g, 4.87 mmol) was added to a saturated solution of $[S_4N_3]Cl$ (1 g, 4.87 mmol; prepared as described by Jolly and Maguire[10]) in 98% formic acid (20 cm^3) with stirring at room temperature. The resulting crystalline solid was filtered off, washed with 98% formic acid and toluene and dried *in vacuo* (yield 1.7 g, 30%). M.p. 203–208°C. Analysis. Calc. for $Cl_{13}N_9S_{12}Sb_2$: Cl 42.1%, N 10.37%; found Cl 42.5%, N 8.4%.

Vibrational Spectra: (Raman in brackets) for $S_4N_3^+$: 1173 m (1176 vw), 1137 w, 1025 s (1026 vw), 674 m (648 vw) (614 m), 569 m (569 w), 470 m (444 w), 339 s, 253 w (259 m) (211 vw); for $SbCl_6^-$ 351 s (331 vs, 285 m) cm^{-1}.

Crystal Data: $Cl_{13}N_9S_{12}Sb_2$, M_r = 1215.2, monoclinic $P2_1/c$, Z = 4, a = 9.623(1), b = 22.916(3), c = 15.976(3) Å, β = 106.55(1)°, V = 3376.9(7) A^3, D_c = 2.39 gcm^{-3}, $\lambda(MoK_\alpha)$ = 0.7073 A, μ = 33.9 cm^{-1}, $F(000)$ = 2312, T = 295 K.

Data Collection: A single crystal of dimensions 0.09 × 0.09 0.27 mm was obtained by recrystallisation from 98% formic acid. Intensity data were collected on a Siemens $P4$ diffractometer using graphite monochromated Mo-K_α radiation. Accurate cell dimensions were derived from setting angles of 20 reflections in the 2θ range 4–27°. Intensity data were measured using ω-scans ($2\theta_{max}$ = 50°), using variable scan speed. Two standard reflections remeasured every 50 reflections showed no significant intensity variation. 6326 reflections were measured, merged into 5957 unique reflections (R_{int} = 1.99%) with 4009 being considered observed [$F > 4.0\sigma(F)$]. Range of hkl: $-11 \le h \le 10$, $0 \le k \le 27$, $0 \le 1 \le 18$. Lorentz and polarization as well as a numerical absorption correction (face indexed crystal, principal faces 100, −100, 0-2-1, 0-2-1, 0-21, 021, 02-1) maximum and minimum transmission factors 0.766 and 0.700 respectively were applied.

Structure Analysis and Refinement: The structure was solved by the heavy atom method and all atoms refined anisotropically. Two reflections (−3 0 4 and −2 1 3) which had $|F_0| << |F_c|$ and were suspected of being affected by extinction were removed. Full matrix least-squares refinement on F_0 converged to R = 0.038, wR = 0.040 and S = 1.00. A total of 325 parameters were refined, weighting scheme $w^{-1} = \sigma^2(F) + 0.00055F^2$, largest and mean Δ/σ 0.030 and 0.004, largest difference peak 0.71 eA^{-3} and largest difference hold −0.53 eA^{-3}. Computations were carried out on a Vaxstation 3100 model 76 using SHELXTL PLUS.[11]

Vibrational Spectroscopy: IR spectra were recorded from 2000–250 cm^{-1} using a PE 1720X spectrometer as KB4 discs. FT Raman spectra were obtained using a PE 1760X spectrometer with Raman accessory.

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