refinements allowing the occupancy of the water sites to vary were tried. Starting occupancies in various cases were 0.5 and 1.0. In all cases the occupancies refined very close to 1.0 with very similar R_1 and R_2 factors given here. Similar problems have been observed by us previously. (R. Faggiani, B. Lippert, C. J. L. Lock, and B. Rosenberg, *Inorg. Chem.*, **17**, 1941 (1978).)

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(26) $R_1 = \sum||F_o| - |F_c||/\sum|F_o|$; $R_2 = [\sum w(|F_o|^2 - |F_c|^2)/\sum wF_o^2]^{1/2}$. All calculations were carried out on a CDC-6400 computer. The programs DATCO3, ABSORB, and DATRDN from the X-ray 71 package were used for preliminary treatment of data. The full-matrix least-squares program CUDLS, Fourier program, SYMFOU, and least-squares-planes program, PALS, were written locally by J. S. Stephens, J. S. Rutherford, and P. G. Ashmore, respectively. Diagrams were prepared using the program ORTEP by C. K. Johnson, Report ORNL 3794, U.S. Atomic Energy Commission, Oak Ridge, Tenn., revised June 1965.

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(30) In each plane mentioned all atoms were included in the refinement and were given unit weight. The esd in each atom position with respect to the plane is 0.015 Å.

(31) IR intensities: vs = very strong, s = strong, m = medium, w = weak, vw = very weak, sh = shoulder, b = broad. Raman intensities are relative to the strongest Raman band at 556 cm^{-1} with arbitrary intensity 10.

(32) According to space group C_i^1 and $Z = 1$ the D_{2h} symmetry of the free dimer is reduced to C_i site symmetry.

Preparation, Vibrational Spectra, and Crystal Structure of Dithionitronium Hexachloroantimonate(V), (S₂N)(SbCl₆)

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Dithionitronium hexachloroantimonate(V), $(S_2N)(SbCl_6)$, has been prepared by the reactions of S_7NH, S_7NBCl_2, and $1,4\text{-}S_6N_2H_2$ with $SbCl_5$ in liquid SO_2. The structure of the compound has been determined by single-crystal X-ray diffraction. The orthorhombic crystal, space group $I222$, has cell dimensions $a = 9.299$ (3) Å, $b = 7.976$ (3) Å, and $c = 7.070$ (2) Å and has two formula units in the unit cell. Intensities were measured using Mo Kα radiation and a Syntex $P2_1$ diffractometer. The crystal structure was determined by standard methods and refined to $R_1 = 0.0377$, $R_2 = 0.0375$. The crystal is composed of linear S_2N^+ cations (N–S = 1.464 (3) Å) and approximately octahedral $SbCl_6^-$ anions (Sb–Cl = 2.351 (3), 2.363 (2) Å). Infrared and Raman spectra of the solid compound are reported.

Introduction

We have recently studied the reactions of S_4N_4 and $S_3N_3Cl_3$ with certain group 5 pentahalides which have both oxidizing and Lewis acid properties and we have shown that the cyclic cation $S_4N_4^{2+}$ is obtained by the reaction of S_4N_4 with $SbCl_5$ or SbF_5 and also by the oxidation of $S_3N_3Cl_3$ with $SbCl_5$.[1]

This work has now been extended to the sulfur imides with particular emphasis on the behavior of heptasulfur imide and 1,4-hexasulfur diimide with Lewis acids. In the only previous study of the Lewis acid chemistry of S_7NH, Heal[2] isolated the dichloro- and dibromo(heptasulfur imido)boron derivatives of S_7NH by means of a simple condensation reaction of the imide with the appropriate boron trihalide. We have now shown that S_7NH and $1,4\text{-}S_6N_2H_2$ do not undergo analogous condensation reactions with $SbCl_5$ but a complex oxidative process produces the dithionitronium cation S_2N^+. That this species has not been previously reported is somewhat surprising in view of its relative stability and fact that the analogus NO_2^+ has been known for over 30 years.

Experimental Section

Heptasulfur imide was prepared according to the method of Becke-Goehring.[3] The product was crystallized twice from benzene to yield platelike crystals of mp 113 °C (lit. mp[4] 113 °C). The $1,4\text{-}S_6N_2H_2$ was prepared by the late Dr. F. P. Olsen according to the method described by Heal.[5] The sample was recrystallized twice from benzene and its purity checked by melting point, 130–131 °C (lit. mp[5] 130, 133 °C), and its solution infrared spectrum.[6] Boron trichloride (Matheson of Canada Ltd.) was distilled into a glass storage vessel that had been previously flame-dried under vacuum. The sample was then degassed several times to remove any HCl present. Antimony pentachloride (J. T. Baker) was used without further purification. Sulfur dioxide (Canadian Liquid Air) was stored as a liquid over phosphoric oxide prior to use.

The Reaction of Heptasulfur Imide with SbCl₅. Heptasulfur imide (0.001 mol, 0.287 g) and $SbCl_5$ (0.002 mol, 0.717 g) were each transferred in a drybox to separate bulbs of a double-bulb reaction vessel fitted with a medium glass frit. Sulfur dioxide (5 mL) was then condensed at −196 °C into each bulb and the apparatus was flame-sealed. The mixtures were then allowed to warm to room temperature. The $SbCl_5$ completely dissolved in the SO_2 at room temperature but as S_7NH is only moderately soluble in liquid SO_2 some remained undissolved. The $SbCl_5$ solution was then poured through the glass frit into the bulb containing the S_7NH. There was an immediate reaction with the formation of a deep red-brown solution. After 48 h of shaking, a yellow powder formed which was characterized as S_8, by means of its Raman spectrum. After filtration at room temperature and slow removal of the solvent, an orange crystalline material was obtained which was shown to be S_2NSbCl_6. The reaction must be allowed to proceed for at least 48 h prior to filtration to ensure that the S_2NSbCl_6 is not contaminated with sulfur. Hydrogen chloride produced during the reaction was identified by means of its infrared spectrum, and $SbCl_3$ sublimed from the reaction mixture was characterized by comparison of its Raman spectrum with that of a pure sample.

The Reaction of 1,4-S₆N₂H₂ with SbCl₅. This reaction was carried out in essentially the same manner as described above using 0.0014 mol (0.317 g) of $1,4\text{-}S_6N_2H_2$ and 0.0057 mol (1.705 g) of $SbCl_5$. A yellow powder was formed, which was characterized as elemental sulfur by means of its Raman spectrum. After filtration of the mixture at room temperature and slow removal of solvent, an orange crystalline material formed which was shown to be S_2NSbCl_6. Hydrogen chloride

and $SbCl_3$ were also identified as reaction products as described above.

The Reaction of S_7NBCl_2 with $SbCl_5$. The compounds S_7NH (0.002 mol, 0.5448 g) and $SbCl_5$ (0.004 mol, 1.3631 g) were transferred in the drybox to separate bulbs of a double-bulb reaction vessel. This vessel was fitted with a glass frit as well as a Roto-flo valve between the frit and the bulb containing the $SbCl_5$. In addition the bulb containing the S_7NH was equipped with a stirring bar. Boron trichloride (0.004 mol, 0.5288 g) and SO_2 (5 mL) were condensed onto the S_7NH at −196 °C. the solution was allowed to warm to −48 °C (1-hexanol slush bath) and maintained at this temperature for approximately 1 h until all the S_7NH was consumed to yield the heptasulfur imide–boron dichloride. It is important not to allow the mixture to warm to a higher temperature as a red tar-like material is then produced.

After SO_2 was condensed onto the $SbCl_5$, the resulting solution was poured onto the S_7NBCl_2, at −48 °C, by opening the Roto-flo valve. The reaction proceeded as described above, and after filtration of the sulfur that was precipitated, the solvent was removed to yield large orange crystals that were characterized as $(S_2N^+)(SbCl_6^-)$.

Spectroscopic Measurements. Raman spectra were recorded on a Spex Industries Model 1400 0.75-m Czerny-Turner double monochromator using a Spectra Physics Model 164 argon ion laser giving up to 900 mW at 5145 Å.

Electron spin resonance spectra were obtained on a Jeolco Model JES 3BS-X spectrometer. The g values were obtained by comparison with a sample of Mn^{2+} in MgO ($g = 1.981$) and are accurate to ±0.001.

Infrared spectra were obtained on a Perkin-Elmer grating infrared spectrometer, Type 283. Samples were prepared using Nujol that had been dried over sodium wire. Spectra were obtained in the range 4000–200 cm^{-1} using CsI windows. All materials sensitive to moisture were handled in a Vacuum Atmospheres drybox, Model HE-43, equipped with a drying train, Model HE-373-B.

Collection of X-ray Diffraction Data. A yellow, nearly cylindrical crystal of the compound $(S_2N)(SbCl_6)$ was sealed in a fused quartz capillary tube. The crystal was 0.075 mm in radius and 0.2 mm in length and was mounted such that the [233] direction was roughly along the goniometer axis. Precession photographs of zero and first layers suggested the crystal was orthorhombic and the systematic absences $h + k + l = 2n + 1$ suggested the space groups $I222$ (No. 23), $I2_12_12_1$ (No. 24), $Imm2$ (No. 44), or $Immm$ (No. 71). It was not possible to measure the density of the crystal because of decomposition in air, but the volume of the cell was about 530 Å^3. The formula assumed was $(S_xN_y)(SbCl_6)$ and the volume of $SbCl_6^-$ was considered to be roughly that of six chlorine atoms (namely 6 × 35 = 210 Å^3). On this basis it seemed likely that $Z = 2$. Since the special positions are fourfold in space group $I2_12_12_1$, this space group was rejected. An analysis of the hkl and $\overline{h}kl$ reflections using NORMSF suggested the crystal was noncentric leaving $I222$ and $Imm2$. The former was chosen for initial treatment, and the structure was successfully refined in this space group. Refinement in $I222$ changing x, y, z to $-x, -y, -z$ for each atom showed no significant difference, however, and in the absence of other physical evidence for the lack of a center of symmetry final refinement was done in space group $Immm$.[8] The crystal was transferred to a Syntex $P2_1$ diffractometer. Accurate parameters were obtained from a least-squares fit of χ, ϕ, and 2θ for 15 medium angle (20° < 2θ < 35°) reflections: $a = 9.299$ (3) Å, $b = 7.976$ (3) Å, $c = 7.070$ (2) Å (λ 0.710 69 Å for Mo Kα at 23 °C). With $Z = 2$, ρ_{calcd} was 2.61 g cm^{-3}. The linear absorption coefficient was 44.8 cm^{-1} and thus μR was 0.34. A^* varied from 1.59 to 1.65. Intensities were measured on the Syntex $P2_1$ diffractometer using graphite-monochromatized Mo Kα radiation for the quadrant $h,k,\pm l$ up to $2\theta = 55°$. Data were collected using a coupled θ-(crystal)–2θ(counter) scan 1° on either side of the peak, scan rates varying from 8.37 to 29.3°/min, and were selected by the program supplied with the machine.[9] The stability of the instrument was monitored by measuring a standard reflection (211) after every 15 reflections. The counting esd of the standard reflection was 2.15% and an analysis of the standard counts showed an overall esd of 4.4% with no systematic variation with time. The intensity of a reflection, I, and its esd, $\sigma(I)$, were calculated as outlined previously.[10] A total of 356 independent reflections were recorded of which 334 had $I > 3\sigma(I)$ and 22 had $3\sigma(I) > I > \sigma(I)$. No corrections were made for absorption. This would produce a maximum error in F of 3%. The Lorentz–polarization factor and method of calculating F and $\sigma(F)$ have been given previously.[10]

Table I. Atomic Parameters and Temperature Factors (Å^2)^a (×10^3)

	x	y	z	U_{11}	U_{22}	U_{33}
Sb	0	0	0	35.6 (6)	35.1 (6)	36.1 (6)
Cl(1)	0	294.7 (4)	0	111 (3)	34 (1)	64 (2)
Cl(2)	177.8 (2)	0	238.9 (3)	46 (1)	81 (1)	44 (1)
S	500	183.4 (5)	0	108 (3)	55 (2)	85 (3)
N	500	0	0	37 (7)	53 (8)	42 (7)

^{a} Anisotropic temperature factors U_{ij} were obtained from $\beta_{ij} = 2\pi^2 b_i b_j U_{ij}$ where the β_{ij}'s appears as a temperature effect of the form $\exp[-(\beta_{11}h^2 + ... + 2\beta_{12}hk + ...)]$ and b_i and b_j are the reciprocal lattice vectors.

Solution of the Structure. The antimony atom was found from a three-dimensional Patterson synthesis, and a three-dimensional electron difference map revealed the chlorine and sulfur atoms. Two cycles of refinement followed by a further difference synthesis revealed the remaining nitrogen atom. Full-matrix refinement of these atom positions using anisotropic temperature factors and minimizing $w(|F_o| - |F_c|)^2$ proceeded smoothly and was terminated at $R_1 = 0.0320$, $R_2 = 0.0321$.[11] A Cruickshank weighting scheme with weight equal to $(4.088 - 0.1033|F_o| + 0.001032F_o^2)^{-1}$ was used and in the final cycle of refinement no parameter shifted by more than 0.17 of its esd. Corrections were made for secondary extinction ($g = 4.53 \times 10^{-8}$) by the method of Larson.[12]

The final difference map showed little variation, the largest peak being 1.3 e/Å^3 (0.07, 0.7, 0) and the deepest valley being −1.2 e/Å^3 (0, 0.78, 0), both close to Cl(1). Throughout the refinement the scattering curves were taken from ref 13a, and anomalous dispersion corrections[13b] were applied to the curves for Sb, Cl, and S. The atom parameters are listed in Table I.

Results and Discussion

Preparation of $(S_2N)(SbCl_6)$. The simple reaction between S_7NH and BCl_3 to give the (heptasulfur imido)boron dichlorides is a direct consequence of the known acidity of the hydrogen atom in S_7NH and the fact that boron trichloride has no oxidizing ability.

The reaction between S_7NH and $SbCl_5$ is much more complex. It seems reasonable to suggest that the first step is the loss of the acidic proton from S_7NH with the formation of a (heptasulfur imido)antimony tetrachloride analogous to the compound formed in the reaction with boron trichloride.

$$S_7NH + SbCl_5 \rightarrow S_7NSbCl_4 + HCl$$
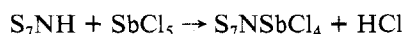
Indeed we showed that S_7NBCl_2, formed by the reaction of S_7NH with BCl_3, reacts with $SbCl_5$ to give $(S_2N)(SbCl_6)$. This reaction must then be followed by a series of rather complex reactions in which the S_7N ring is oxidized by Sb(V) which is reduced to $SbCl_3$ with the formation of SN_2^+ and S_8. It is interesting that the red-brown solutions obtained from the above reactions exhibited an ESR signal consisting of one sharp line with $g = 2.016$ G. This can probably be attributed to the radical S_5^+ which has g values reported in the range 2.013 and 2.016 and which is obtained when sulfur is oxidized by SbF_5 or AsF_5 or by certain strong oxyacids.[14] It is noteworthy that the formation of S_2N^+ from the S_7N ring leaves an S_5 fragment. Presumably S_8 is then formed from the S_5 fragment by a series of complex reactions.

The dithionitronium cation can also be obtained from the reaction of $1,4-S_6N_2H_2$ with $SbCl_5$. The solution obtained from this reaction exhibited a five-line ESR spectrum, $g = 2.002$, $a = 3.15$ G. This is consistent with a radical containing two equivalent nitrogen atoms. A signal due to the S_5^+ radical was not observed.

Again, as in the S_7NH system, the first step may be the formation of the (hexasulfur diimido)antimony tetrachloride which then reacts further to produce the products. The identity of the radical is not known. Comparison of the g value and coupling constant with those of $S_3N_2^{+}$[15] tends to rule out the cyclothiodithiazyl cation as a possibility.
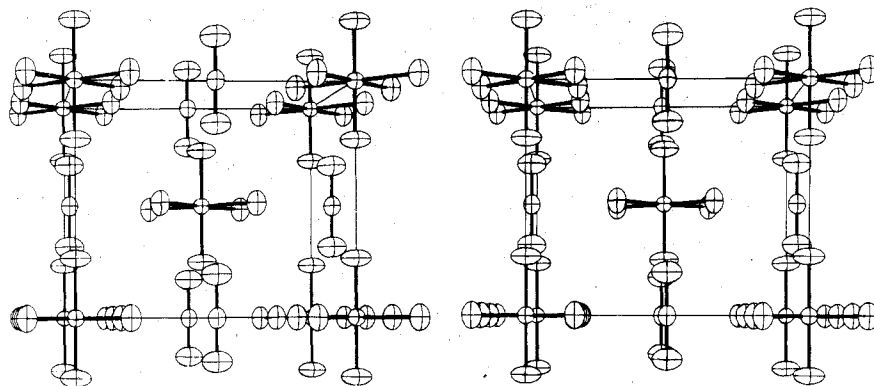
Figure 1. Stereogram (stereosopic pair of perspective projections) of $(S_2N)(SbCl_6)$. a and b are parallel to the top and side of the page, respectively, and the view is down c.

Table II. Selected Interatomic Distances (Å) and Angles (deg)[a]

Sb–Cl(1)	2.351 (3)	Sb–Cl(2)	2.363 (2)
		S–N	1.463 (4)
Cl(1)–Sb–Cl(2)	90,	Cl(2)–Sb–Cl(2)[a]	90
Cl(1)–Sb–Cl(2)[a]	90	Cl(2)–Sb–Cl(2)[b]	90

[a] Atoms labeled a and b are related to those in Table I by: (a) $\bar{x}, 0, z$; (b) $\bar{x}, 0, \bar{z}$.

The Crystal Structure of $(S_2N)(SbCl_6)$.

The crystal is composed of S_2N^+ cations and $SbCl_6^-$ anions. The S_2N^+ cation is linear, has $D_{\infty h}$ local symmetry, and has short SN bonds (1.462 (2) Å). The $SbCl_6^-$ anion is approximately octahedral; Sb–Cl(1) (2.352 (2) Å) and Sb–Cl(2) (2.363 (2) Å) are significantly different, and of the cis Cl–Sb–Cl angles only Cl(1)–Sb–Cl(2) (88.6 (4), 91.4(2)°) differs significantly from 90°.

The packing within the crystal is illustrated in Figure 1. The S_2N^+ cations lie parallel to b in the center of the a edge, with the hexachloroantimonate ions on the corner of the cell, with Sb–Cl(1) along b, and with the Sb–Cl(2) bonds roughly bisecting the angle between a and c. The principal contact in the b direction is between Cl(1) atoms on different anions. The contacts between the S_2N^+ group and $SbCl_6^-$ are principally in planes parallel to ac. Each nitrogen atom has four nearest-neighbor Cl(2) atoms, at the corners of a rough square, and each S atom has four Cl(1) atoms, again at the corners of a very rough square.

The packing is based on cubic close packing of the chlorine and sulfur atoms, but there are marked distortions caused by the bonding within the cation and anion. The edges of this cubic close packed cell lie along a and the [011] and [01$\bar{1}$] directions. The dimensions of this cell are 9.299, 10.66, and 10.66 Å with an angle between the last two sides of 83.1°. These should be compared with a = 10.47 Å for an ideal close-packed cell of chlorine atoms.

The principal distortion is caused by bonding within the S_2N^+ group. In the b direction the S–S distance within the group is 2.93 Å and between groups 5.05 Å, rather than the ideal equal distances of 3.7 Å. The converse effect is reflected in the Cl(1)–Sb–Cl(1) unit where the corresponding Cl(1)–Cl(1) distances are 4.70 Å (intra) and 3.28 Å (inter). This causes a marked distortion in the x = 0 and x = $^1/_2$ layers of the ideal close-packed cell such that, instead of being square, the unit is kite shaped with the kite axis along y (see Figure 2). The pairs of adjacent sides have lengths of 4.70 and 6.02 Å, respectively. As can be seen the distortion is in the opposite direction at x = $^1/_2$. The remaining distortion is caused by the arrangement of the Cl(2) atoms and shows in the x parameter (0.1778 rather than 0.2500). Thus, as can be seen in Figure 2, the Cl(2) atoms close to y = 0 are at x = 0.178 because they can fit more easily between the more widely spaced atoms in the x = 0 layer than between the closely
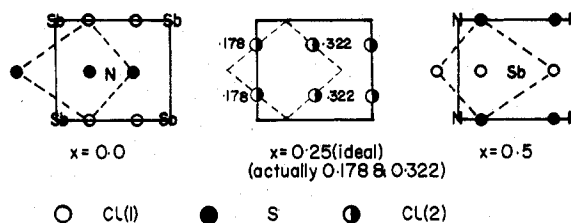

Figure 2. Sections through the cell showing chlorine and sulfur atoms. The continuous line shows the outline of the present cell, and the dotted line shows the outline of distorted close packed cell.

Table III. Raman and Infrared Spectra of $S_2N^+SbCl_6^-$ and CS_2

| $(S_2N^+)(SbCl_6^-)$ | | CS_2[a] | | |
R, cm^{-1} solid	IR, cm^{-1} solid	R, cm^{-1}	IR, cm^{-1}	assignment
	1498 m		1523	ν_3 S_2N^+ (CS_2)
766 (17)		796		$2\nu_2$ S_2N^+ (CS_2)
747 (2)				$2\nu_2$ $^{32}S^{34}SN^+$ ($C^{32}S^{34}S$)
688 (44)		656.5		ν_1 S_2N^+ (CS_2)
680 (8)		648.3	396.7	ν_1 $^{32}S^{34}N^+$ ($C^{32}S^{34}S$)
	374 m			ν_2 S_2N^+ (CS_2)
333 (100)				$\nu_1(A_{1g})$ $SbCl_6^-$
	320 s			$\nu_3(T_{1a})$ $SbCl_6^-$
293 (12)				$\left.\right\}\nu_2(E_g)$ $SbCl_6^-$
283 (8)				
180 (26)				$\left.\right\}\nu_5(T_{2g})$ $SbCl_6^-$
175 (48)				
167 (4)				
78 (100)				$\left.\right\}$ lattice modes
62 (76)				

[a] Reference 21.

packed atoms in the x = $^1/_2$ layer. The opposite argument applies to the Cl(2) atoms close to y = $^1/_2$, and the x parameter is 0.322.

The SN bond in S_2N^+ (1.46 Å) is shorter than the CS bond in the isoelectronic CS_2 molecule (1.55 Å)[16] just as the NO bond in NO_2^+ (1.10 Å)[17] is shorter than the CO bond in the isoelectronic CO_2 molecule (1.16 Å).[18] These differences are consistent with the smaller expected covalent radius of nitrogen than of carbon. All of these molecules have bond lengths that are smaller than those predicted from double-bond covalent radii such as those given by Pauling.[19] This might be taken to indicate that all these molecules have bond orders greater than two, i.e. that a simple valence-bond structure such as S=N$^+$=S is not an adequate representation of the molecule as the bonds have some triple-bond character.[19,20] On the other hand these short bond lengths may simply reflect the inadequancy of the concept of additive covalent radii particularly as applied to multiple bonds.

Infrared and Raman Spectra. The infrared and Raman spectra of solid $(S_2N)(SbCl_6)$ are given in Table III. The

spectra can be interpreted in terms of the ionic structure $(S_2N^+)(SbCl_6^-)$. In the Raman spectrum of the solid the three bands at 333, 293, and 175 cm^{-1} can be readily assigned as ν_1 (A$_{1g}$), ν_2 (E$_g$), and ν_3 (T$_{2g}$) of an octahedral SbCl$_6^-$ ion. As the site symmetry of SbCl$_6^-$ is D_{2h}, the degeneracy of the E$_g$ and T$_{2g}$ modes is lifted and they are observed as a doublet and a triplet, respectively. In the infrared spectrum the band at 320 cm^{-1} may be assigned as ν_3 (T$_{1u}$) of SbCl$_6^-$. In addition to the above mentioned bands, the most prominent band in the Raman spectrum is that at 688 cm^{-1} which may clearly be assigned as the single Raman-active fundamental of the linear triatomic S$_2$N$^+$. The analogous band of the isoelectronic CS$_2$ molecule is observed at 656.5 cm^{-1}.[21] However, in addition to this band there are two additional bands: a moderately intense band at 766 cm^{-1} and a very weak band at 680 cm^{-1}. The former is assigned as 2ν_2 which should normally be very weak but appears to have its intensity enhanced by Fermi resonance with ν_1. A similar band is observed at 648 cm^{-1} in the Raman spectrum of CS$_2$ and is similarly assigned to 2ν_2 enhanced by Fermi resonance with ν_1.[16] The weak band at 680 cm^{-1} can be assigned as ν_1 of the ^{32}S^{34}SN$^+$ molecule for which the calculated value of ν_1 is 678 cm^{-1}. The other Raman-inactive but infrared-active fundamentals of the S$_2$N$^+$ ion, ν_2 and ν_3, are observed at 374 and 1498 cm^{-1}, respectively, and have frequencies close to the corresponding bands for CS$_2$. Satisfactory solution Raman spectra of (S$_2$N)(SbCl$_6$) could not be obtained due to interference of solvent lines, low solubility, or reaction with the solvent.

Registry No. (S$_2$N)(SbCl$_6$), 67556-29-0; S$_7$NH, 293-42-5; S$_7$NBCl$_2$, 67556-30-3; 1,4-S$_6$N$_2$H$_2$, 3925-67-5; SbCl$_5$, 7647-18-9.

Supplementary Material Available: A table of the moduli of the observed and calculated structure amplitudes (2 pages). Ordering information is given on any current masthead page.

References and Notes

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(6) J. Nelson, *Spectrochim. Acta, Part A,* **27**, 1165 (1971).
(7) All calculations were carried out on a CDC-6400 computer. The programs DATCO3, ABSORB, and DATDRN were used for preliminary treatment of data as was the program NORMSF. The full-matrix least-squares program, CUDLS, and Fourier program, SYMFOU, were written locally by J. S. Stephens and J. S. Rutherford, respectively. The cell diagram was prepared using the program ORTEP by C. K. Johnson, U.S. Atomic Energy Commission Report ORNL 3794, revised June 1965.
(8) Refinements were tried in both space groups *I*222 and *Immm*. Refinement in *I*222 was terminated at $R_1 = 0.0411$, $R_2 = 0.0416$ (630 reflections, 26 variables). All atom parameters were transformed $x, y, z \to -x, -y, -z$ and refinement in *I*222 was terminated at $R_1 = 0.0414$, $R_2 = 0.0418$. The first refinement proceeded rapidly to a maximum shift/error of 0.02, whereas the second was less rapid and stabilized at a maximum shift/error of 0.16. Nevertheless, the application of the Hamilton test (W. C. Hamilton, *Acta Crystallogr.,* **18**, 502 (1965)) shows that the two refinements are not significantly different. Thus on this basis, and in the absence of any other evidence of an acentric space group (the results from NORMSF can be used as an indicator only and not as direct evidence), we have made the final refinement in the space group *Immm*.
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Crystal Structure and Raman Spectral Study of Ligand Substitution in Mn$_3$[Co(CN)$_6$]$_2$·xL

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Ligand substitution in the Prussian blue analogue Mn$_3$[Co(CN)$_6$]$_2$·xL has been studied using X-ray crystallography and Raman spectroscopy. The structure of the methanol-substituted species, Mn$_3$[Co(CN)$_6$]$_2$·12CH$_3$OH, is quite similar to the parent hydrated form; the space group is *Fm3m* with a = 10.550 (3) Å. The unit cell contains $1^1/_3$ formula units and both coordinated and zeolitic methanol molecules. The coordinated methanol species form $^1/_3$ of the ligand environment of the manganese atoms. The remaining methanols occupy the tetrahedral holes in the lattice and are H bonded to the coordinated methanol species. The final R and R_w values for 137 reflections were 4.4 and 5.2%, respectively. Raman scattering has been employed to study the relative importance of hydrogen-bonding ability and size of L in determining the rate with which various ligands substitute into the lattice. A possible explanation for the semipermeable membrane properties of these compounds has been proposed.

Introduction

The structure of pseudo Prussian blue salts, such as Mn$_3$[Co(CN)$_6$]$_2$·xH$_2$O, is usually based on a model proposed by Ludi.[1–3] Recently, detailed X-ray and neutron diffraction studies of Mn$_3$[Co(CN)$_6$]$_2$·12H$_2$O have yielded a more satisfactory model of the metal cyanide and the hydrogen-bonded water structure.[4] However, in spite of the several structural studies of the hydrated Prussian blue complexes, there are still questions concerning the zeolitic water structure in these materials. A clear understanding of the water network is essential if we are to properly model the H$_2$O transport in these semipermeable membranes.

Recently, we reported a single-crystal Raman study of Mn$_3$[Co(CN)$_6$]$_2$·xL (M = Mn^{II}, Cd^{II}) where H$_2$O was re-