

The Crystal Structure of Ammonium Tris(pentasulfido)platinum(IV) Dihydrate

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Ammonium tris(pentasulfido)platinum(IV) dihydrate, $(\text{NH}_4)_2\text{Pt}(\text{S}_5)_3 \cdot 2\text{H}_2\text{O}$, crystallizes in space group *Cc* with unit-cell dimensions $a = 15.67$, $b = 9.925$, $c = 12.94$ Å, $\beta = 92.74^\circ$ and $Z = 4$. The final structure parameters were based on 2450 observed reflections collected by counter methods. The structure was refined by least-squares methods to a conventional *R* index of 5.2%. The anion consists of three bidentate five-membered sulfur chains octahedrally coordinated to a central platinum atom so as to form, with platinum, three six-membered rings in chair configurations. The ammonium ions and water molecules alternate in a chain through the structure. The range of Pt-S distances is 2.365 ± 0.007 to 2.428 ± 0.008 Å.

Introduction

Ammonium tris(pentasulfido)platinum(IV) dihydrate was first prepared by Hofmann & Höchtlen (1903). They suggested that the compound contained three pentasulfide ligands but offered no suggestions about the coordination to platinum. A structure suggestion given by R. A. Krause of this department was that there were three *cis* bidentate S_5 ligands octahedrally coordinated to the platinum ion. Since compounds for which pure sulfur ligands coordinated to metal ions have been suggested are rare,† it was decided to undertake the structure determination.

Experimental

$(\text{NH}_4)_2\text{Pt}(\text{S}_5)_3 \cdot 2\text{H}_2\text{O}$ was prepared according to the procedure of Hofmann & Höchtlen (1903) by R.A. Krause of this department. The red crystals formed in this preparation were found invariably to be twinned. Single crystals, which were in the form of triangular plates, were cut from these crystals and were used for intensity measurements.

After the structure of the anion was solved with preliminary film data, a set of intensity data was collected on a manually operated General Electric single crystal orienter with Zr-filtered Mo radiation, pulse height selection, and a scintillation counter. The reciprocal lattice nets were collected for which $h = 0, \pm 1, \pm 2, \pm 3$; $k = 0, -1, -2$; $l = 0, \pm 1, \pm 2, \pm 3, \pm 4$ and for which 2θ was less than or equal to 50 degrees. A total of 2578 reflections were collected of which 128 were unobserved (no peak was observed on the recorder using the highest available sensitivity). The data were corrected for Lorentz-polarization effects and

were also corrected for absorption by the procedure described by Wuensch & Prewitt (1965) with the use of Prewitt's program *ACACA* (1965). The crystal used for this part of the work was a triangular plate of dimensions $0.143 \times 0.143 \times 0.215$ mm and 0.072 mm thick.

Crystal data

The crystals were examined by precession and Weissenberg methods which indicated Laue symmetry of $2/m$ with systematic absences occurring only in the general hkl reflections for $h+k = 2n+1$ and in the $h0l$ reflections for $l = 2n+1$. The probable space group was thus either *C2/c* or *Cc*.

The cell dimensions were determined from measurements taken on an accurately aligned single crystal orienter using Zr-filtered Mo radiation. They are: $a = 15.674 \pm 0.004$, $b = 9.925 \pm 0.005$, $c = 12.937 \pm 0.007$ Å, and $\beta = 92.74 \pm 0.05^\circ$.

The density was measured by the flotation method with a mixture of bromoform ($d = 2.890$ g.cm⁻³) and 1,1,2,2-tetrachloroethane ($d = 1.600$ g.cm⁻³). The observed density was 2.44 ± 0.02 g.cm⁻³ while the calculated densities, based on four molecules per unit cell and one or two water molecules per formula unit are 2.42 g.cm⁻³ and 2.47 g.cm⁻³ respectively. The compound was analyzed in duplicate for nitrogen, sulfur and platinum. The results are:

	%N	%S	%Pt	Number of H ₂ O
Theoretical	3.74	64.28	26.08	2
	3.84	65.88	26.72	1
Observed	3.57	64.13	25.97	
(our results)				
Observed	3.64	64.37	26.00	
(Hofmann & Höchtlen, 1903)				
	3.86	64.81	25.83	
		65.21	25.76	

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† An S_5 bidentate ligand coordinated to titanium has recently been reported for $(\text{C}_5\text{H}_5)_2\text{TiS}_5$ by Köpf, Block & Schmidt (1968). Their conclusion was based on nuclear magnetic resonance evidence.

The density measurement indicates that there is water present. Our analyses, and those of Hofmann &

Höchtlen (1903) both fit well with two water molecules per formula unit, *i.e.* $(\text{NH}_4)_2\text{PtS}_{15}\cdot 2\text{H}_2\text{O}$.

Structure determination

The structure determination, until the final refinement stages, was carried out with photographic data. The preliminary investigation of this compound indicated the space group to be either $C2/c$, which is centrosymmetric, or Cc , which is non-centrosymmetric. The platinum atom must be placed in a special fourfold position if $C2/c$ is chosen. This position was assumed to be $(0, 0, 0; \frac{1}{2}, \frac{1}{2}, 0) + 0, y, \frac{1}{4}; 0, \bar{y}, \frac{3}{4}$ since the other special fourfold positions require both that additional reflections be weak (since Pt would make no contribution), which was not observed, and that the anion be centrosymmetric, which was not considered likely. This position would serve just as well in Cc with $x=0$ and $z=\frac{1}{4}$ arbitrarily chosen for Pt to fix the origin.

A y parameter of 0.20 for the Pt was determined from a Patterson line synthesis along $[0, y, \frac{1}{2}]$. This positional parameter as well as scale and overall temperature factors were refined by the method of least-squares using Busing, Martin & Levy's *ORFLS* program (1962). The y value converged to 0.2102 while the unweighted reliability factor, $R = \Sigma(|F_o| - |F_c|) / \Sigma|F_o|$, was 32.5%. This position is, of course, also compatible with the general fourfold position of space group Cc .

An electron density map was calculated using the observed amplitudes with phases calculated from the platinum atoms alone. Since the platinum arrangement is centrosymmetric, the resulting map was centrosymmetric. If the structure were also centrosymmetric, it should have been visible from this map. However, there were over thirty important peaks in one fourth of the cell volume, instead of the fifteen or so expected in the centrosymmetric case, which indicated that the structure belonged to space group Cc and was non-centrosymmetric.

From the initial Fourier result it was clear that we were faced with the familiar problem of a structure superimposed on its center related structure. The problem of sorting out the correct structure was accomplished (not without false attempts) by adding small groups of sulfur atoms, beginning with an assumed octahedral environment around Pt, and taking advantage of some enhancement effects as correctly placed atoms were added in the calculations. Each correct addition of a sulfur atom reduced R by about 1%. The prediction that the anion contained three five-membered sulfur rings coordinated to a central platinum ion, made by Professor Krause before we began the investigation, proved to be correct. (Hofmann & Höchtlen (1903) also suggested three five-membered sulfur groups, but, of course, they did not suggest a coordination scheme.) After least-squares refinement of individual layer scale factors, positional parameters, and individual atom isotropic temperature factors, the un-

weighted and weighted R indices were 18.7% and 20.6%.

The structure was refined further by the use of anisotropic temperature factors in the form $\exp[-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + 2\beta_{12}hk + 2\beta_{13}hl + 2\beta_{23}kl)]$.

The refinement was carried out in stages using blocks of parameters until all parameters converged. The unweighted and weighted R indices were 13.3 and 16.4% at this stage.

A difference electron density map was then calculated in an attempt to locate the ammonium ions and water molecules. Only three peaks were found that seemed to be possible sites for H_2O and NH_4^+ , although four sites were needed for the two H_2O and the two NH_4^+ .

At this point in the refinement the bond length and angle ranges, average values and estimated standard deviations were: Pt-S, 2.28–2.54, 2.43, 0.03 Å; S-S, 1.98–2.15, 2.05, 0.05 Å; S-S-S, 97.8–116.1, 104.8, 5°; Pt-S-S, 103.0–113.0, 109.4, 2.5°; S-Pt-S, 90.5–96.4, 92.8, 2.5° (Jones & Katz, 1967).

Refinement

The refinement of the anion and the placing of the ammonium ions and water molecules was determined by data collected on the single crystal orienter. In the initial stages of the refinement, Friedel-related structure factors were averaged. When R dropped to 8.6% with only the platinum and sulfur atoms included, a difference electron density map was calculated in order to locate the ammonium ions and water molecules. Six positive regions were found which were more than 2.2 Å away from the platinum and sulfur atoms. Two of the positions, which were within 2.5 Å of sulfur atoms, when refined isotropically as ammonium ions, resulted in temperature factors greater than 50. The other four positions, which were in fact the highest positive regions found, were also refined as ammonium ions. The unweighted and weighted R indices dropped to 7.3 and 8.8%, and the isotropic temperature factors all remained below 10.

The structure was then refined using all 2450 observed reflections (*i.e.* without averaging Friedel related pairs). The unweighted and weighted R indices were 8.4 and 10.2%. The refinement was continued with anomalous dispersion corrections, both real and imaginary parts, for platinum and sulfur. The weighted and unweighted R indices increased to 10.5 and 12.5%, which indicated that the correct structure was related by a center of symmetry to the one refined. Refinement of this center related structure resulted in final isotropic unweighted and weighted R indices of 7.3 and 9.2%.

As it was not possible to determine definitely which of the four peaks found were ammonium ions and which were water molecules, the scattering factor curves of the ammonium ion and oxygen (used for water) were simply averaged.

The following Hughes-type weighting scheme, based on the assumption that intensities of intermediate magnitude should be weighted more than weak or strong intensities, was introduced: $|w| = |F_o|/130$ for $|F_o| \leq 130$; $|w| = 1$ for $130 < |F_o| < 260$; $|w| = 260/|F_o|$ for $|F_o| \geq 260$. After refinement the weighted R was 7.7% while the unweighted R was unchanged. The structure was then refined using anisotropic temperature factors by full-matrix least-squares analysis until the final

parameter shifts were less than one-tenth the standard errors. The resulting unweighted and weighted R indices were 5.2 and 6.2%, and the standard deviation for an observation of unit weight was 1.45. The final positional parameters, anisotropic temperature factors, and observed and calculated structure factor amplitudes are listed in Tables 1, 2 and 3.

Computations for the initial part of the structure determination were carried out on an IBM-7040 computer. The refinement of the structure was carried out on an IBM360-65 computer. The scattering factor curves of S^0 and O^0 (used for water) were taken from *International Tables for X-ray Crystallography* (1962), while the Pt^{4+} curve was from Thomas & Umeda (1957). The ammonium scattering factor curve was that of Davis & Whitaker (1966), while anomalous dispersion values were those of Cromer (1965).

Table 1. Final positional parameters and their standard deviations* for $(NH_4)_2Pt(S_5)_3 \cdot 2H_2O$ (all parameters are times 10^4)

	x/a	y/b	z/c
Pt	0 (0)	2103 (1)	7500 (0)
S(1)	627 (5)	1265 (8)	5900 (6)
S(2)	1812 (4)	2082 (9)	5640 (6)
S(3)	2625 (5)	1175 (9)	6597 (7)
S(4)	2271 (4)	2078 (9)	7983 (6)
S(5)	1141 (5)	1248 (8)	8449 (6)
S(6)	9395 (5)	2783 (10)	9180 (6)
S(7)	8598 (5)	4421 (9)	9028 (8)
S(8)	4433 (5)	1021 (8)	8775 (8)
S(9)	4810 (4)	737 (7)	7240 (8)
S(10)	692 (5)	4222 (7)	7220 (7)
S(11)	9370 (5)	9975 (7)	7939 (7)
S(12)	4147 (5)	3943 (8)	6621 (7)
S(13)	3084 (4)	4847 (8)	6057 (6)
S(14)	8615 (4)	1611 (8)	5442 (6)
S(15)	8767 (4)	2833 (9)	6673 (6)
X(1)	6178 (15)	614 (24)	4964 (19)
X(2)	7349 (19)	797 (29)	8506 (24)
X(3)	6326 (15)	3080 (28)	8049 (19)
X(4)	6505 (18)	3133 (33)	5900 (24)

* Standard deviations, as calculated by *ORFLS*, are given in parentheses.

Discussion

Geometry of the anion

A stereoscopic illustration of the $Pt(S_5)_3^{2-}$ anion was drawn with the use of Johnson's program *ORTEP* (1965) and is shown in Fig. 1. The bond distances, angles, and their standard errors were calculated by the *ORFFE* program of Busing, Martin, & Levy (1964) and are listed in Table 4.

The platinum ion is octahedrally coordinated by six sulfur atoms at an average distance of 2.39 Å, which is approximately equal to the sum of their ionic radii*.

* Goldschmidt (1929) lists an atomic radius of 1.74 Å for S^{2-} , and Ahrens (1952) gives the atomic radius of Pt^{4+} as 0.65 Å.

Table 2. Final thermal parameters and their standard deviations* of $(NH_4)_2Pt(S_5)_3 \cdot 2H_2O$

Anisotropic parameters are times 10^4 ; isotropic parameters are times 10^2 .

	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Pt	16 (0)	31 (1)	26 (1)	-1 (1)	-5 (0)	3 (2)
S(1)	26 (3)	59 (8)	51 (5)	12 (4)	-8 (3)	-2 (6)
S(2)	28 (3)	80 (7)	55 (5)	-8 (6)	6 (3)	8 (8)
S(3)	19 (3)	84 (10)	79 (7)	7 (5)	-16 (4)	-20 (8)
S(4)	29 (2)	65 (7)	61 (5)	-8 (5)	-19 (3)	-9 (8)
S(5)	30 (3)	66 (8)	41 (5)	2 (5)	-16 (4)	8 (6)
S(6)	44 (4)	84 (9)	40 (5)	-27 (6)	4 (4)	-12 (8)
S(7)	28 (3)	91 (9)	80 (7)	-3 (5)	14 (4)	-11 (8)
S(8)	36 (4)	71 (8)	102 (8)	1 (5)	-2 (5)	-40 (8)
S(9)	22 (4)	45 (7)	101 (9)	2 (4)	-16 (4)	5 (7)
S(10)	24 (3)	39 (7)	55 (6)	1 (4)	-1 (4)	3 (6)
S(11)	32 (3)	50 (7)	45 (5)	-9 (5)	-10 (4)	14 (6)
S(12)	35 (3)	50 (7)	57 (6)	-11 (4)	-10 (4)	-6 (6)
S(13)	28 (3)	83 (8)	52 (6)	-14 (5)	-15 (4)	-10 (7)
S(14)	26 (3)	92 (9)	40 (5)	-14 (4)	-15 (3)	9 (6)
S(15)	27 (3)	51 (7)	60 (5)	11 (5)	-8 (3)	2 (8)
B						
X(1)			395 (52)			
X(2)			443 (72)			
X(3)			533 (50)			
X(4)			756 (81)			

* Standard deviations, as calculated by *ORFLS*, are given in parentheses.

Table 3. Observed and calculated structure amplitudes

Columns are -k, l, |Fobs|, |Fcalc|.

Table with columns for h, k, l, |Fobs|, |Fcalc|. The table lists observed and calculated structure amplitudes for various Miller indices (h, k, l). The data is organized into a grid with multiple columns and rows, showing values for different reflections.

Table 3 (cont.)

A large table with multiple columns of numerical data, organized in a grid-like structure. The table contains various numbers, some with signs, and is divided into sections by labels like 'H=5', 'H=7', 'H=9', 'H=10', 'H=11', 'H=12', 'H=13', 'H=14', 'H=15', 'H=16', 'H=17', 'H=18', 'H=19', 'H=20'. The data appears to be a list of coordinates or values for a specific study.

The structure of the orthorhombic form of sulfur has been refined by Abrahams (1955). If three contiguous sulfur atoms are removed from the eight-membered ring found in orthorhombic sulfur, the *cis* conformation of the pentasulfide ion results. The S-S bond lengths reported by Abrahams range from 2.031 to 2.043 Å. The S-S-S bond angles range from 98.3 to 100.6°. The bond distances agree quite well with the values we report, but the bond angle range is narrower than ours, which may be an indication of strain in the sulfur rings of the $\text{Pt}(\text{S}_5)_3^-$ anion.

The structure of $\text{BaS}_4 \cdot \text{H}_2\text{O}$, a compound with a S_4^{2-} group, has also been reported by Abrahams (1954). The S-S bond distances and S-S-S bond angles are 2.02, 2.03, 2.07 Å and 104.1 and 104.9°, and the dihedral angles are 74.1 and 77.2°. These values are similar to those observed in the S_3^- ligand.

Determination of the water and ammonium ions

As previously discussed, four peaks which could be attributed to the two water molecules and two ammonium ions were located on a difference electron density map. Since the total number of electrons is ten for NH_4^+ as well as for H_2O , distinguishing NH_4^+ from H_2O is not always easy. In this case we did not succeed in making the distinction.

The four positions located formed a chain through holes in the anion packing. We must assume that H_2O and NH_4^+ alternate in this chain, since it is not reasonable to assume that two NH_4^+ ions would be next to each other. Both charge repulsion and the difficulty of establishing hydrogen bonding argue against a scheme in which NH_4^+ and H_2O do not alternate. Not only does alternation maintain a coordination number of four for N, it permits the same coordination number for O and in addition makes possible a continuous chain of NH_4^+ to H_2O hydrogen bonds. The distances found between adjacent peaks are 2.78, 2.83, 2.85, and 2.93 Å, which agree well with observed values for hydrogen bond lengths. Fuller (1959) has listed the range for hydrogen bonds of the type $\text{R-NH}_3^+ \cdots \text{OH}_2$ as 2.68 to 2.96 Å. Battelle & Trueblood (1965), for example, reported in $(\text{NH}_4)_2\text{SO}_3 \cdot \text{H}_2\text{O}$ a $\text{NH}_4^+ \cdots \text{OH}_2$ hydrogen bond length of 2.82 Å. Assuming alternation of NH_4^+ and H_2O then, if one could identify definitely even one of the peaks as an ammonium ion or as a water molecule, a complete assignment could be made. However, we were unable to make any definite assignment, since neither peak heights nor isotropic temperature factors alternated. A consideration of the environment of the groups did not provide us with the necessary clues either; all have reasonably close approaches to sulfur atoms and would, as ammonium ions, be reasonably well placed to balance the anion charges. This final assignment was therefore not made, and, to that extent, the structure determination is incomplete.

Effect of refinement on parameters

Some bond distances and angles changed considerably during the course of the refinement. At different stages anomalous dispersion corrections were introduced and then anisotropic thermal parameters. Allowing for vibration anisotropy had a much greater effect on the position parameters than correcting for anomalous dispersion.

Cruickshank & McDonald (1967) have discussed the errors in position and thermal parameters caused by neglect of the imaginary part of the dispersion correction, or even worse, the inclusion of $\Delta f''$ but for the inverse of the true structure. In class *m* (*b* axis unique) which is a polar class and the class to which $(\text{NH}_4)_2\text{PtS}_{15} \cdot 2\text{H}_2\text{O}$ belongs, there could be errors in *x* or in *z* if the measurements were for *h* or *l* of one sign only. However, we measured the hemisphere with *k* of one sign only, so that both signs for *h* and *l* were measured. (Indeed, since there is a true mirror, not Friedel symmetry, the other hemisphere is also produced.) Thus there should be no first-order errors in *x* or *z* from an uncorrected least-squares calculation, or even the $\Delta f''$ correction were of the wrong sign. Of course, the thermal parameters should be too large and the observed and calculated structure factor agreement should be poorer if the anomalous dispersion corrections were omitted or included incorrectly. These conclusions are generally borne out by the data of Table 7 (no anomalous dispersion corrections), Table 8 (anomalous dispersion accounted for incorrectly), and Table 9 (anomalous dispersion accounted for correctly). The corresponding *R* indices, as indicated earlier, change dramatically: 8.4, 10.5, and 7.3%.

It can be seen by comparing Table 1 with Table 9 that some positional parameters changed considerably during anisotropic refinement. The effects on bond distances and angles are pronounced: some bond dis-

Table 7. *Isotropic parameters and their standard deviations* with no anomalous dispersion corrections*

Positional parameters are times 10^4 ; temperature factors are times 10^2 .

	<i>x/a</i>	<i>y/b</i>	<i>z/c</i>	<i>B</i>
Pt	0 (0)	2103 (1)	7500 (0)	153 (2)
S(1)	624 (6)	1255 (10)	5889 (8)	214 (16)
S(2)	1808 (6)	2067 (11)	5638 (8)	287 (18)
S(3)	2627 (7)	1168 (12)	6597 (10)	281 (21)
S(4)	2268 (6)	2080 (11)	7972 (8)	299 (19)
S(5)	1133 (6)	1237 (11)	8461 (8)	255 (18)
S(6)	9383 (7)	2787 (12)	9172 (9)	301 (20)
S(7)	8594 (7)	4424 (12)	9015 (10)	354 (22)
S(8)	4436 (8)	1027 (13)	8770 (10)	407 (24)
S(9)	4817 (7)	738 (11)	7233 (9)	317 (21)
S(10)	695 (6)	4220 (10)	7222 (8)	245 (18)
S(11)	9371 (6)	9967 (10)	7947 (8)	243 (17)
S(12)	4147 (6)	3952 (11)	6608 (8)	274 (18)
S(13)	3074 (6)	4835 (11)	6056 (8)	267 (18)
S(14)	8606 (6)	1629 (10)	5443 (8)	264 (18)
S(15)	8766 (6)	2833 (11)	6674 (8)	256 (17)

* Standard deviations, as calculated by ORFLS, are given in parentheses.

Table 8. *Isotropic parameters and their standard deviations* with incorrect sign of $\Delta f''$ †*Positional parameters are times 10^4 ; temperature factors are times 10^2 .

	x/a	y/b	z/c	B
Pt	0 (0)	2103 (1)	7500 (0)	144 (3)
S(1)	623 (7)	1259 (12)	5888 (10)	239 (20)
S(2)	1811 (8)	2064 (14)	5639 (11)	332 (24)
S(3)	2627 (8)	1164 (14)	6591 (12)	313 (26)
S(4)	2265 (8)	2077 (14)	7974 (11)	344 (24)
S(5)	1136 (7)	1239 (13)	8454 (10)	285 (22)
S(6)	9387 (8)	2784 (15)	9167 (11)	338 (25)
S(7)	8591 (9)	4422 (15)	9016 (12)	390 (28)
S(8)	4437 (10)	1027 (17)	8767 (13)	444 (31)
S(9)	4819 (8)	739 (14)	7237 (11)	356 (27)
S(10)	693 (8)	4220 (13)	7126 (10)	277 (22)
S(11)	9370 (7)	9966 (13)	7941 (10)	269 (21)
S(12)	4148 (8)	3953 (14)	6606 (11)	308 (23)
S(13)	3071 (8)	4833 (13)	6057 (10)	296 (23)
S(14)	8607 (8)	1629 (13)	5443 (10)	296 (23)
S(15)	8768 (8)	2835 (14)	6668 (10)	293 (22)

* Standard deviations, as calculated by ORFLS, are given in parentheses.

† Structure amplitudes calculated with the correct structure and incorrect sign of $\Delta f''$ equal structure amplitudes based on the inverse structure and the correct sign of $\Delta f''$.Table 9. *Isotropic parameters and their standard deviations* with correct sign of $\Delta f''$* Positional parameters are times 10^4 ; temperature factors are times 10^2 .

	x/a	y/b	z/c	B
Pt	0 (0)	2103 (1)	7500 (0)	148 (2)
S(1)	625 (5)	1256 (9)	5890 (7)	228 (15)
S(2)	1809 (6)	2067 (10)	5637 (7)	300 (16)
S(3)	2626 (6)	1167 (10)	6599 (8)	298 (18)
S(4)	2269 (6)	2081 (10)	7972 (8)	308 (17)
S(5)	1133 (7)	1239 (10)	8462 (7)	268 (16)
S(6)	9385 (6)	2787 (11)	9172 (8)	311 (17)
S(7)	8595 (7)	4425 (11)	9014 (9)	365 (20)
S(8)	4438 (7)	1024 (12)	8760 (9)	421 (22)
S(9)	4816 (6)	735 (10)	7233 (9)	333 (19)
S(10)	695 (6)	4220 (9)	7223 (7)	257 (16)
S(11)	9371 (5)	9968 (9)	7948 (7)	252 (15)
S(12)	4147 (6)	3952 (10)	6610 (8)	288 (17)
S(13)	3075 (7)	4834 (10)	6056 (7)	283 (16)
S(14)	8606 (6)	1629 (9)	5444 (7)	278 (16)
S(15)	8766 (5)	2834 (10)	3325 (7)	269 (15)

* Standard deviations, as calculated by ORFLS, are given in parentheses.

tances changed by almost 0.1 \AA and some bond angles changed by as much as 0.8° . One would, of course, not be surprised by any great changes in parameters if there were high correlation among parameters; however, no such correlation was observed.

Using Hamilton's (1965) significance test, we tested the hypothesis that all atoms vibrate isotropically. The R factor ratio is 1.48, the dimension of the hypothesis is 80, and the number of degrees of freedom for the refinement is 2345. From Hamilton's table we find $\mathcal{P}_{80,2345,0.005} = 1.04$. Since 1.04 is less than the R factor

ratio of 1.48, the hypothesis that all atoms vibrate isotropically can be rejected at the 0.5% significance level, *i.e.* we are quite sure that there is anisotropic motion.

Packing of the unit cell

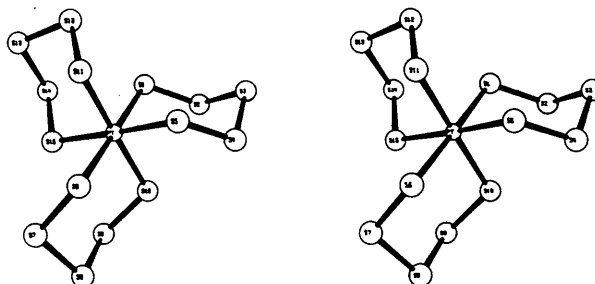
A stereoscopic illustration of the unit cell and its contents was drawn using Johnson's (1965) ORTEP program and is shown in Fig. 2. The origin is in the lower left corner, and the right handed coordinate system has the z axis vertical, the x axis horizontal, and the y axis pointing away from the viewer.

The large circles in the drawing indicate the positions of the water molecules and the ammonium ions. These units are seen to form chains weaving around the anions in the z direction. This is particularly noticeable around the best resolved ring in the Figure.

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Fig. 1. Stereoscopic illustration of the $\text{Pt}(\text{S}_5)_3^{2-}$ anion.

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The Crystal Structure of the 2:1 Complex between Antimony Trichloride and Naphthalene

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Crystals of the 2:1 complex between antimony trichloride and naphthalene are monoclinic, $a=9.154$, $b=9.368$, $c=11.989$ Å, $\beta=122^\circ 40'$, space group $P2_1/c$. The structure consists of SbCl_3 molecules stacked in the bc plane alternating with layers of naphthalene molecules in the plane $x=\frac{1}{2}$. The antimony atoms exist in a 4-coordinate, distorted sp^3d trigonal bipyramidal environment, with two chlorine atoms occupying equatorial positions, 2.347 and 2.348 Å away while the third equatorial position is filled by the antimony lone electron pair. The third chlorine atom occupies one axial position 2.367 Å from antimony, while the other axial position is utilized in bonding to the π -system of the naphthalene molecule. The distances from the antimony atom to the carbon atoms of the ring vary from 3.36 to 3.74 Å, and the distance from the antimony atom to the plane of the ring is 3.2 Å. The structure has been refined using anisotropic full-matrix least-squares refinement, the final R index being 0.091 for all 2566 reflexions used, and 0.072 for the 2034 observed terms only.

Introduction

Complexes between antimony trichloride and aromatic hydrocarbons have been known for many years. In the earliest work (Smith & Davies, 1882), the complex between antimony trichloride and naphthalene was reported, and incorrectly analysed as a 3:2 adduct. Menshutkin (1911, 1912*a, b*), who studied the eutectic diagrams of antimony trihalides with a large number of organic compounds, defined the composition of these intermolecular compounds as maxima in the phase diagrams. He showed that a series of complexes of antimony trihalides with aromatic hydrocarbons or substituted hydrocarbons could be made, and that the most common ratios for these were 1:1, 2:1 or 4:1. He found that the melting point of the antimony trichloride-naphthalene 2:1 adduct (85°) was higher than that of antimony trichloride (73°) or of naphthalene (80°). To determine the nature of the bonding forces between the constituents, an extensive study of antimony trihalide-aromatic hydrocarbon complexes

was undertaken. Preliminary reports on some of these compounds have already been published (Szymański, 1963; Hulme, 1966; Cushen, Hulme & Szymański, in press). A knowledge of the structure of these compounds is important in view of the known catalytic properties of antimony trichloride in Friedel-Crafts reactions (Olah, 1963), and the possible relation of these structures to the reaction intermediates. We here report a more detailed account of the 2:1 adduct between antimony trichloride and naphthalene, whose structure was previously solved in projection and described elsewhere (Szymański, 1963).

Experimental

Antimony trichloride and naphthalene in 2:1 molar ratio were dissolved in hot $60\text{--}80^\circ$ petroleum spirit. The solution on cooling deposited a mass of fine crystals, which were then left to stand in the mother liquor for several weeks in a sealed flask. From the mass a number of excellently formed acicular crystals grew. The forms exhibited were $\{011\}$, $\{100\}$, and less prominently $\{110\}$. Chemical analysis, and quantitative estimation of the naphthalene ultraviolet absorption

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