Crystal and Molecular Structure of Tris(hexaamminerhodium(III)) Tetrakis(trichlorostannato(II))(Tetrachlorostannato(II))rhodate(I) Hexachlorostannate(II) Tetrahydrate

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The crystal and molecular structure of the title compound, $[Rh(NH_3)_6]_3[Rh(SnCl_3)_4(SnCl_4)]$ $[SnCl_6] \cdot 4H_2O$, has been determined by the single-crystal X-ray diffraction method. The compound crystallizes in the monoclinic system, space group $P2/n$ with $a = 16.581(2)$, $b = 11.010(4)$, $c = 16.024(2)$ Å, $\beta = 90.76(1)$, and two molecules per unit cell. The structure was solved by Patterson's method and refined by the least-squares technique to give a final R factor of 0.031. The three cations, $[Rh(NH_3)_6]^{3+}$, are a regular octahedron with an average Rh–N bond length of 2.07 Å. The rhodium anion, $[Rh(SnCl_3)_4(SnCl_4)]^{5-}$, is a trigonal bipyramid with the two axial Rh–Sn bonds, 2.493 Å in length, and the three equatorial bonds, 2.546, 2.540, and 2.540 Å. One of the three tin atoms in the equatorial trigonal plane forms a distorted trigonal bipyramid with two short Sn–Cl bonds 2.384 Å in length and two long bonds, 2.733 Å. The other four tin atoms have a distorted tetrahedral arrangement with an average Sn–Cl bond length of 2.42 Å. The tin anion, $[SnCl_6]^{4-}$, which is not coordinated to rhodium, forms extremely long Sn–Cl bonds of 2.763, 2.800, and 2.893 Å in a distorted octahedral arrangement.

Introduction

Although many platinum metal complexes with trichlorostannato(II) ligand, $SnCl_3^-$, have been obtained by a number of workers, the structure of only a few of them has been determined by X-ray analysis. In the case of $[(\pi\text{-}C_3H_5)Pd(PPh_3)SnCl_3] \cdot 0.4Me_2CO$ (*1*) and $[Ir(SnCl_3)(C_8H_{12})_2]$ (*2*), $SnCl_3^-$ coordinated to palladium or iridium through tin, which formed a tetrahedral arrangement. On the other hand, in $[(C_8H_{12})_3Pt_3(SnCl_3)_2]$ (*3*), $SnCl_3^-$ coordinated above and below the triangular three platinum atoms to form a trigonal bipyramidal metal atom cluster. An attempt was also made to determine the structural

details of $[Ph_3(CH_3)P]_3[Pt(SnCl_3)_5]$ (*4*), but it was not successful because of the disorder in the structure.

One of the present authors has reported some interesting trichlorostannato complexes of rhodium(III) and rhodium(I) (*5*) obtained by the reaction of rhodium(III) with tin(II) in hydrochloric acid solution. Rhodium(III) formed a six-coordinate complex series, $[RhCl_n(SnCl_3)_{6-n}]^{3-}$, where $n = 2$, 3, and 4, and rhodium(I) seemed to form a five-coordinate complex formulated as $[M(NH_3)_6]_3[Rh(SnCl_3)_5]$ $[SnCl_3]Cl_4 \cdot 4H_2O$, where M = Rh(III) and Ir(III). The rhodium(I) complex salt showed extremely pronounced polychroism and was thought to have a quite anisotropic struc-
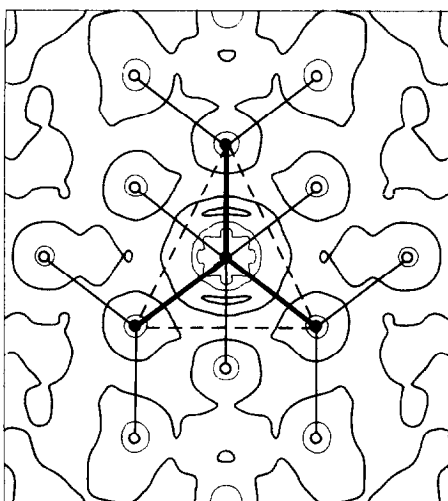
Fig. 1. Patterson map and the corresponding vector set on the *ab* plane.

Experimental

Collection and Reduction of the Data

The crystalline sample of the salt, $[Rh(NH_3)_6]_3[RhSn_6Cl_{22}] \cdot 4H_2O$, was quite stable and showed no signs of decomposition after being exposed to X rays for two weeks in air at room temperature. The preliminary X-ray photographs using $CuK\alpha$ radiation showed the crystals to be of the monoclinic system. The observed systematic absences $h0l$ for $h + l =$ odd, suggested one or the other of the two space groups Pn and $P2/n$. A pillar-shaped crystal of approximate dimensions $0.2 \times 0.2 \times 0.4$ mm was mounted on a RIGAKU AFC automatic single-crystal four-circle diffractometer. The lattice parameters, obtained by a least-squares

refinement using 20 high-angle reflections, were $a = 16.581(2)$, $b = 11.010(4)$, $c = 16.024(2)$ Å, and $\beta = 90.76(1)$. The observed density of 2.58 g cm^{-3}, measured by flotation in tribromomethane–tetrachloromethane, was in good agreement with that of 2.589 g cm^{-3} calculated for two formula units in the unit cell. Diffraction data were collected over the θ range from 55 to 0° using $MoK\alpha$ radiation monochromated by a graphite crystal. In-

ture. Its Mössbauer spectra also showed the presence of noncoordinated tin(II). In order to obtain further information on the structural details which could explain these observations, this salt was studied in the present work described in this paper.

TABLE I

FINAL ATOMIC COORDINATES AND ISOTROPIC THERMAL PARAMETERS

Atom	X	Y	Z	B (Å²)
SnA	2489(0)	−56(0)	944(0)	1.7
SnB	1262(0)	−1399(0)	2483(0)	1.9
SnV	2500(0)	2271(1)	2500(0)	2.2
SnF	2500(0)	5008(1)	7500(0)	1.9
RhA	2500(0)	−41(1)	2500(0)	1.2
Rh1	5000(0)	−5000(0)	0(0)	1.4
Rh2	5000(0)	5000(0)	5000(0)	1.5
Rh3	2500(0)	135(1)	7500(0)	1.6
ClA1	1380(1)	669(2)	110(1)	2.6
ClA2	2484(1)	−2058(2)	373(1)	2.4
ClA3	3473(1)	694(2)	−4(1)	3.0
ClB1	180(1)	−1336(2)	1431(1)	3.0
ClB2	382(1)	−1425(2)	3686(1)	2.9
C1B3	1364(1)	−3574(2)	2393(2)	3.5
ClV1	2649(2)	3626(2)	1348(1)	3.7
ClV2	881(1)	2634(3)	2270(2)	4.1
ClF1	3822(1)	3315(2)	7715(1)	3.2
ClF2	2370(1)	4813(3)	9236(1)	3.5
ClF3	1320(1)	6760(2)	7302(2)	3.7
O1	4482(5)	−1611(7)	6026(5)	5.0
O2	4904(6)	−1684(8)	−1058(5)	5.7
N11	4197(4)	−6420(6)	−204(4)	2.4
N12	4077(4)	−3739(7)	−97(5)	3.0
N13	5191(4)	−4848(7)	−1274(4)	2.8
N21	5911(4)	3762(7)	5187(5)	3.6
N22	4194(4)	3578(7)	4856(6)	3.8
N23	4761(5)	5021(9)	6263(4)	3.9
N31	2662(5)	−1199(6)	6606(4)	2.7
N32	2325(5)	1511(6)	8362(4)	2.7
N33	1268(4)	117(8)	7246(5)	3.2

Note. Estimated standard deviations are given in parentheses. Positional parameters are multiplied by 10⁴.

TABLE II

ANISOTROPIC TEMPERATURE FACTORS

Atom	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
SnA	22(0)	37(0)	10(0)	−2(0)	−2(0)	0(0)
SnB	15(0)	44(0)	19(0)	−7(0)	−2(0)	2(0)
SnV	33(0)	28(1)	17(0)	0(0)	1(0)	0(0)
SnF	16(0)	40(1)	20(0)	0(0)	0(0)	0(0)
RhA	13(0)	25(1)	9(0)	0(0)	−1(0)	0(0)
Rh1	12(0)	29(1)	16(0)	1(0)	−1(0)	−3(0)
Rh2	12(0)	30(1)	18(0)	1(0)	1(0)	3(0)
Rh3	17(0)	37(1)	12(0)	0(0)	−1(0)	0(0)
ClA1	25(1)	61(2)	21(1)	9(1)	−4(1)	7(1)
ClA2	26(1)	36(2)	25(1)	−2(1)	−3(1)	−8(1)
ClA3	27(1)	75(2)	22(1)	−17(1)	1(1)	10(1)
ClB1	24(1)	86(2)	22(1)	−4(1)	−8(1)	5(1)
ClB2	22(1)	88(2)	21(1)	−6(1)	1(1)	4(1)
ClB3	31(1)	38(2)	51(1)	−4(1)	−1(1)	5(1)
ClV1	44(1)	72(2)	27(1)	−2(1)	2(1)	18(1)
ClV2	25(1)	95(3)	47(1)	16(1)	−2(1)	0(1)
ClF1	33(1)	52(2)	35(1)	−3(1)	−5(1)	−6(1)
ClF2	20(1)	116(3)	25(1)	0(1)	3(1)	−1(1)
ClF3	29(1)	65(2)	45(1)	−4(1)	−5(1)	−8(1)
O1	39(3)	87(8)	65(4)	0(4)	−2(3)	15(5)
O2	69(5)	94(8)	50(4)	−34(5)	−12(3)	1(5)
N11	17(2)	38(6)	33(3)	−7(3)	−1(2)	−3(3)
N12	18(3)	53(7)	42(4)	15(3)	−3(2)	−11(4)
N13	29(3)	80(7)	14(2)	−7(4)	−1(2)	−1(4)
N21	17(3)	68(8)	56(4)	13(4)	4(3)	23(5)
N22	20(3)	57(7)	65(5)	−12(4)	10(3)	−16(5)
N23	34(3)	124(10)	21(3)	5(5)	−(2)	3(5)
N31	40(3)	44(6)	15(2)	4(4)	0(2)	−5(3)
N32	42(3)	53(6)	10(2)	5(4)	1(2)	−3(3)
N33	18(3)	81(8)	36(3)	−2(4)	−3(2)	−5(4)

Note. The factor is given by $\exp[-(B_{11}h^2 + B_{22}k^2 + \cdots + 2B_{12}hk + 2B_{13}hl + \cdots)]$ and is multiplied by 10^4. Estimated standard deviations are given in parentheses.

tensities were measured using the ω-scanning technique in the lower angular region, and 2θ-ω scanning above 2θ = 30° at a ω-scan speed of 2°/min.

The diffraction intensities were monitored by 3 standard reflections for every 100 reflections recorded. The observed intensities were corrected for the ordinary Lorentz and polarization factors, but no absorption correction ($\mu R = 0.49$) was applied, and 4558 statistically significant independent reflections with $|F| > 3\sigma(F)$, where σ is the standard deviation based on counting statistics, were obtained.

Structure Determination and Refinement

From the extinction rule, two space groups, Pn and P2/n, were possible. The statistical intensity distribution showed a peculiar behavior, which suggested that some of the atoms would be situated at special positions, but the distinction between the two space groups was not possible. Therefore, the structure analysis was begun by assuming the low-symmetry space group Pn. As shown in Fig. 1, the distribution of the Patterson function on the ab plane is consistent with the vector set of the centered triangle, which suggests the existence of the trigonal bipyramidal metal atom cluster, with the trigonal plane parallel to the ab plane, and one of its vertices along the b axis. In this space group, the x, z coordinates of the central rhodium atom could be arbitrarily chosen to be 0.25, 0.25. The y coordinate was determined in order to give the lowest R factor ($R = \Sigma||F_0| - |F_c||/\Sigma|F_0|$) for the calculated structure factor of the six atoms in the bipyramidal group. A subsequent Fourier synthesis revealed four atoms, which would correspond to three rhodium atoms and one tin. At this stage tin could not be distinguished from rhodium, and a second Fourier synthesis was carried out to give some additional atomic parameters. Then, after repetition of the Fourier synthesis, the atomic parameters of the six tin, four rhodium, and twenty-two chlorine atoms were determined. The sixth tin atom could be distinguished from the cationic rhodium because it had to form some tin-chlorine bonds (cationic rhodiums are coordinated octahedrally by six nitrogen atoms). At this stage all the atomic coordinates were carefully examined, and they were found to satisfy P2/n symmetry with very good accuracy. Therefore, the space group was changed to P2/n. These nineteen atomic parameters were refined by three cycles of isotropic least squares; and then three cycles of least-squares refinement with anisotropic temperature factors reduced R to 0.094. Difference Fourier synthesis revealed two

TABLE IV

OCTAHEDRAL ARRANGEMENT OF $[Rh(NH_3)_6]^{3+}$
AROUND $[SnCl_6]^{4-}$. INTERATOMIC DISTANCES (Å)

SnF–Rh1	5.7276(8)	Rh3–Rh1	7.8411(16)
–Rh2	5.8026(8)	–Rh2	7.8967(16)
–Rh3	5.3650(24)		

oxygen and nine nitrogen atoms. The nitrogen atoms had to exist within the range of Rh–N bond length; hence the nitrogen atoms could be distinguished from the oxygen atoms. Thus, all of the atomic parameters in the complicated salt, except for the hydrogen atoms, were determined. Three more cycles of the anisotropic least-squares refinements were performed, and the R factor converged to 0.031.

In Table I and II, the final atomic and thermal parameters are listed, and in Table III,[1] the final observed and calculated structure factors.

Calculations were performed using the UNICS III universal program system (6) and the FACOM 230-75 computer of this Institute.

Description of the Structure and Discussion

The crystal structure of $[Rh(NH_3)_6]_3$ $[RhSn_6Cl_{22}] \cdot 4H_2O$ consists of three cations, $[Rh(NH_3)_6]^{3+}$, two kinds of anions, $[Rh(SnCl_3)_4(SnCl_4)]^{5-}$ and $[SnCl_6]^{4-}$, and four molecules of water of crystallization. The atomic arrangement in the asymmet-

[1] See NAPS document No. 03595 for 25 pages of supplementary material. Order from ASIS/NAPS c/o Microfiche Publications, P.O. Box 3513, Grand Central Station, New York, New York 10017. Remit in advance for each NAPS Accession number. Institutions and organizations may use purchase orders when ordering, however, there is a billing charge for this service. Make checks payable to Microfiche Publications. Photocopies are $5.00. Microfiche are $3.00. Outside of the U.S. and Canada, Postage is $3.00 for a photocopy or $1.50 for a fiche.
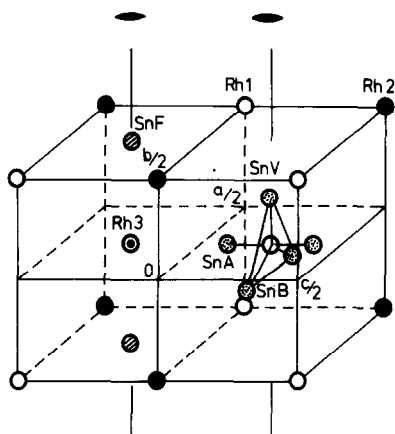

FIG. 2. Arrangement of metal atoms in the assymmetric unit.

ric unit is shown in Fig. 2. Two of the cationic rhodium atoms (RH1 and 2) are on the inversion center and the other one (RH3) is on the twofold axis $(x, y, z = \frac{1}{4}, 0.0136, \frac{3}{4})$. The noncoordinate tin(II)
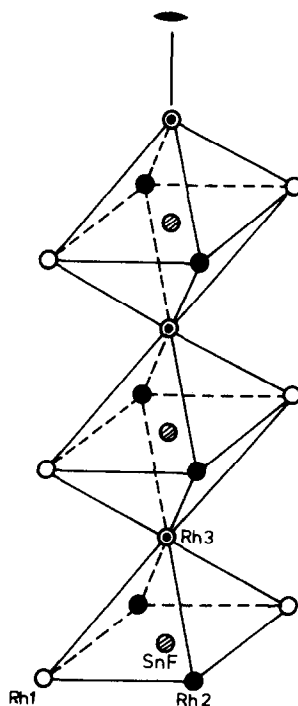

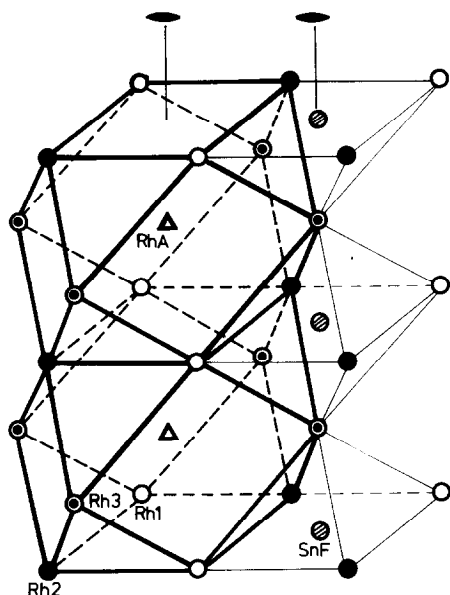FIG. 3. Octahedral arrangement of cations around $[SnCl_6]^{4-}$ ion.

FIG. 4. Tetradecahedral arrangement of cations around $[Rh(SnCl_3)_4(SnCl_4)]^{5-}$ ion.

and angles in the two units. The octahedron is linked at the Rh3 position in series along the twofold axis (–Rh3–SnF–Rh3–), and the tetradecahedron is linked in series along the twofold axis by sharing its tetragonal plane (Rh1 Rh1 Rh2 Rh2) on the ac plane. Every tetradecahedron shares eight trigonal planes (Rh1 Rh2 Rh3) with eight octahedrons which surround the tetradecahedron to form a hexahedral arrangement around the tetradecahedron.

The molecular structure of the cations is a regular octahedron with an average Rh–N bond length of 2.075 Å as shown in Table VI. These values are reasonable in comparison with that of $[Rh(NH_3)_5H][ClO_4]_2$ (7). The molecular structure of the $SnCl_6^{4-}$
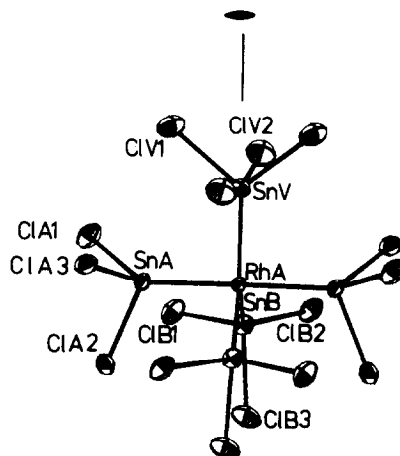
(SnF) in the $SnCl_6^{4-}$ group also exists on the twofold axis $(\frac{1}{4}, 0.5008, \frac{3}{4})$. $[Rh(SnCl_3)_4(SnCl_4)]^{5-}$ ion has a trigonal bipyramidal structure with the trigonal plane parallel to the ab plane and the axial Sn–Rh–Sn perpendicular to the ab plane. The vertex tin(SnV) and central rhodium(RhA) of the trigonal plane are on the other twofold axis.

The crystal structure of this salt is characterized by two kinds of arrangement of the cations around the two anions. As Fig. 3 and 4 show, one is the almost regular octahedron with $SnCl_6^{4-}$ ion at the center and the other is the tetradecahedron with $[Rh(SnCl_3)_4(SnCl_4)]^{5-}$ at the center. Tables IV and V show the interatomic distances

TABLE V

TETRADECAHEDRAL ARRANGEMENT OF $[Rh(NH_3)_6]^{3+}$ AROUND $[Rh(SnCl_3)_4(SnCl_4)]^{5-}$. INTERATOMIC DISTANCES (Å)

RhA–Rh1	8.0294(17)	Rh3–Rh1	7.8411(16)
–Rh2	7.9747(17)	–Rh2	7.8967(16)
–Rh3	8.0144(10)		

TABLE VI

INTERATOMIC DISTANCES (Å)

	$[Rh(SnCl_3)_4(SnCl_4)]^{5-}$		
RhA–SnA	2.4928(5)	SnB–ClB1	2.4455(22)
–SnB	2.5404(8)	–ClB2	2.4334(21)
–SnV	2.5449(15)	–ClB3	2.4055(25)
SnA–ClA1	2.3959(21)	SnV–ClV1	2.3893(25)
–ClA2	2.3863(21)	–ClV2	2.7340(24)
–ClA3	2.3919(22)		
	$[SnCl_6]^{4-}$		
SnF–ClF1	2.8942(24)	SnF–ClF3	2.7631(26)
–ClF2	2.8009(22)		
	$[Rh(NH_3)_6]^{3+}$		
Rh1–N11	2.077(6)	Rh2–N23	2.067(7)
–N12	2.070(7)	Rh3–N31	2.072(6)
–N13	2.076(6)	–N32	2.073(6)
Rh2–N21	2.054(7)	–N33	2.078(6)
–N22	2.070(7)		
	$[Rh(NH_3)_6]^{3+}$—H_2O—Cl^-		
O1 –N21	3.127(11)	O2 –N11	3.254(10)
–N22	3.404(11)	–N12	3.070(11)
–N23	3.756(13)	–N13	3.534(11)
–N31	3.202(10)	–N33	3.353(11)
–ClA1	3.404(8)	–ClA3	3.348(9)
–ClB1	3.502(8)	–ClB2	3.539(8)
–ClV2	3.241(8)	–ClV2	3.318(8)
–ClF3	3.502(8)	–ClF3	3.304(8)

Note. Estimated standard deviations are given in parentheses.
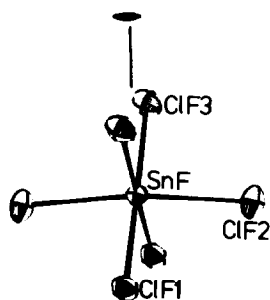
FIG. 5. Molecular structure of [SnCl₆]⁴⁻.

FIG. 6. Molecular structure of [Rh(SnCl₃)₄(SnCl₄)]⁵⁻.

ion, shown in Fig. 5, is very interesting with respect to its coordination number and the bond lengths of Sn–Cl. Although few tin(II) compounds have been reported to form an octahedral six-coordinate complex, the present tin(II) anion has a distorted octahedral configuration with extremely long Sn–Cl bond lengths of 2.763, 2.800, and 2.893 Å. Tin(II) generally forms a trigonal pyramid as shown in

$SnCl_2 \cdot 2H_2O$ (8) and $KCl \cdot SnCl_3 \cdot 2H_2O$ (9) and the Sn–Cl bond lengths of these complexes are in the range 2.54–2.63 Å. In $SnCl_2$ (8), which also forms a trigonal pyramid with bridging chlorine, there are

TABLE VII

BOND ANGLES (Å)

[Rh(SnCl₃)₄(SnCl₄)]⁵⁻			
SnA –RhA–SnB	89.40(2)	RhA –SnB–ClB1	125.18(6)
–SnV	90.40(2)	–ClB2	119.41(6)
SnB –RhA–SnV	126.07(3)	–ClB3	121.94(6)
RhA –SnA –ClA1	123.46(5)	ClB1–SnB–ClB2	96.00(7)
–ClA2	112.96(5)	–ClB3	92.23(9)
–ClA3	129.55(6)	ClB2–SnB–ClB3	94.56(9)
ClA1–SnA –ClA2	95.46(7)	RhA –SnV–ClV1	128.66(6)
–ClA3	93.16(7)	–ClV2	98.41(6)
ClA2–SnA –ClA3	94.26(8)	ClV1–SnV–ClV2	85.19(9)
[SnCl₆]⁴⁻			
ClF1–SnF –ClF2	84.29(7)	ClF2–SnF –ClF3	95.96(8)
–ClF3	175.83(7)		
[Rh(NH₃)₆]³⁺			
N11 –Rh1 –N12	91.2(2)	N22 –Rh2 –N23	89.2(3)
–N13	90.7(2)	N31 –Rh3 –N32	178.0(2)
N12 –Rh1 –N13	89.7(3)	–N33	89.7(3)
N21 –Rh2 –N22	89.2(3)	N32 –Rh3 –N33	89.5(3)
–N23	90.8(3)		
[Rh(NH₃)₆]³⁺—H₂O			
N21 –O1 –N31	95.6(3)	N11 –O2 –N33	125.2(3)
N23 –O1 –N31	103.1(3)	N12 –O2 –N33	117.5(3)
		N13 –O2 –N33	127.2(3)
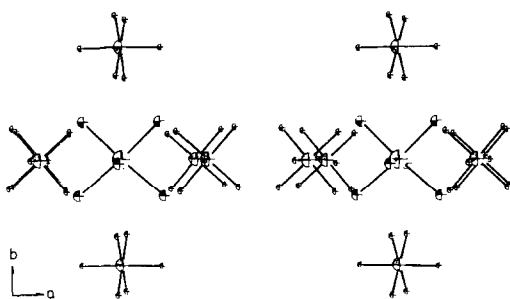
FIG. 7. Stereoscopic view of the packing in the octahedron with [SnCl$_6$]$^{4-}$ at the center.

-Sn-Cl-Sn-Cl- chains with bond length of 2.78 Å.

As shown in Fig. 6, the molecular structure of the [Rh(SnCl$_3$)$_4$(SnCl$_4$)]$^{5-}$ ion also has a unique stereochemistry. In general, tin(II) is coordinated to metal as an SnCl$_3^-$ group through an apex tin of a trigonal pyramid. Tables VI and VII show that, for this ion, the two axial SnA and the two equatorial SnB show the ordinary feature of the coordinated SnCl$_3^-$ in the bond-length values for RhA–SnA (2.493 Å) and RhA–SnB (2.540 Å), and in the Sn–Cl bond-length range (2.386–2.446 Å). On the other hand, the vertex tin atom (SnV) forms a distorted trigonal bipyramid with an ordinary Rh–Sn bond, 2.545 Å in length, and two short equatorial and two long axial Sn–Cl bonds, 2.389 and 2.733 Å, respectively. Two tri-
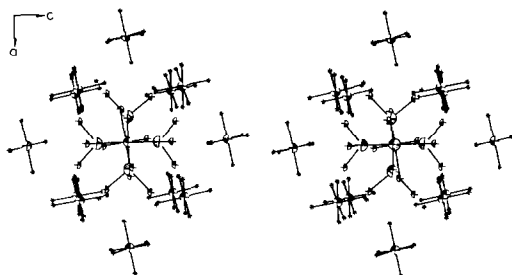
gonal planes, the RhA centered and the SnV centered, are linked by the RhA–SnV bond, and cross each other almost at right angles.

Four molecules of water of crystallization exist near the cations on the inversion center with N–O distances of 3.071 Å for O2-N12 and 3.203 Å for O1-N31, as shown in Table VI.

This salt shows pronounced polychroism, a phenomenon that can be explained from the crystal and its molecular structure. As shown in Fig. 2, the crystal axes of the salt coincide with those of the rhodium anion, thus causing the violet color of this salt. Hence, the single crystal of this salt may be extremely anisotropic and is expected to show polychroism. This anion seems to correspond to the purple species (5) which exists in hydrochloric acid solution. The strange features of the vertex tin in the trigonal plane may be related to the fact that the purple species was precipitated as a variety of salts depending on the cation: for example, the yellow M_3[RhSn$_5$Cl$_{15}$] for alkylammonium ion, the reddish-brown [Rh(en)$_3$]$_3$[RhSn$_6$Cl$_{22}$], and this violet salt.

In earlier work Mössbauer spectra also suggested the presence of noncoordinated tin(II) in this salt, and the present results obtained from X-ray analysis are in agreement with this earlier finding.

FIG. 8. Stereoscopic view of the packing in the tetradecahedron with [Rh(SnCl$_3$)$_4$(SnCl$_4$)]$^{5-}$ at the center.

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