structure; Na1 with site symmetry $\bar{1}$ and Na2 on *m*. Na1 is surrounded by two S, two N and two water O atoms forming a distorted octahedron. These polyhedra share edges N3—S2 forming chains $^1_\infty[NaO_2N_{2/2}S_{2/2}]$ parallel to [010]. Each dedt links two different chains *via* the *trans*-positioned S2 and N3 atoms. Na2 coordinates four water O atoms (2 × O1, 2 × O2), one S1 and one N3 atom. Na2 polyhedra form pairs by edge-sharing [O(2)—O(2)] and these pairs are connected with the Na1 octahedra *via* common O1 and N3 atoms (Fig. 2).

As a result, short and long O1—O1 distances alternate along [010]. The Na—O and Na—N distances correspond to usually observed bond lengths (Colapietro, Domenicano & Vaciago, 1968). A sodium–sulfur coordination is mainly found in inorganic compounds with Na—S distances in the range 2·8–3·1 Å (Mereiter, Preisinger & Guth, 1979).

There are two crystallographically different water molecules (site symmetries 1 and 2) interspersed between the layers of dedt ions which build up a symmetric set of hydrogen bonds with respect to the mirror planes. The molecule $H_2O(1)$ connects two dedt ions in $y = 0$ and $y = 0·5$ *via* an unusually short S···H contact (S1···H11 = 2·25 Å) and an N—H hydrogen bridge (N4···H12 = 1·94 Å), while $H_2O(2)$ is associated with two anions within the same layer ($y = 0$ or 0·5) *via* H2···S2 contacts with H···S = 2·50 Å. The distances O···*X* (*X* = S2, N4) are in the range given by Kuleshova & Zorkii (1981) and Chiari & Ferraris (1982) while the O1···S1 distance is at the low end of usually observed values (3·23–3·31 Å).

It is expected that hydrogen bonds as well as the charge and size of a metal cation in the salts of dedt (Table 3) will lead to deviations from planarity of the ligand. Nevertheless no systematic trend within the known compounds is observed. Although the metal cation in the present species is small ($r_{Na^+} = 0·97$, $r_{Ba^{2+}} = 1·34$ Å; Shannon & Prewitt, 1969), dedt is situated on a mirror plane and forms an effective and symmetric set of hydrogen bonds.

Table 3. *Maximum deviations from planarity of* dedt *in some ionic compounds* (Å)

Compound	Δ	Reference
$Ba(dedt).3H_2O$	0·10	Hummel & Wolf (1985)
$Sr(dedt).5H_2O$	0·04	Hummel & Wolf (1986)
$Ca(dedt).5H_2O$	0·10	Wolf & Hummel (1985)
$K_2(dedt).H_2O$	0·03	Hummel (1985)

References

CHIARI, G. & FERRARIS, G. (1982). *Acta Cryst.* B**38**, 2331–2341.
COLAPIETRO, M., DOMENICANO, A. & VACIAGO, A. (1968). *J. Chem. Soc. Chem. Commun.* pp. 572–573.
GERMAIN, G., MAIN, P. & WOOLFSON, M. M. (1971). *Acta Cryst.* A**27**, 368–376.
HUMMEL, H. U. (1985). *Acta Cryst.* C**41**, 1591–1592.
HUMMEL, H. U. & WOLF, C. (1985). *Z. Naturforsch. Teil B*, **40**, 1638–1643.
HUMMEL, H. U. & WOLF, C. (1986). *Z. Naturforsch.* In the press.
International Tables for X-ray Crystallography (1974). Vol. IV. Birmingham: Kynoch Press. (Present distributor D. Reidel, Dordrecht.)
KULESHOVA, L. N. & ZORKII, P. M. (1981). *Acta Cryst.* B**37**, 1363–1366.
MEREITER, K., PREISINGER, A. & GUTH, H. (1979). *Acta Cryst.* B**35**, 19–25.
SHANNON, R. D. & PREWITT, C. T. (1969). *Acta Cryst.* B**25**, 925–946.
SHELDRICK, G. M. (1976). *SHELX76*. A program for crystal structure determination. Univ. of Cambridge, England.
SÖDERBÄCK, E. (1963). *Acta Chem. Scand.* **17**, 362–376.
WOLF, C. & HUMMEL, H. U. (1985). *J. Chem. Soc. Dalton Trans.* pp. 43–45.

Acta Cryst. (1987). C**43**, 43–46

Di-μ-hydroxo-[tetrakis(tetrahydrothiophene 1-oxide)]diplatinum(II) Nitrate

BY F. D. ROCHON AND FRANCE GUAY

Département de chimie, Université du Québec à Montréal, CP 8888, *succ. A, Montréal, Canada H*3*C* 3*P*8

(*Received* 19 *August* 1985; *accepted* 5 *August* 1986)

Abstract. $[Pt_2(OH)_2(C_4H_8OS)_4](NO_3)_2$, $M_r = 964·82$, triclinic, $P\bar{1}$, $a = 6·036$ (2), $b = 10·848$ (5), $c = 11·737$ (10) Å, $\alpha = 69·97$ (6), $\beta = 75·63$ (5), $\gamma = 80·30$ (3)°, $V = 696·4$ (8) Å^3, $Z = 1$, $D_x = 2·300$, $D_m = 2·29$ (2) Mg m^{-3}, λ(Mo $K\alpha$) = 0·71069 Å, μ(Mo $K\alpha$) = 10·479 mm^{-1}, $F(000) = 460$, $T = 295$ K, $R = 0·043$, and $wR = 0·041$ for 3044 unique observed reflections. The hydroxo-bridged dimer has a center of symmetry. The coordination around the Pt^{II} atom is square-planar. The Pt—S bond distances are 2·203 (2) and 2·209 (2) Å and the Pt—O distances are 2·045 (5) and 2·050 (5) Å. The Pt—O—Pt′ angle is 100·0 (3)°

0108-2701/87/010043-04$01.50

while the O—Pt—O′ angle is 80·0 (2)°. The NO_3^- is very disordered and is hydrogen-bonded to the bridged-hydroxo group. The packing consists of layers of cations parallel to the *ac* plane and centered at $y = 0$, and separated by layers of nitrate ions.

Introduction. The crystal structure of a hydroxo-bridged platinum compound with dimethyl sulfoxide, $[(Me_2SO)_2Pt(OH)_2Pt(Me_2SO)_2](ClO_4)_2$, isolated from an aqueous solution of *cis*-$[Pt(Me_2SO)_4](ClO_4)_2$ was recently reported (Rochon, Kong & Melanson, 1985). The method was not found suitable for the synthesis of dimers with other sulfoxides. Therefore, a new method involving the precipitation of the halide ligands of *cis*-$[Pt(sulfoxide)_2X_2]$ with a silver salt was developed. This study of the aqueous reactions of *cis*-$[Pt(sulfoxide)_2X_2]$ with several silver salts was recently reported (Rochon, Kong & Girard, 1986). Monomers of types *cis*-$[Pt(sulfoxide)_2(ClO_4)_2]$ and *cis*-$[Pt(sulfoxide)_2(SO_4)]$ and hydroxo-bridged oligomers were isolated. Dimers, *cis*-$[Pt(sulfoxide)_2(OH)]_2^{2+}$ and possibly a trimer were characterized by IR and ^1H NMR. The different platinum(II) species with ethyl methyl sulfoxide were also studied by ^{195}Pt NMR (Rochon & Girard, 1986). In order to confirm the structure of the different species, we have decided to undertake the crystal structure analysis of several of these compounds. Recently we reported the crystalline structure of *cis*-$[PtCl_2(TMSO)_2]$ [TMSO = tetrahydrothiophene 1-oxide ('tetramethylenesulfoxide')] (Melanson, de la Chevrotière & Rochon, 1985). In this paper we report the structure of a dimer, *cis*-$[\{Pt(OH)(TMSO)_2\}_2](NO_3)_2$. Other dimeric and trimeric compounds did not give crystals suitable for X-ray diffraction methods.

Experimental. The title compound was prepared from the aqueous reaction of *cis*-$[PtCl_2(TMSO)_2]$ with $AgNO_3$ according to the recently published method (Rochon, Kong & Girard, 1986). The crystals were slowly recrystallized in water.

Rectangular plate, dimensions (mm): 0·056 (001–00$\bar{1}$) × 0·094 (010–0$\bar{1}$0) × 0·754 (100–$\bar{1}$00); density by flotation in a CCl_4–CH_2Br_2 solution; space group $P\bar{1}$; Syntex $P\bar{1}$ diffractometer; graphite-monochromatized Mo $K\alpha$ radiation; cell parameters from refined angles of 15 centered reflections (2θ range: 7–22°); 4126 independent reflections measured up to $2\theta < 60°$ by θ–2θ scan technique, range of *hkl*: $h = 0\rightarrow8$, $k = -15\rightarrow15$, $l = -15\rightarrow16$; standard reflections 301, 030 and 003; variations <3%; 1082 reflections with $I_{net} < 2{\cdot}5\sigma(I)$ unobserved, $\sigma(I)$ calculated as in Melanson & Rochon (1975); absorption correction based on equations of crystal faces, transmission factors from 0·326 to 0·581; data corrected for Lorentz and polarization effects; 3044 unique observed reflections; atomic scattering factors of Cromer & Waber (1965) for Pt, S, O, N, C and of Stewart, Davidson & Simpson (1965) for H; anomalous-dispersion terms of Pt and S from Cromer (1965).

Patterson map showed position of Pt; other atoms (except H) located by structure factors and Fourier map calculations; nitrate ion very disordered as shown by the very high thermal factors; isotropic secondary-extinction correction (Coppens & Hamilton, 1970); $w = 1/\sigma^2(F)$; H atoms on the C atoms fixed at calculated positions (C—H = 0·95 Å) with isotropic $B = 6{\cdot}0$ Å^2. Ratio of maximum least-squares shift to e.s.d. in final refinement cycle (on *F*): <0·2 for the dimeric cation and up to 0·7 for the nitrate ion; $\rho_{max} = 1{\cdot}26$ (close to Pt), $\rho_{min} = -0{\cdot}65$ e Å^{-3} in final difference Fourier synthesis, standard deviation of an observation of unit weight 1·58. $R = 0{\cdot}045$ and $wR = 0{\cdot}043$, calculations on a Cyber 171 with programs of Melanson & Rochon (1975).*

Discussion. The refined atomic parameters and temperature factors are listed in Table 1. Bond distances and angles are in Table 2. A view of the molecular cation is shown in Fig. 1. The ion $[\{Pt(OH)(C_4H_8SO)_2\}_2]^{2+}$ is a centrosymmetric dimer bridged by hydroxo groups. The coordination around the Pt atom is square-planar. As expected the TMSO ligands are bonded to Pt through their S atoms. The $S_2PtO_2PtS_2$ moiety is planar. The deviations from the weighted best plane calculated through the eight atoms are Pt 0·0006 (4), S(1) −0·005 (2), S(2) −0·007 (2) and O(3) −0·016 (8) Å. This is similar to the structures of $[(Me_2SO)_2Pt(OH)_2Pt(Me_2SO)_2](ClO_4)_2$ (Rochon, Kong & Melanson, 1985), $[(NH_3)_2Pt(OH)_2Pt(NH_3)_2](NO_3)_2$ (Stanko, Hollis, Schreifels & Hoeschele, 1977; Faggiani, Lippert, Lock & Rosenberg, 1977) and $[(NH_3)_2Pt(OH)_2Pt(NH_3)_2]CO_3.2H_2O$ (Lippert, Lock, Rosenberg & Zvagulis, 1978). But it is different from the structure of $[\{P(Et)_3\}_2Pt(OH)_2Pt\{P(Et)_3\}_2](BF_4)_2$ (Bushnell, 1978), which contains a bent hydroxo bridge. The dihedral angle between the two planes in the phosphine structure is 36·4°. Therefore sulfoxides seem to have more similarities with amines than with phosphine compounds.

The angles around the Pt atom show considerable strain inside the four-membered ring. The O(3)—Pt—O(3′) angle is reduced to 80·0 (2)° while the Pt—O(3)—Pt′ angle is 100·0 (3)°. These values are very close to those found in $[\{Pt(OH)(Me_2SO)_2\}_2]^{2+}$, and in $[\{Pt(OH)(NH_3)_2\}_2]^{2+}$ but are slightly different from those found in a chlorine bridged dimer where the Cl—Pt—Cl′ = 84·7° and Pt—Cl—Pt′ = 93·3° (Rochon

* Lists of structure factors, anisotropic thermal parameters, H coordinates, deviations from best planes, equations of weighted least-squares planes and data on the nitrate ion have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 43316 (22 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 1. *Positional parameters with their e.s.d.'s and equivalent isotropic temperature factors* ($\times 10^4$) *in* $[Pt_2(OH)_2(TMSO)_4]^{2+}$

$$U_{eq} = \tfrac{1}{3}\sum_i\sum_j U_{ij}a_i^*a_j^*\mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	U_{eq}(Å^2)
Pt	604·6 (6)	−18·4 (2)	−1373·7 (2)	340
S(1)	1310 (3)	1483 (2)	−3210 (1)	352
S(2)	1131 (4)	−1553 (2)	−2283 (1)	354
O(1)	60 (12)	1442 (6)	−4112 (5)	600
O(2)	3210 (11)	−1504 (5)	−3238 (5)	532
O(3)	108 (13)	1284 (4)	−401 (4)	662
C(1)	970 (16)	3118 (6)	−3126 (7)	470
C(2)	2544 (19)	3853 (8)	−4312 (9)	675
C(3)	4715 (18)	2972 (9)	−4556 (9)	645
C(4)	4323 (16)	1516 (8)	−3881 (8)	536
C(5)	−1305 (17)	−1594 (8)	−2883 (8)	529
C(6)	−1305 (24)	−3054 (10)	−2738 (11)	812
C(7)	−195 (28)	−3908 (10)	−1754 (13)	1001
C(8)	975 (17)	−3188 (7)	−1208 (7)	507

Table 2. *Bond distances* (Å) *and angles* (°) *in* $[Pt_2(OH)_2(TMSO)_4]^{2+}$

Pt—S(1)	2·203 (2)	S(2)—C(5)	1·794 (10)
Pt—S(2)	2·209 (2)	S(2)—C(8)	1·791 (8)
Pt—O(3)	2·045 (5)	C(1)—C(2)	1·52 (1)
Pt—O(3')	2·050 (5)	C(2)—C(3)	1·51 (1)
S(1)—O(1)	1·459 (7)	C(3)—C(4)	1·53 (1)
S(2)—O(2)	1·455 (6)	C(5)—C(6)	1·53 (1)
S(1)—C(1)	1·785 (8)	C(6)—C(7)	1·45 (2)
S(1)—C(4)	1·794 (10)	C(7)—C(8)	1·51 (2)
S(1)—Pt—S(2)	89·5 (1)	O(1)—S(1)—C(1)	109·3 (4)
S(1)—Pt—O(3)	95·1 (2)	O(1)—S(1)—C(4)	109·9 (4)
S(1)—Pt—O(3')	175·0 (2)	O(2)—S(2)—C(5)	109·8 (4)
S(2)—Pt—O(3)	175·4 (2)	O(2)—S(2)—C(8)	109·7 (4)
S(2)—Pt—O(3')	95·5 (2)	C(1)—S(1)—C(4)	94·3 (4)
O(3)—Pt—O(3')	80·0 (2)	C(5)—S(2)—C(8)	94·8 (4)
Pt—O(3)—Pt'	100·0 (3)	S(1)—C(1)—C(2)	103·0 (6)
Pt—S(1)—O(1)	116·0 (3)	S(1)—C(4)—C(3)	106·0 (6)
Pt—S(1)—C(1)	112·8 (3)	S(2)—C(5)—C(6)	103·9 (7)
Pt—S(1)—C(4)	112·5 (3)	S(2)—C(8)—C(7)	105·3 (7)
Pt—S(2)—O(2)	115·0 (3)	C(1)—C(2)—C(3)	109 (1)
Pt—S(2)—C(5)	112·6 (3)	C(2)—C(3)—C(4)	111 (1)
Pt—S(2)—C(8)	113·2 (3)	C(5)—C(6)—C(7)	112 (1)
		C(6)—C(7)—C(8)	114 (1)

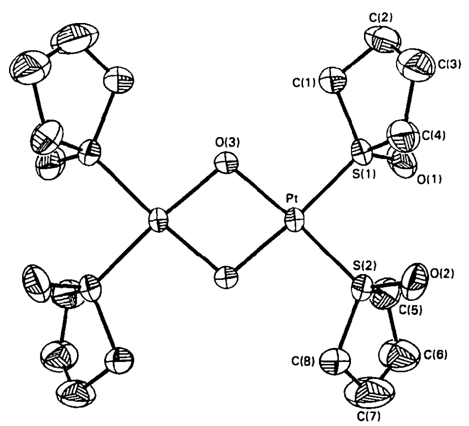

Fig. 1. Labeled diagram of the cation $[Pt_2(OH)_2(C_4H_8SO)_4]^{2+}$. The ellipsoids correspond to 50% probability.

& Melanson, 1981). The strain inside the four-membered ring also causes some deformations in the O—Pt—S angles [95·1 (2), 95·5 (2), 175·0 (2) and 175·4 (2)°]. Only the S—Pt—S angle is normal [89·5 (1)°]. The Pt—O bond distances (2·05 Å) agree well with the values (2·02–2·07 Å) found in the Me_2SO and ammine hydroxo dimers, but are shorter than the values (2·09–2·17 Å) found in the bent phosphine dimer.

The Pt—S bonds [2·203 (2) and 2·209 (2) Å] are normal and agree with values found in *cis*-$[PtCl_2(TMSO)_2]$ (Melanson, de la Chevrotière & Rochon, 1985) and in other Pt–sulfoxide compounds (Melanson & Rochon, 1975, 1977, 1978*a,b*, 1984; Rochon, Kong & Melanson, 1985; Lock, Speranzini & Powell, 1976). The S atoms in the TMSO molecules are in an approximately tetrahedral environment. The Pt—S—O angles [115·0 (3) and 116·0 (3)°] are larger than the tetrahedral values as observed in the Pt–sulfoxide structures described above. The Pt—S—C angles are also larger than the tetrahedral values (112·5 to 113·2°) as observed in *cis*-$[PtCl_2(TMSO)_2]$, whereas these angles are normal in other Pt–sulfoxide compounds. This deformation is caused by a considerable strain inside the five-membered ring. This strain is confirmed by the small C—S—C angles (94·3 and 94·8°) as observed in *cis*-$[PtCl_2(TMSO)_2]$. The S—O, S—C bond distances are normal and agree well with the values found in the above references. The C—C bond distances are also normal except C(6)—C(7) = 1·45 Å. This is caused by some disorder in the position of C(7), as demonstrated by its large temperature factors (U_{eq} = 0·100 Å^2).

The weighted least-squares plane was calculated through each five-membered ring of the ligand. The atom-to-plane distances (Å) are S(1) 0·013 (2), C(1) −0·306 (8), C(2) 0·322 (10), C(3) 0·057 (11), C(4) −0·251 (9) for the first ring and S(2) 0·010 (2), C(5) −0·256 (9), C(6) 0·259 (12), C(7) 0·197 (15), C(8) −0·180 (8) for the second ring. The first plane makes an angle of 57° with the platinum plane while the equivalent angle for the second ligand is 124°. The angles between the two TMSO ligands is 69°. The two independent O atoms of the *cis* TMSO ligands are on opposite sides of the platinum plane.

The nitrate ion is very disordered. It was impossible to resolve completely the disorder. The nitrate group presented is the best chemical model for the cluster of peaks determined by X-ray diffraction. The average N—O bond distance is 1·14 (6) Å but the thermal factors are extremely high (U_{eq}: 0·20 to 0·36 Å^2). The angles vary from 114 (5) to 124 (5)°.

The packing of the molecules is shown on Fig. 2. The main feature of the structure consists in the arrangement of the dimeric cations in layers parallel to the *ac* plane and centered at $y = 0$. These layers are separated by the nitrate ions. Besides the ionic attraction,

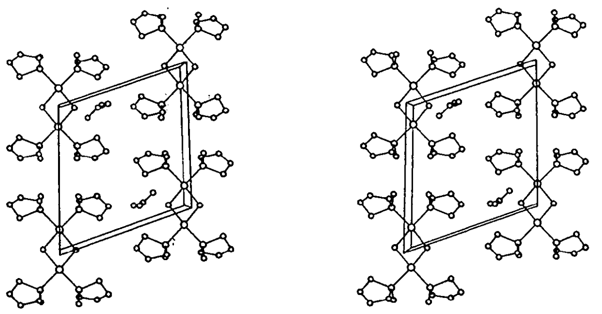

Fig. 2. Stereoscopic diagram of the crystal packing (*c* axis vertical, view down *a* axis).

hydrogen bonding is important to stabilize the crystal. The bridged-hydroxo groups are hydrogen-bonded to the nitrate ion. The distances O(3)—H···O(4) = 3·20 (2) and O(3)—H···O(5) = 2·94 (2) Å [transformation on O(4) and O(5): $-x$, $1-y$, $-z$] and the angles Pt—O(3)···O(4) = 83·7 (4), Pt′—O(3)···O(4) = 111·1 (4), Pt—O(3)···O(5) = 116·6 (4) and Pt′—O(3)···O(5) = 113·0 (4)°, close to the tetrahedral value.

Grateful acknowledgments are made to the Natural Sciences and Engineering Research Council of Canada, to the Ministère de l'Education (FCAR) and the Société Saint-Jean Baptiste for financial support.

References

BUSHNELL, G. W. (1978). *Can. J. Chem.* **56**, 1773–1778.
COPPENS, P. & HAMILTON, W. C. (1970). *Acta Cryst.* A**26**, 71–83.
CROMER, D. T. (1965). *Acta Cryst.* **18**, 17–23.
CROMER, D. T. & WABER, J. T. (1965). *Acta Cryst.* **18**, 104–109.
FAGGIANI, R., LIPPERT, B., LOCK, C. J. L. & ROSENBERG, B. (1977). *J. Am. Chem. Soc.* **99**, 777–781.
LIPPERT, B., LOCK, C. J. L., ROSENBERG, B. & ZVAGULIS, M. (1978). *Inorg. Chem.* **17**, 2971–2975.
LOCK, C. J. L., SPERANZINI, R. A. & POWELL, J. (1976). *Can. J. Chem.* **54**, 53–58.
MELANSON, R., DE LA CHEVROTIÈRE, C. & ROCHON, F. D. (1985). *Acta Cryst.* C**41**, 1428–1431.
MELANSON, R. & ROCHON, F. D. (1975). *Can. J. Chem.* **53**, 2371–2374.
MELANSON, R. & ROCHON, F. D. (1977). *Acta Cryst.* B**33**, 3571–3573.
MELANSON, R. & ROCHON, F. D. (1978*a*). *Acta Cryst.* B**34**, 941–943, 1125–1127.
MELANSON, R. & ROCHON, F. D. (1978*b*). *Inorg. Chem.* **17**, 679–681.
MELANSON, R. & ROCHON, F. D. (1984). *Acta Cryst.* C**40**, 793–795.
ROCHON, F. D. & GIRARD, L. (1986). *Can. J. Chem.* **64**. In the press.
ROCHON, F. D., KONG, P. C. & GIRARD, L. (1986). *Can. J. Chem.* **64**, 1897–1902.
ROCHON, F. D., KONG, P. C. & MELANSON, R. (1985). *Acta Cryst.* C**41**, 1602–1605.
ROCHON, F. D. & MELANSON, R. (1981). *Acta Cryst.* B**37**, 690–692.
STANKO, J. A., HOLLIS, L. S., SCHREIFELS, J. A. & HOESCHELE, J. D. (1977). *J. Clin. Hematol. Oncol.* **7**, 138–168.
STEWART, R. F., DAVIDSON, E. R. & SIMPSON, W. T. (1965). *J. Chem. Phys.* **42**, 3175–3187.

Acta Cryst. (1987). C**43**, 46–48

$1H^+,1'H^+$-2,2′-Bipyridinium Di-μ-chloro-bis[dichloro(phenyl)antimonate(III)]

BY HANS PREUT AND FRIEDO HUBER

Fachbereich Chemie, Universität Dortmund, Postfach 500 500, *D*-4600 *Dortmund* 50, *Federal Republic of Germany*

AND GIUSEPPE ALONZO

Istituto di Chimica Generale, Università di Palermo, Via Archirafi 26, *I*-90123 *Palermo, Italy*

(*Received* 25 *June* 1985; *accepted* 5 *August* 1986)

Abstract. $[C_{10}H_{10}N_2][Sb_2Cl_6(C_6H_5)_2]$, $M_r = 768·6$, monoclinic, $I2/c$, $a = 14·095$ (9), $b = 11·649$ (5), $c = 15·954$ (8) Å, $\beta = 98·07$ (6)°, $V = 2593·6$ Å^3, $Z = 4$, $D_x = 1·968$ Mg m^{-3}, Ag $K\alpha$, $\lambda = 0·56087$ Å, $\mu = 1·4$ mm^{-1}, $F(000) = 1480$, $T = 291$ (1) K, final $R = 0·028$ for 2072 [$I > 3\sigma(I)$] unique diffractometer data. Two $C_6H_5SbCl_2$ units are linked by two slightly unsymmetrically bridging Cl atoms to form the anionic moiety $(C_6H_5)_2Sb_2Cl_6$ with each Sb having distorted square-planar (pseudo-octahedral) coordination neglecting a very weak intermolecular Sb···Cl contact. Phenyl groups are in apical positions. No bonding contacts exist to the bipyridinium cation.

Introduction. The first structural proposal made for halomonophenylantimonates(III) was based on Mössbauer data, but no decision was possible between monomeric units $[C_6H_5SbX_3]^-$ with pseudo trigonal-

0108-2701/87/010046-03\$01.50