The electronic spectrum of $[Co(Ph_2PCH=CHPPh_2)_2-(O_2)][PF_6]$ in frozen solution at 77 K has been reported and an assignment proposed from experimental comparisons.[6] Our assignment, based on transition energies for $Co(PH_3)_4(O_2)^+$ computed by the spin-polarized transition-state method,[12] is in general agreement. We ascribe the bands at 1.6 sh (ϵ 75), 2.16 (ϵ 1170), 2.6 sh (ϵ 1200), and 3.10 μm^{-1} (ϵ 24500) to O_2^{2-} $\pi^*_\perp \rightarrow d_{xz}$, $d_{z^2-x^2} \rightarrow d_{xz}$, $d_{z^2-x^2} \rightarrow d_{y^2}$, and $\pi^*_{||} \rightarrow d_{xz}$, d_{y^2} transitions, respectively, using the orbital designations in Figure 1.[13] Gray et al. denote the last transition as $\sigma(P) \rightarrow d\sigma^*(Co)$.[6] The $6b_1$ orbital, which we call O_2^{2-} $\pi^*_{||}$, does have about 30% PH_3 lone-pair character (see Figure 2); alternatively, the difference between 2 PH_3 and $Ph_2PCH=CHPPh_2$ orbital energies may become significant this deep in the energy-level diagram.

Though these nonrelativistic calculations do qualitatively reproduce the observed order of stability, Co $\gg$ Ir > Rh, they quantitatively place the Ir and Rh complexes quite close in energy.[9] A good illustration at the orbital level is that the Rh- and Ir-complex $6b_1$ orbitals do differ in *energy* (Figure 1) but not significantly in $M-O_2$ *overlap* (Figure 2). The experimental difference in stability between the Ir and Rh complexes appears to be somewhat greater.[5,6] Relativistic corrections should preferentially decrease the atomic d–s and d–p energy splittings for Ir.[14] This is exactly what would be required to bring the calculated strength of peroxide bonding for Ir closer to that for Co. Very recent fully relativistic calculations on $Pt(PH_3)_2(O_2)$ explicitly support this hypothesis.[15]

(12) Ziegler, T.; Rauk, A.; Baerends, E. J. *Theor. Chim. Acta* **1977**, *43*, 261.
(13) The calculated energies for the spin-allowed transitions are 2.23, 2.95, 3.02, and 3.27/3.30 μm^{-1}, respectively. The spin-forbidden O_2^{2-} $\pi^*_\perp \rightarrow d_{xz}$ transition is calculated at 1.57 μm^{-1} (1 hartree = 21.947463 6 μm^{-1}).
(14) (a) Pitzer, K. S. *Acc. Chem. Res.* **1979**, *12*, 271. (b) Pyykko, P.; Desclaux, J. P. *Ibid.* **1979**, *12*, 276.
(15) Case, D. A.; Norman, J. G., Jr.; Osborne, J. A., work in progress.

For a long time, the very weak base ClO_4^- has been considered as a poor ligand despite the synthesis and spectroscopic studies of copper and iron perchlorates by Hathaway et al. in 1961.[2] In 1973, Rosenthal[3] underlined the lack of bibliography about perchlorate complexes. Overcoming the difficulties in the synthesis and handling of strong perchlorating reagents like anhydrous $HClO_4$, Cl_2O_6, and $ClOClO_3$ allowed Rosolvskii et al., ourselves, and Christe et al. to synthesize anhydrous perchlorato complexes of B,[4] Al,[5] Co,[6] Zr,[7] Hf,[8] Ti,[9] Cr,[10] Fe,[11] Ga,[12] Ni,[13,14] Pd,[14] and Sn.[15]

Although the isolated complexes crystallize poorly, their molecular structures could generally be deduced from infrared and Raman spectra. Fortunately, single crystals of a tin perchlorato complex were grown in $SnCl_4$, and their crystal structure determination gave the first evidence for an entirely inorganic perchlorato complex: $[Sn_3O_2Cl_4(ClO_4)_4]_2$.[15] Good agreement was obtained between X-ray and vibrational spectroscopy data.

Interesting results concerning the ClO_4 ligand can be expected from the well-known ability of $SbCl_5$ to react with basic ligands to form (i) addition complexes, $SbCl_5L$, and (ii) substitution complexes, $SbCl_4L$ and $SbCl_3L_2$; in the last 10 years, the $SbCl_5-H_2O$[16] and $SbCl_5-Me_2SO$[17] compounds have been reported. The carboxylate,[18,19] phosphate,[20] and sulfinate[21] ligands have been shown to be able to substitute Cl atoms.

So far, only $[(CH_3)_2Sb(ClO_4)]_2O$,[22] an antimony(V) perchlorato complex with the unidentate ClO_4, has been prepared and studied by X-ray diffraction.

In this paper are presented the syntheses of two new perchlorato complexes, $Sb_8Cl_{24}O_5(ClO_4)_6$ and $Sb_2Cl_6(OH)(O)(ClO_4)$, together with the spectroscopic investigations concerning both compounds and the crystal structure of the latter. For the first time, precise geometrical data for a strongly bonded bidentate ClO_4 group are given.

(2) Hathaway, B. J.; Underhill, A. E. *J. Chem. Soc.* **1961**, 3091.
(3) Rosenthal, M. R. *J. Chem. Educ.* **1973**, *50*, 331.
(4) Chausse, T.; Pascal, J. L.; Potier, A.; Potier, J. *Nouv. J. Chim.* **1981**, *5*, 261.
(5) Nikitina, Z.; Karelin, A. I.; Rosolovskii, V. Ya. *Russ. J. Inorg. Chem.* (*Engl. Transl.*) **1980**, *25*, 71.
(6) Loginov, S. V.; Nikitina, Z. K.; Rosolovskii, V. Ya. *Bull. Acad. Sci. USSR, Div. Chem. Sci.* (*Engl. Transl.*) **1977**, *26*, 1351; *Russ. J. Inorg. Chem.* (*Engl. Transl.*) **1978**, *23*, 178.
(7) Babaeva, V. P.; Rosolovskii, V. Ya. *Bull Acad. Sci. USSR, Div. Chem. Sci.* (*Engl. Transl.*) **1977**, *26*, 445; *Russ. J. Inorg. Chem.* (*Engl. Transl.*) **1978**, *23*, 527.
(8) Babaeva, V. P.; Rosolovskii, V. Ya. *Russ. J. Inorg. Chem.* (*Engl. Transl.*) **1979**, *24*, 206.
(9) (a) Babaeva, V. P.; Rosolovskii, V. Ya. *Bull. Acad. Sci. USSR, Div. Chem. Sci.* (*Engl. Transl.*) **1974**, *23*, 2330; **1975**, *24*, 2278. (b) Schack, C. J.; Pilipovich, D.; Christe, K. O. *J. Inorg. Nucl. Chem., Suppl.* **1976**, *76*, 207.
(10) Chaabouni, M.; Chausse, T.; Pascal, J. L.; Potier, J. *J. Chem. Res., Synop.* **1980**, *3*, 72.
(11) Chaabouni, M.; Pascal, J. L.; Pavia, A. C.; Potier, J.; Potier, A. *C. R. Hebd. Seances Acad. Sci. Ser. C* **1978**, *287*, 41.
(12) Chaabouni, M.; Pascal, J. L.; Potier, A.; Potier, J. *J. Chem. Res., Synop.* **1977**, *3*, 80; *J. Chim. Phys. Phys.-Chim. Biol.* **1977**, *74*, 1083.
(13) Loginov, J. V.; Nikitina, Z. K.; Rosolovskii, V. Ya. *Russ. J. Inorg. Chem.* (*Engl. Transl.*) **1980**, *25*, 562.
(14) Chaabouni, M.; Pascal, J. L.; Potier, J. *C. R. Hebd. Seances Acad. Sci., Ser. C* **1980**, *29*, 125.
(15) Belin, C.; Chaabouni, M.; Pascal, J. L.; Potier, J.; Roziere, J. *J. Chem. Soc., Chem. Commun.* **1980**, 105.
(16) Roziere, J.; Potier, J.; Picotin, G.; Vitse, P. *Rev. Chim. Miner.* **1977**, *14*, 66.
(17) Burgard, M.; Brunette, J. P.; Leroy, M. J. F. *Inorg. Chem.* **1976**, *15*, 1225.
(18) Koller, F. J.; Schwarz, W.; Schmidt, A. *Z. Naturforsch. B: Anorg. Chem., Org. Chem.* **1979**, *34B*, 563.
(19) Blösl, S.; Schwarz, W.; Schmidt, A. *Z. Anorg. Allg. Chem.* **1981**, *474*, 51.
(20) Laber, R. A.; Schmidt, A. *Z. Anorg. Allg. Chem.* **1977**, *428*, 29.
(21) Binder, G. E.; Schmidt, A. *Z. Anorg. Allg. Chem.* **1977**, *430*, 263.
(22) Fergusson, G.; March, F. C.; Ridley, D. R. *Acta Crystallogr., Sect. B* **1975**, *B31*, 1260.

Contribution from the Laboratoire des Acides Minéraux, LA 79 CNRS, Université des Sciences et Techniques du Languedoc, 34060 Montpellier Cédex, France

Two New Perchlorato Complexes. The Oxochloro(perchlorato)antimony Complexes Sb₂Cl₆(OH)(O)(ClO₄) and Sb₈Cl₂₄(O₅)(ClO₄)₆: Synthesis, Vibrational Spectroscopy, and X-ray Structural Determination of (μ-Hydroxo)(μ-oxo)(perchlorato)bis[trichloroantimony(V)], Sb₂Cl₆(OH)(O)(ClO₄)

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In the course of systematic studies on the substitution of chlorine atoms by perchlorato ligands in nontransitional or transitional element chlorides, we have examined the behavior of $SbCl_5$ toward the strong perchlorating reagent Cl_2O_6.

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Experimental Section

SbCl$_5$ (Merck, for synthesis, 99%) was used without purification. The vacuum line allowing the synthesis and the purification of Cl$_2$O$_6$ and the handling of anhydrous perchlorates have been previously described.[23]

A first approach to the molecular structure of the synthesized complexes was made by IR and Raman spectroscopy. Infrared spectra were recorded on a Perkin-Elmer 180. For Raman spectra, a Dilor spectrometer connected to a Tracor TN 1710 modular multichannel computer (Northern Instruments) was used with a Spectra-Physics argon laser (5145-Å line and 150 mW). Sensitivity and calibration of spectrometers are indicated elsewhere.[4] For IR, the finely powdered samples were pressed between two silicon plates ((111) cleavage). A poly(chlorotrifluoroethylene) oil (Merck Uvasol) had to be used for mulls in the 4000–1300-cm^{-1} range in order to observe OH stretching modes. For Raman spectra, samples were sealed under vacuum in 5–8 mm o.d. Pyrex tubes.

Preparation of the Complexes. *Caution!* Cl$_2$O$_6$ and perchlorates are highly explosive compounds, particularly on contact with organic compounds and under shock. The reactions have to be carried out with caution and continuously checked.

Sb$_8$Cl$_{24}$O$_5$(ClO$_4$)$_6$. A 3.10-g (0.018 mol) quantity of Cl$_2$O$_6$ is added to react with 8.49 g (0.028 mol) of SbCl$_5$ at −180 °C in a Pyrex reactor. The mixture is allowed to warm slowly to 10 °C. When Cl$_2$O$_6$ dissolves, the reaction starts quickly; formation of gases (ClO$_2$, Cl$_2$, and sometimes ClOClO$_3$) is observed, and these are periodically removed. A pale orange product progressively precipitates to give a white deposit, after 1.5–2 h. The unreacted SbCl$_5$ is pumped out.

The white product, formulated as Sb$_8$Cl$_{24}$O$_5$(ClO$_4$)$_6$, is produced from a complex reaction:

$$8SbCl_5 + 16Cl_2O_6 \rightarrow$$
$$Sb_8Cl_{24}O_5(ClO_4)_6 + 5Cl_2O_7 + 8Cl_2 + 16ClO_2$$
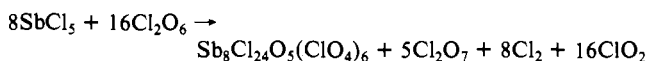
The formation of Cl$_2$O$_7$ and ClO$_2$ was checked by infrared spectroscopy. Anal. Calcd for Sb$_8$Cl$_{24}$O$_5$(ClO$_4$)$_6$: Sb, 38.93; ClO$_4^-$, 23.85; Cl$^-$, 34.01. Found: Sb, 38.84; ClO$_4^-$, 24.65; Cl$^-$, 33.24. IR: 1280 (sh); 1265 (s); 1250 (s); 1235 (sh); 1140 (s); 1130 (sh); 1020 (m); 930 (w); 855 (m); 835 (sh); 712 (w); 685 (w); 640 (m); 585 (m); 538 (s); 508 (s); 475 (sh); 410 (sh); 390 (s); 378 (sh); 300 (s); 270 (sh); 225 (w) cm^{-1}. Raman: 1295 (60); 1280 (sh); 1275 (35); 1260 (20); 1150 (80); 1142 (60); 1035 (110); 895 (15); 865 (40); 848 (55); 726 (50); 690 (15); 653 (80); 637 (sh); 629 (85); 600 (sh); 591 (50); 524 (150); 500 (sh); 493 (40); 474 (60); 467 (sh); 418 (325); 407 (400); 392 (400); 383 (1000); 378 (sh); 317 (25); 282 (25); 242 (275); 233 (180); 211 (140); 180 (165); 170 (220); 156 (235); 146 (310); 138 (300); 126 (230); 105 (175); 85 (75); 77 (60) cm^{-1} (relative intensities are given in parentheses).

Sb$_2$Cl$_6$(OH)(O)(ClO$_4$). If the previously synthesized compound Sb$_8$Cl$_{24}$O$_5$(ClO$_4$)$_6$ is kept standing with SbCl$_5$ in an evacuated and sealed Pyrex tube at 5 °C for 1–3 weeks, it is progressively consumed while colorless single crystals grow. X-ray studies (vide infra) allow the formulation Sb$_2$Cl$_6$(OH)(O)(ClO$_4$), and the presence of a hydrogen atom suggests that slight hydrolysis has occurred, because SbCl$_5$ was probably not strictly anhydrous:

$$Sb_8Cl_{24}O_5(ClO_4)_6 + 3H_2O \rightarrow$$
$$4Sb_2Cl_6(OH)(O)(ClO_4) + 2HClO_4$$
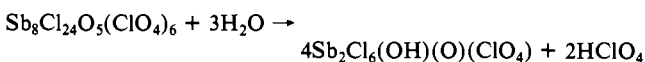
IR: 3300, 2850–21200 (w, br); 1695 (w); 1485 (w); 1270 (s); 1255 (s); 1142 (s); 1030 (w); 930 (w); 860 (s); 840 (s); 705 (sh); 680 (m); 648 (m); 545 (w); 508 (m); 455 (sh); 398 (s); 388 (sh); 315 (m); 305 (m); 230 (s); cm^{-1}. Raman: 3350, 2920, 2602, 2502, 2140 (1, br); 1603 (1, br); 1475 (1, br); 1284 (sh); 1276 (16); 1263 (sh); 1149 (25); 1035 (1); 879 (15); 860 (18); 853 (sh); 675 (sh); 651 (42); 637 (36); 603 (12); 539 (1); 520 (1); 500 (sh); 474 (30); 445 (12); 424 (36); 400 (1000); 386 (sh); 318 (6); 255 (sh); 240 (460); 204 (42); 159 (300); 141 (810); 120 (45); 105 (25); 36 (66) cm^{-1}.

X-ray Data Collection. The crystals were examined under a microscope in a dry box filled with nitrogen since they are highly hygroscopic; they were protected by wetting with poly(chlorotrifluoroethylene) oil and mounted in thin-wall Lindemann glass capillaries. They were tested through preliminary oscillation and Weissenberg photographs and found to be monoclinic. A rod-shaped

crystal of dimensions 0.18 × 0.26 × 0.64 mm which gave the best diffraction spots was investigated on a Nonius CAD-4 automatic diffractometer.

The preliminary orientation search confirmed that the crystal was monoclinic. Integrated intensities were collected at room temperature (25 °C). The profile analysis of a few low-angle reflections indicated that an ω–$^4/_3\theta$ scan method was the most appropriate for data collection. Scan ranges were calculated from the formula Sr = $A + B$ tan θ, where A depends on the mosaic spread of the crystal and B allows for increasing peak width due to Kα_1 and Kα_2 splitting: A and B were chosen as 1.2 and 0.35°, respectively. For each reflection, the calculated scan angle was extended by 25% on either side to estimate the background count. Cell parameters were obtained by least-squares refinement of angular positions of 25 reflections automatically centered on the diffractometer: $a = 9.477$ (1) Å, $b = 20.884$ (4) Å, $c = 13.588$ (1) Å, $\beta = 90.90$ (1)°, and $V = 2688$ Å^3.

The data were collected in the two octants hkl and $hk\bar{l}$, in the range $2 < 2\theta < 50°$. During data collection, the intensities of 3 standard reflections were checked after every 57 reflections. The loss in intensities was less than 13% but was taken into account in data reduction. The data were corrected for the effects of absorption by Gaussian integration[24] with $\mu = 54.5$ cm^{-1}. From 5211 collected reflections, the final data set consisted of 3168 independent reflections with $I > 3\sigma(I)$. Systematic absences of reflections $h0l$ and $0k0$ with, respectively, $h + k$ and k odd confirmed the nonstandard space group $P2_1/n$.

Structure Solution and Refinement. The structure was solved by direct methods in space group $P2_1/n$. The output from the Fourier step of MULTAN[25] contained all the atoms except a few oxygen atoms. After a few cycles of positional and isotropic thermal parameter refinement, $R = \sum ||F_o| - |F_c||/\sum|F_o| = 0.12$. At this stage, a subsequent Fourier difference map clearly indicated the remaining atoms. All atoms were refined with anisotropic thermal parameters; convergence was obtained by minimizing the function $w(|F_o| - |F_c|)^2$ with $w^{-1} = \sigma_{count}^2(F^2)/4F^2 + (0.02F)^2$ and using the final data set corrected for absorption. The final agreement factors were $R(F) = 0.036$ and $R_w(F) = 0.044$ for 271 variables and 3168 reflections. The final Fourier map was flat except for residual peaks around antimony atoms less than 1.8 e/Å^3. In the final cycle of refinement the shifts in antimony and chlorine parameters were zero in position and <0.4σ (esd) in temperature factor while the changes in oxygen parameters were <.15σ in position and <0.56σ in temperature factor.

The scattering factors were taken from Doyle and Turner,[26] and the crystallographic programs used[27] were MULTAN, FORDAP for Fourier summations, ORXLFS 3 for least-squares refinement, ORFFE 3 for molecular and error functions, and ORTEP II, the thermal ellipsoid program for molecular plots.

X-ray Results and Discussion

The final positional parameters for 30 atoms in Sb$_2$Cl$_6$(OH)(O)(ClO$_4$) are listed in Table I and bond distances and bond angles in unit A are given in Table II; listings of observed and calculated structure factors and bond angles and distances in unit B as well as thermal parameters are given in the supplementary material.

The asymmetric unit contains two independent molecules of the title compound. Each of them can be described as a dimeric trichloroantimony(V) oxide stabilized through the protonation by perchloric acid. Each antimony atom is hexacoordinated to three chlorine atoms, to one oxygen atom of the perchlorato ligand, to a bridging oxygen, and to the hydroxo group in a fairly distorted octahedral environment, as shown by the listing of interatomic angles. The geometry of the molecule is depicted in Figure 1. A first glance at the

(23) Chaabouni, M. Thesis, Université des Sciences et Techniques du Languedoc, Montpellier, 1979.

(24) Busing, W. R.; Levy, H. A. *Acta Crystallogr.* **1957**, *10*, 180.

(25) Main, P.; Woolfson, M. M.; Germain, G. "MULTAN, a Computer Program for the Automatic Solution of Crystal Structures"; University of York, Printing Unit: York, England, 1971.

(26) Doyle, P. A.; Turner, P. S. *Acta Crystallogr., Sect. A* **1968**, *A24*, 390.

(27) The computer programs that were used in performing the necessary calculations with their accession names in the "World List of Crystallographic Computer Programs", 3rd ed., are as follows: Fourier summation, FORDAP; least-squares refinement, ORXLFS 3; error analysis of distances and angles, ORFFE 3; structural drawings, ORTEP II.

Table I. Final Positional Parameters for Atoms in Sb$_2$Cl$_6$(OH)(O)(ClO$_4$)

	unit A				unit B		
atom	x	y	z	atom	x	y	z
Sb(1)	0.11247 (7)	0.20305 (5)	0.28036 (5)	Sb(3)	0.77281 (8)	0.06155 (3)	0.64527 (5)
Sb(2)	0.44394 (7)	0.18183 (3)	0.29602 (5)	Sb(4)	0.76228 (8)	0.03570 (3)	0.87697 (5)
Cl(11)^a	0.0949 (4)	0.2203 (2)	0.1149 (2)	Cl(31)	0.5392 (3)	0.0807 (2)	0.6213 (2)
Cl(12)	−0.0135 (4)	0.2902 (1)	0.3308 (3)	Cl(32)	0.8044 (4)	−0.0120 (2)	0.5238 (2)
Cl(13)	0.9385 (3)	0.1277 (1)	0.2889 (2)	Cl(33)	0.8549 (4)	0.1499 (2)	0.5671 (2)
Cl(21)	0.4966 (4)	0.1901 (2)	0.1337 (2)	Cl(41)	0.5253 (3)	0.0491 (2)	0.8931 (2)
Cl(22)	0.6116 (3)	0.2486 (2)	0.3592 (3)	Cl(43)	0.8357 (4)	0.1006 (2)	0.0014 (2)
Cl(23)	0.5595 (3)	0.0875 (1)	0.3257 (2)	Cl(42)	0.7847 (3)	−0.0606 (1)	0.9552 (2)
O(121)^b	0.2936 (7)	0.2473 (3)	0.2965 (4)	O(341)	0.7493 (7)	−0.0052 (3)	0.7465 (4)
O(122)	0.2611 (7)	0.1317 (3)	0.2691 (4)	O(342)	0.7836 (7)	0.1099 (3)	0.7775 (4)
Cl(A)	0.2573 (3)	0.1912 (1)	0.5041 (2)	Cl(B)	0.0810 (3)	0.0491 (1)	0.7725 (2)
O(1)A	0.3813 (8)	0.1655 (3)	0.4529 (5)	O(1)B	0.9910 (7)	0.0204 (3)	0.8495 (5)
O(2)A	0.1344 (7)	0.1794 (4)	0.4381 (5)	O(2)B	0.0007 (8)	0.0410 (3)	0.6787 (5)
O(3)A	0.2389 (9)	0.1557 (4)	0.5895 (5)	O(3)B	0.1028 (10)	0.1127 (4)	0.7922 (6)
O(4)A	0.2730 (9)	0.2571 (4)	0.5185 (6)	O(4)B	0.2028 (8)	0.0124 (4)	0.7659 (6)

^{a} The first digit corresponds to the antimony atom to which it is attached. ^{b} The two first digits correspond to the antimony atoms to which it is attached.

Table II. Bond Distances (A) and Angles (Deg) for Unit A in Sb$_2$Cl$_6$(OH)(O)(ClO$_4$)

Sb(1)-O(121)	1.959 (6)	Sb(2)-O(121)	1.975 (6)
Sb(1)-O(122)	2.059 (6)	Sb(2)-O(122)	2.053 (6)
Sb(1)-O(2)A	2.207 (7)	Sb(2)-O(1)A	2.247 (7)
Sb(1)-Cl(11)	2.280 (3)	Sb(2)-Cl(21)	2.275 (3)
Sb(1)-Cl(12)	2.288 (3)	Sb(2)-Cl(22)	2.271 (3)
Sb(1)-Cl(13)	2.283 (3)	Sb(2)-Cl(23)	2.286 (3)
Cl(A)-O(1)A	1.477 (7)	Cl(A)-O(3)A	1.390 (8)
Cl(A)-O(2)A	1.479 (7)	Cl(A)-O(4)A	1.398 (8)

O(121)-Sb(2)-O(122)	75.3 (3)	O(121)-Sb(1)-O(122)	75.6 (2)
O(121)-Sb(2)-O(1)A	84.3 (2)	O(121)-Sb(1)-O(2)A	85.9 (3)
O(121)-Sb(2)-Cl(22)	94.3 (2)	O(121)-Sb(1)-Cl(11)	94.9 (2)
O(121)-Sb(2)-Cl(21)	96.9 (2)	O(121)-Sb(1)-Cl(13)	162.1 (2)
O(121)-Sb(2)-Cl(23)	160.0 (2)	O(121)-Sb(1)-Cl(12)	92.9 (2)
O(122)-Sb(2)-O(1)A	81.8 (3)	O(122)-Sb(1)-O(2)A	81.7 (2)
O(122)-Sb(2)-Cl(22)	164.5 (2)	O(122)-Sb(1)-Cl(11)	94.6 (2)
O(122)-Sb(2)-Cl(21)	93.6 (2)	O(122)-Sb(1)-Cl(13)	90.0 (2)
O(122)-Sb(2)-Cl(23)	89.6 (2)	O(122)-Sb(1)-Cl(12)	163.6 (2)
O(1)A-Sb(2)-Cl(22)	85.9 (2)	O(2)A-Sb(1)-Cl(11)	175.9 (2)
O(1)A-Sb(2)-Cl(21)	174.8 (2)	O(2)A-Sb(1)-Cl(13)	81.6 (2)
O(1)A-Sb(2)-Cl(23)	80.5 (2)	O(2)A-Sb(1)-Cl(12)	85.9 (2)
Cl(22)-Sb(2)-Cl(21)	99.0 (1)	Cl(11)-Sb(1)-Cl(13)	96.8 (1)
Cl(22)-Sb(2)-Cl(23)	97.6 (1)	Cl(11)-Sb(1)-Cl(12)	98.0 (1)
Cl(21)-Sb(2)-Cl(23)	97.1 (1)	Cl(13)-Sb(1)-Cl(12)	98.8 (1)
O(4)A-Cl(A)-O(1)A	109.9 (5)	O(3)A-Cl(A)-O(4)A	115.0 (5)
O(4)A-Cl(A)-O(2)A	109.3 (5)	O(3)A-Cl(A)-O(1)A	108.1 (5)
O(1)A-Cl(A)-O(2)A	106.2 (4)	O(3)A-Cl(A)-O(2)A	108.0 (5)

distances between antimony atoms and bridging oxygens allowed the location of the hydroxo group, since hydrogen atoms were not located on the final Fourier difference map. These are O(122) in unit A and O(342) in unit B, whose mean distances to antimony atoms, respectively 2.056 (6) and 2.065 (6) Å, are longer. These distances are similar to those observed in analogous compounds Sb$_2$Cl$_6$(OH)(O)(L) by Schmidt et al.[18,19] (L = CH$_3$CO$_2$[18] and L = CCl$_3$CO$_2$[19]), where the perchlorato ligand is replaced by acetato or trichloroacetato ligands, respectively.

This is the second time a strongly coordinated bidentate perchlorato ligand has been encountered in an inorganic compound. The lengths of bridging Cl–O bonds are clearly longer than the terminal ones (mean value of 1.48 against 1.38 Å). Such a comparison generally provides a good quantification of the degree of the interaction between the ligand and the metal; for instance in the compound [Sn$_3$O$_2$Cl$_4$(ClO$_4$)$_4$]$_2$, recently described,[15] these distances were respectively 1.46 and 1.33 Å. In the same way, the comparison of angles between terminal–terminal bonds and bridging–bridging bonds (mean values of 115.0 and 1C5.8°) would lead to the same conclusions.
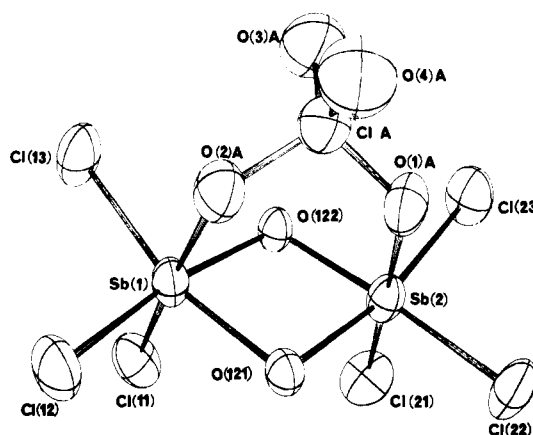

Figure 1. ORTEP diagram of a Sb$_2$Cl$_6$(OH)(O)(ClO$_4$) unit. Thermal ellipsoids are shown at the 50% probability level.

The comparison of the geometric data for compound Sb$_2$Cl$_6$(OH)(O)(L) (L = ClO$_4$,CCl$_3$CO$_2$,[19] CH$_3$CO$_2$[18]) shows that the SbO distances between metal and ligand decrease in the above order. This is, of course, due to the increase in basicity of the anions ClO$_4^-$ < CCl$_3$CO$_2^-$ < CH$_3$CO$_2^-$.

The geometries of molecular units A and B are similar. The packing in the unit cell is illustrated in Figure 2; the units A and B are linked to each other through a medium-strength hydrogen bond O(122)···O(341) (2.651 (9) Å) in an approximate cross arrangement. Each pair of units A and B is oriented along chains through weak interaction between the free hydroxo group, O(322), and the remaining bridging oxygen O(121). The distance between O(342) and O(121) is fairly long and would suggest van der Waals interaction rather than hydrogen bonding (2.996 (9) Å).

Infrared and Raman spectra are consistent with X-ray data; a splitting observed between IR and Raman frequencies agrees with the C_{2h} factor group corresponding to the $P2_1/n$ space group.

The broad band observed between 3600 and 2000 cm^{-1} in the IR spectrum and related to the Raman line at 2980 cm^{-1} is characteristic of the medium-strength hydrogen bond (d_{O-O} = 2.651 Å)[28] while the Raman line at 3350 cm^{-1} is assigned to the practically free OH vibrator (O(322)).

The three groups of lines occurring around 860, 1145, and 1270 cm^{-1} are assigned to the stretching modes in bidentate ClO$_4$ groups as in [Sn$_3$O$_2$Cl$_4$(ClO$_4$)$_4$]$_2$ and known perchlorato complexes.

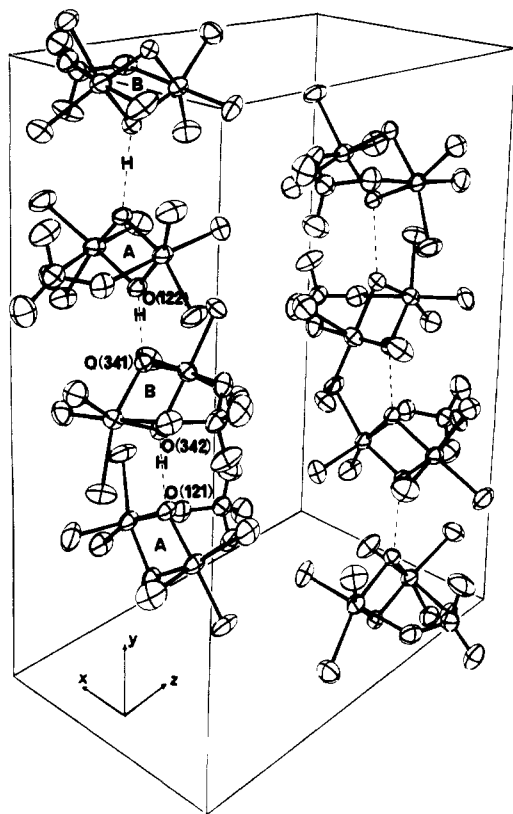(28) Claydon, M. F.; Sheppard, N. *J. Chem. Soc. D* **1969**, 1431.

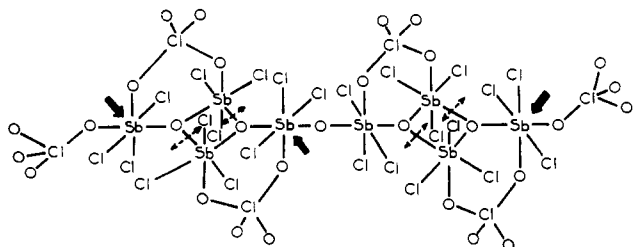**Figure 2.** Molecular arrangement of the two independent molecules in the unit cell.

Figure 3. Hypothetical structure for $Sb_8Cl_{24}O_5(ClO_4)_6$, showing the attack of water (dark arrows) and breaking of bonds (broken arrows) leading to $Sb_2Cl_6(OH)(O)(ClO_4)$.

The other significant stretchnig modes of SbCl and SbO bonds range from 200 to 550 cm^{-1}, and they are assigned as follows: 539 and 445 (R) and 545 and 455 (IR) to ν(Sb–O) ring, 424 and 305 (R and IR) to ν(SbCl), and 240 (R) and 230 (IR) to ν(Sb–O) (oxygen of ClO_4).

The structure of the compound $Sb_8Cl_{24}O_5(ClO_4)_6$ remains a challenging problem which could be approached by comparison with the structure of the $Sb_2Cl_6(OH)(O)(ClO_4)$ complex and with the use of spectroscopic data.

The only differences between their spectra are for $Sb_8Cl_{24}O_5(ClO_4)_6$ the lack of a broad band characteristic of an OH bond between 2100 and 3350 cm^{-1} and the presence of lines at 1295 (R), 1280 (IR), 1035 (R), 1020 (IR), 726 (R), and 712 cm^{-1} (IR), which describe the stretching modes of an unidentate ClO_4 group.

The coexistence of unidentate and bidentate ClO_4 groups in $Sb_8Cl_{24}(O)_5(ClO_4)_6$ as in the tin complex[15] allows us to imagine a basic skeleton composed of octahedrally surrounded antimony atoms linked to each other through tricoordinate and bicoordinate oxygen atoms as in the Sb_2O_5 frame.[29] The completion of the atomic arrangement around Sb is ensured

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(29) Jansen, M. *Angew. Chem., Int. Ed. Engl.* **1978,** *17,* 137.

by uni- and bidentate perchlorato groups and chlorine atoms as shown in Figure 3. This model is particularly in agreement with the two Raman lines observed at 242 and 233 cm^{-1} and assigned to Sb–O stretching vibrations between the metal and, respectively, the bidentate and monodentate perchlorates.

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Synthesis and Molecular and Crystal Structure of Tetrakis(tetraphenylarsonium) Tetrakis(dithiooxalato-*S*,*S'*)(μ-*trans*-dithiooxalato)diindate(III), $[(C_6H_5)_4As]_4[(O_2C_2S_2)_2In(SOC_2SO)In(S_2C_2O_2)_2]$

Ljubo Golič,[1a] Nada Bulc,[1a] and Wolfgang Dietzsch*[1b]

Although 1,2-dithiooxalate (dto) is among the classical sulfur ligands,[2] in the last years much work has been done on the coordination chemistry and characterization of this ligand showing some interesting points. Thus, the dithiooxalate has the highest ligand field strength of all known geminal and vicinal dithio ligands.[3] Coucouvanis and co-workers have shown that the presence of four donor atoms in the dithiooxalate dianion and the possibilities of charge delocalization on any two of these atoms result in a multifunctional ligand with unique coordination properties.[4] X-ray structure determinations and other studies demonstrate the ability of the ligand to coordinate to the central metal ion by two sulfur or two oxygen donor atoms, respectively.[4d,f,h] Further, dithiooxalate may coordinate simultaneously to more than one metal ion in polynuclear complexes that form when various parent dithiooxalate complexes react with coordinately unsaturated species. If $M(PR_3)_2^+$ cations (M = Cu, Ag) are used, surprisingly, in the cases of iron or tin tris(dithiooxalates) a ligand reorganization from S,S chelation to O,O chelation to the central metal ion was found and confirmed by X-ray structure analysis.[4f,h] At present there is no evidence for such bridging dithiooxalate in the trans form proposed in few cases from infrared studies.[4e,g] In the $(Ph_4As)_4[In_2(dto)_5]$ complex salt

(1) (a) Edvard Kardelj University of Ljubljana. (b) Karl Marx University of Leipzig.
(2) For example: (a) Jones, H. O.; Tasker, H. S. *J. Chem. Soc.* **1909,** *95,* 1904. (b) Robinson, C. S.; Jones, H. O. *Ibid.* **1912,** *101,* 62. (c) Cox, E. G.; Wardlaw, W.; Webster, K. C. *Ibid.* **1935,** 1475.
(3) (a) Latham, A. R.; Hascall, V. C.; Gray, H. B. *Inorg. Chem.* **1965,** *4,* 788. (b) Lockyer, T. N.; Martin, R. L. *Prog. Inorg. Chem.* **1980,** *27,* 223.
(4) (a) Coucouvanis, D. *J. Am. Chem. Soc.* **1970,** *92,* 707. (b) Coucouvanis, D.; Coffman, R. E.; Piltingsrud, D. *Ibid.* **1970,** *92,* 5004. (c) Coucouvanis, D. *Ibid.* **1971,** *93,* 1786; (d) Coucouvanis, D.; Baenziger, N. C.; Johnson, S. M. *Ibid.* **1973,** *95,* 3875. (e) Coucouvanis, D.; Piltingsrud, D. *Ibid.* **1973,** *95,* 5556. (f) Hollander, F. J.; Coucouvanis, D. *Inorg. Chem.* **1974,** *13,* 2381. (g) Leitheiser, M.; Coucouvanis, D. *Ibid.* **1977,** *16,* 1611. (h) Hollander, F. J.; Leitheiser, M.; Coucouvanis, D. *Ibid.* **1977,** *16,* 1615. (i) Czernuszewicz, R.; Strommen, D. P.; Nakamoto, K. *Inorg. Chim. Acta* **1979,** *34,* L211.