The error limits reported in Table II represent the ranges of the variables for which $\sigma_{\min} < 1.5\sigma_{\min}$. In all cases $1.5\sigma_{\min} \leq 3N$ where N = number of data points (eq 12). Excellent agreement between the calculated and experimental concentrations could be obtained provided this criterion was met. By contrast, calculations for which $\sigma_{\min} > 3N$ were found to be relatively insensitive to large changes in the variables, exhibiting little or no change in either $\sigma_{\min}$ or the calculated concentrations. These situations arose when the experimental data contained large uncertainties. Thus, a useful empirical criterion for the reliability of the calculated rate constants appears to be $\sigma_{\min} < 3\,N$.

Acknowledgments.—We thank the University Research Council for financial support, E. I. du Pont de Nemours and Co. for a summer fellowship (G. A. T.), the National Science Foundation for a Center of Excellence Grant to the department, Mr. H. B. Dellinger for assistance with some of the experimental work, Professor L. G. Pedersen for invaluable assistance in designing the kinetic analysis program, and Professor T. J. Meyer for several helpful discussions.

Appendix

Case 2: $A00 = A_2 = 100\%,\ A_1 = A_3 = 0$ at $t = 0$

$$\mathrm{A}_1 \underset{k_{21}}{\overset{k_{12}}{\rightleftarrows}} \mathrm{A}_2 \underset{k_{32}}{\overset{k_{23}}{\rightleftarrows}} \mathrm{A}_3$$

$$\mathrm{d}[\mathrm{A}_1]/\mathrm{d}t = k_{21}[\mathrm{A}_2] - k_{12}[\mathrm{A}_1]$$

$$\mathrm{d}[\mathrm{A}_2]/\mathrm{d}t = k_{12}[\mathrm{A}_1] - (k_{21} + k_{23})[\mathrm{A}_2] + k_{32}[\mathrm{A}_3]$$

$$\mathrm{d}[\mathrm{A}_3]/\mathrm{d}t = k_{23}[\mathrm{A}_2] - k_{32}[\mathrm{A}_3]$$

Replacing d/dt by the operator P and recalling that at $t = 0$, $[\mathrm{A}_2] = A00$

$$P[\mathrm{A}_1] = k_{21}[\mathrm{A}_2] - k_{12}[\mathrm{A}_1]$$

$$P[\mathrm{A}_2] - PA00 = k_{12}[\mathrm{A}_1] - (k_{21} + k_{23})[\mathrm{A}_2] + k_{32}[\mathrm{A}_3]$$

$$P[\mathrm{A}_3] = k_{23}[\mathrm{A}_2] - k_{32}[\mathrm{A}_3]$$

Solving these in succession gives

$$[\mathrm{A}_1] = \frac{k_{21}A00(P + k_{32})}{(P + \gamma_1)(P + \gamma_2)}$$

$$[\mathrm{A}_2] = \frac{A00(P + k_{32})(P + k_{12})}{(P + \gamma_1)(P + \gamma_2)}$$

$$[\mathrm{A}_3] = \frac{k_{23}(A00)(P + k_{12})}{(P + \gamma_1)(P + \gamma_2)}$$

where γ_1 and γ_2 are the roots of the quadratic equation

$$\gamma^2 + \gamma(k_{12} + k_{23} + k_{21} + k_{32}) + k_{12}k_{23} + k_{32}k_{21} + k_{12}k_{32} = 0$$

Transforming to the originals (ref 13, eq 8, 12, and 8) gives

$$\begin{aligned}[\mathrm{A}_1] &= \text{eq } 4\\ [\mathrm{A}_2] &= \text{eq } 5\\ [\mathrm{A}_3] &= \text{eq } 6\end{aligned}$$

CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY,
UNIVERSITY OF GUELPH, GUELPH, ONTARIO, CANADA

Organoantimony Compounds. VI.[1] Oxybis(triorganoantimony) Diperchlorates and Their Complexes with Oxygen-Donor Lewis Bases

BY R. G. GOEL* AND H. S. PRASAD

Received December 13, 1971

Preparation and structural aspects of oxybis(triorganoantimony) diperchlorates $(\mathrm{R_3Sb})_2\mathrm{O(ClO_4)_2}$, where R = Ph or Me, have been reinvestigated. Previously reported $(\mathrm{Ph_3Sb})_2\mathrm{O(ClO_4)_2}$ has been shown to be a hydrate. In contradiction to the conclusions reached in previous studies, the anhydrous diperchlorates are indicated to contain pentacoordinate antimony in the solid state. Complexes containing pentacoordinate cations $[(\mathrm{R_3SbL})_2\mathrm{O}]^{2+}$, where L = DMA, DMSO, DPSO, pyO, $\mathrm{Ph_3PO}$, and $\mathrm{Ph_3AsO}$, have also been isolated and characterized by infrared spectroscopic and conductance measurements.

Introduction

Preparation and infrared spectra of oxybis(triorganoantimony) diperchlorates[2,3] $(\mathrm{R_3SbOSbR_3})(\mathrm{ClO_4})_2$, where R = Me or Ph, were reported a few years ago. On the basis of the ir spectroscopic data,[2,3] in the solid state, these compounds were considered to contain the cation $(\mathrm{R_3SbOSbR_3})^{2+}$. Recent studies on the analogous oxybis(triphenylbismuth) diperchlorate[4] showed that this compound exists in two forms, hydrated and anhydrous. The hydrated form is orthorhombic and appears to contain the dihydrated cation $[(\mathrm{Ph_3Bi})_2\mathrm{O}(\mathrm{OH_2})_2]^{2+}$. The anhydrous form is monoclinic and its ir spectrum indicated a nonionic structure. A subsequent single-crystal X-ray diffraction study[5] has now confirmed that in the anhydrous compound the perchlorates are coordinated to bismuth atoms and that each bismuth atom has a slightly distorted trigonal-bipyramidal configuration. Since the perchlorate ir frequencies reported for the oxybis(triphenylantimony) diperchlorate in the previous work[2] were similar to those observed for the hydrated oxybis(triphenylbismuth) diperchlorate,[4] it led us to believe that the previously reported ir data[2] were obtained on the hydrated species. We, therefore, reinvestigated the preparation and structural aspects of oxybis(triphenylantimony) diperchlorate and our results show that the previously reported ir spectrum[2] is in fact due to the hydrated species and

---

(1) Part V: R. G. Goel and D. R. Ridley, *J. Organometal. Chem.*, **38**, 83 (1972).

(2) G. O. Doak, G. G. Long, and L. D. Freedman, *ibid.*, **4**, 82 (1965).

(3) G. G. Long, G. O. Doak, and L. D. Freedman, *J. Amer. Chem. Soc.*, **86**, 209 (1964).

(4) R. G. Goel and H. S. Prasad, *J. Organometal. Chem.*, **36**, 323 (1972).

(5) G. Ferguson, R. G. Goel, F. C. March, D. R. Ridley, and H. S. Prasad, *Chem. Commun.*, 1547 (1971).

that the infrared spectrum of the anhydrous compound is indeed best interpreted in terms of a nonionic structure. We have also reinvestigated trimethylantimony diperchlorate and we find that the infrared spectrum of this compound is also significantly different from that reported[3] previously. To obtain further information on the nature of these diperchlorates, their complexes with several O-donor Lewis bases have also been isolated and characterized by infrared spectroscopy and conductance measurements.

Results and Discussion

Oxybis(triphenyl- and trimethylantimony) Diperchlorates.—The reaction of triphenylantimony dichloride with silver perchlorate, as described in the previous work,[2] afforded hydrated oxybis(triphenylantimony) diperchlorate. However, this compound is obtained more conveniently and in better yield from the reaction of oxybis(triphenylantimony) dichloride with silver perchlorate. Analytical data (Table I), proton nmr, and thermogravimetric measurements indicate that the product is a dihydrate. The nmr spectrum of the hydrated diperchlorate in acetone-d_6 showed a multiplet (centered at δ 7.68) due to the phenyl protons and a single peak (δ 5.21) due to water. The relative intensities of the phenyl and the water peaks were in the ratio 7.8:1. The thermogram of the hydrate showed a weight loss of 3.72% at 165°. The anhydrous oxybis(triphenylantimony) diperchlorate was obtained by treating the hydrated compound with triethyl orthoformate. The anhydrous compound melts at 307° without any explosion. Upon exposure to atmospheric air it is converted into the hydrated form. Both the anhydrous and the hydrated compounds are soluble in polar organic solvents such as alcohol, acetone, and nitromethane. They are also slightly soluble in chloroform and dichloromethane. The oxybis(trimethylantimony) diperchlorate does not form a hydrate and it also is prepared much more conveniently from the metathetical reaction of the oxybis(trimethylantimony) dichloride with silver perchlorate. In contrast to the previously reported method[3] no explosion was observed at any stage of the preparation of this compound by this method. However, the compound exploded at 280° during attempts to determine the melting point. Unlike the phenyl compound it is not soluble in chlorocarbon solvents, but it is soluble in donor solvents such as acetone, alcohol, or nitromethane. It is also soluble in water.

Ir spectra of these compounds were examined in the solid state in the 4000–200-cm^{-1} region. The perchlorate frequencies observed for the anhydrous oxybis(triphenylantimony) diperchlorate are significantly different from those reported in the previous work.[2] Three strong well-resolved perchlorate bands are observed at 1155, 1015, and 868 cm^{-1}. Two other perchlorate bands of medium intensity are also observed at 625 and 400 cm^{-1}. These frequencies are in the same range as those observed for the anhydrous oxybis(triphenylbismuth) diperchlorate[4] as well as other perchlorato complexes.[6–8] In view of the ir data, then, there seems little doubt that in the solid state the anhydrous oxybis(triphenylantimony) diperchlorate has a nonionic structure similar to that for the bismuth compound.[5] The separation of the 1155- and 1015-cm^{-1} frequencies ($\Delta\nu$ = 140 cm^{-1}) which corresponds to the splitting of the ν_3 mode of the ClO_4^- is significantly greater than that for the bismuth compound (100 cm^{-1}). The 868-cm^{-1} frequency which corresponds to the ν_1 mode of the ClO_4^- is significantly lower than that for the bismuth compound (900–920 cm^{-1}). These differences in the perchlorate frequencies between the antimony and the bismuth compounds imply that the Sb–$OClO_3$ bond is stronger than the Bi–$OClO_3$ bond. The spectrum of the hydrated oxybis(triphenylantimony) diperchlorate shows bands at 3300 and 1640 cm^{-1} which can be attributed to the O–H stretching and bending frequencies, respectively. The perchlorate frequencies for the hydrated diperchlorate are observed at 1120, 1050, 928, 625, and 418 cm^{-1}. Except for the 418-cm^{-1} band, these frequencies are similar to those observed for the hydrated bismuth compound as well as to those previously reported[2] for the oxybis(triphenylantimony) diperchlorate. It is, therefore, evident that the previously reported ir data were obtained on the hydrated compound. The perchlorate bands observed for the hydrated compound also indicate the lowering of the perchlorate symmetry.[6] This can be attributed to either hydrogen bonding or coordination. The perchlorate frequencies for the hydrated diperchlorate are also similar to those for the triphenylhydroxyarsonium perchlorate.[9] The splittings of the perchlorate bands in the arsonium perchlorate are certainly due to the hydrogen bonding, since recent X-ray diffraction studies[10] show that in triphenylhydroxyarsonium chloride or bromide the arsenic atom is tetrahedrally bonded to three phenyl rings and to an oxygen atom which is hydrogen bonded to the chloride or bromide ion. It is therefore very likely that the oxybis(triphenylantimony) diperchlorate dihydrate also has an ionic structure in the solid state and that the observed splittings in the perchlorate frequencies for this compound are caused by hydrogen bonding. An indirect support for the ionic formulation of the dihydrate is also provided by the formation of cationic complexes of the diperchlorate with several O-donor ligands (*vide infra*). The Sb–O–Sb stretching frequency and other frequencies observed for the anhydrous as well as the hydrated oxybis(triphenylantimony) diperchlorate are similar to those reported in the previous work.[2]

A very strong perchlorate infrared band between 1150 and 1040 cm^{-1}, partially resolved into three or four components, was reported[3] for the oxybis(trimethylantimony) diperchlorate. For this compound, in this region, we observe two strong well-resolved perchlorate bands at 1132 and 1045 cm^{-1} and a medium perchlorate band at 928 cm^{-1}. The 1045-cm^{-1} band shows a splitting of *ca.* 10 cm^{-1}. Two other perchlorate bands of medium intensity are also observed at 622 and 468 cm^{-1}. Also, a strong band due to the Sb–O–Sb asymmetric stretching frequency reported in the previous work[3] at 775 cm^{-1} is observed at 820 cm^{-1}. The Sb–C stretching frequencies were found to be sim-

---

[6] K. Nakamoto, "Infrared Spectra of Inorganic and Coordination Compounds," Wiley, New York, N. Y., 1970, pp 109, 175.

[7] G. A. Rodley and P. W. Smith, *J. Chem. Soc. A*, 1580 (1967), and references therein.

[8] "Spectroscopic Properties of Inorganic and Organometallic Compounds," Vol. 1, The Chemical Society, London, 1968, p 204.

[9] G. S. Harris and F. Inglis, *J. Chem. Soc. A*, 497 (1967).

[10] G. Ferguson and E. W. Macaulay, *Chem. Commun.*, 1288 (1968).

TABLE I

ANALYTICAL AND CONDUCTANCE DATA

					Molar conductance data			
	% C		% H		Nitromethane		Dichloromethane	
Compound	Calcd	Found	Calcd	Found	Concn, *M*	Λ_M[i]	Concn, *M*	Λ_M[i]
$(Ph_3Sb)_2O(ClO_4)_2$[a]	46.95	46.69	3.28	3.44	2.04×10^{-3}	171.79	2.00×10^{-3}	2.36
$[Ph_3Sb)_2O(ClO_4)_2](H_2O)_2$	45.18	45.45	3.58	3.38	1.00×10^{-3}	181.59	1.03×10^{-3}	2.49
$(Me_3Sb)_2O(ClO_4)_2$[c]	13.11	13.12	3.30	3.34	2.28×10^{-3}	132.19		
$[Ph_3Sb(DMA)]_2O(ClO_4)_2$[a,b]	48.24	48.29	4.41	4.56	1.17×10^{-3}	163.44	5.01×10^{-4}	47.00
$[Me_3Sb(DMA)]_2(ClO_4)_2$[a,b,e]					2.12×10^{-3}	170.45		
$[Ph_3Sb(DMSO)]_2O(ClO_4)_2$[a,b]	44.60	44.81	3.93	4.36	1.57×10^{-3}	166.15	1.06×10^{-3}	30.52
$[Ph_3Sb(DMSO\text{-}d_6)]_2O(ClO_4)_2$[a]	44.10	44.45	3.86[g]	3.98				
$[Me_3Sb(DMSO)]_2O(ClO_4)_2$[a,b,d]	17.04	16.19	4.29	4.61	4.21×10^{-3}	145.79	1.65×10^{-3}	41.24
$[Ph_3Sb(DPSO)]_2O(ClO_4)_2$[a]	54.36	54.31	3.80	3.46	2.22×10^{-3}	159.72	1.65×10^{-3}	22.69
$[Me_3Sb(DPSO)]_2O(ClO_4)_2$[a]	36.43	36.66	3.49	3.71	1.75×10^{-3}	151.71		
$[Ph_3Sb(pyO)]_2O(ClO_4)_2$[f]	49.72	49.63	3.63	3.87	1.03×10^{-3}	175.63	1.03×10^{-3}	34.77
$[Me_3Sb(pyO)_2O(ClO_4)_2$[a]	26.01	26.17	3.82	3.70	2.23×10^{-3}	153.33	1.66×10^{-3}	8.64[h]
$[Ph_3Sb(Ph_3PO)]_2O(ClO_4)_2$	58.52	59.03	4.09	4.34	0.97×10^{-3}	108.06	1.00×10^{-3}	53.10
$[Me_3Sb(Ph_3PO)]_2O(ClO_4)_2$	44.68	44.42	3.94	4.23	1.13×10^{-3}	156.50	0.95×10^{-3}	7.71[h]
$[Ph_3Sb(Ph_3AsO)]_2O(ClO_4)_2$[b]	55.24	55.80	3.86	3.97	1.01×10^{-3}	158.04	2.00×10^{-3}	63.44
$[Me_3Sb(Ph_3AsO)]_2O(ClO_4)_2$[b]	42.28	42.06	4.05	3.90	1.22×10^{-3}	170.81	0.93×10^{-3}	37.33

[a] Hygroscopic. [b] Recrystallized from absolute alcohol containing ligand. [c] Per cent Sb: calcd, 43.38; found, 43.59. [d] Better analyses could not be obtained. [e] Exploded on combustion. [f] Per cent N: calcd, 2.52; found, 2.48. [g] Calcd as H. [h] Conductance increased on adding pyO or Ph_3PO. [i] In ohm^{-1} cm^2 mol^{-1}.

ilar to those reported in the previous work.[3] Although previous workers[3] interpreted the infrared spectrum of this compound in terms of an ionic structure, we consider that the observed lowering of the perchlorate symmetry is caused by coordination. However, on comparing the perchlorate frequencies for this compound with those for the analogous phenyl derivative, it is evident that the coordination in the methyl compound is weaker. As reported later in this paper, no significant splittings are observed for the perchlorate bands in the spectra of the cationic complexes of oxybis(triorganoantimony) diperchlorates. Thus it is not very likely that the observed lowering of the perchlorate symmetry is caused by the solid-state effects. Incomplete crystal structure data[11] for this compound have been reported recently and on the basis of these data an ionic structure containing the $[(CH_3)_3SbOSb(CH_3)_3]^{2+}$ cation and the ClO_4^- anion has been concluded. However, the distance between the perchlorate oxygen atom and the antimony atom is reported to be 2.20 Å which is even shorter than the Sb–C distance reported to be 2.26 Å. Obviously the reported Sb–O(ClO_4) bond distance cannot be correct and structural conclusions based on these data can only be misleading.

Ir spectra for the anhydrous and the hydrated oxybis(triphenylantimony) diperchlorate were also determined in dichloromethane. Due to the interference with the solvent bands, spectra were, however, obtained only for the 1200–950-cm^{-1} region. In this region, both the anhydrous as well as the hydrated diperchlorates showed two strong perchlorate bands at 1160 and 1015 cm^{-1}. Under similar conditions the spectrum of tetraethylammonium perchlorate showed a single perchlorate band at *ca.* 1100 cm^{-1}. Molar conductances for these compounds in dichloromethane which are shown in Table I are very close to those for the analogous bismuth compounds.[4] However, they are much lower than those for ionic perchlorates (*vide infra*). Thus, the ir and conductance data in dichloromethane suggest that the anhydrous as well as the hydrated oxybis(triphenylantimony) diperchlorate exists as either ion pairs or nonionic species in this solvent. As shown in Table I, molar conductances for the hydrated as well as the anhydrous diperchlorate in nitromethane correspond to those for 1:2 electrolytes.[12] The oxybis(trimethylantimony) diperchlorate is also dissociated in nitromethane. However, its ir spectrum and conductance could not be measured in dichloromethane, due to its insolubility in this solvent.

Complexes of Oxybis(triphenyl- and trimethylantimony) Diperchlorates.—Treatment of oxybis(triphenyl- and trimethylantimony) diperchlorates with O-donor Lewis bases resulted in the formation of cationic complexes of the type $[(R_3SbL)_2O](ClO_4)_2$. In this study complexes were isolated and characterized for L = dimethylacetamide (DMA), dimethyl sulfoxide (DMSO), diphenyl sulfoxide (DPSO), pyridine *N*-oxide (pyO), triphenylphosphine oxide (Ph_3PO), and triphenylarsine oxide (Ph_3AsO). The analytical data for the complexes are shown in Table I. All the complexes are white crystalline compounds and are soluble in polar organic solvents. Complexes of DMA, DMSO, DPSO, and pyO are sensitive to the atmospheric moisture; others can be handled in the air. The DMA complex of oxybis(trimethylantimony) diperchlorate is explosive. Several explosions occurred during handling and attempted analysis of this compound.

Important ir frequencies for the complexes together with their assignments are listed in Table II. These assignments have been made by comparing the spectra (4000–200-cm^{-1} region, in the solid state) of the complexes with those of the free ligands and the anhydrous organoantimony diperchlorates. Since the CH_3 rocking vibrations[13,14] in DMSO occur in the same spectral region as ν(SO), the assignments for the ν(SO) frequency in DMSO complexes were confirmed by studying the DMSO-d_6 complex. For each complex the perchlorate bands are observed at *ca.* 1100 and 625 cm^{-1}, which are characteristics of a free perchlorate ion.[6] No splitting is observed for either of these bands, except in the case of $[Me_3Sb(Ph_3AsO)]_2(ClO_4)_2$, for

---

[11] H. W. Baird, *J. Elisha Mitchell Sci. Soc.*, **86**, 173 (1970). We thank Professor G. O. Doak for a copy of this reference.

[12] R. S. Drago, "Non Aqueous Solvent Systems," T. C. Waddington, Ed., Academic Press, New York, N. Y., 1965, p 235.

[13] M. T. Forel and M. Tranquille, *Spectrochim. Acta, Part A*, **26**, 1023 (1970).

[14] W. D. Horrocks, Jr., and F. A. Cotton, *Spectrochim. Acta*, **17**, 134 (1961).

TABLE II

INFRARED DATA[a] (CM^{-1})

Compound	ν(XO)		ν(Sb–O)	Anion freq
	Complex	Free ligand		
$[Ph_3Sb(DMA)]_2O(ClO_4)_2$	1600 s 1600 s[b]	1640 s[d] 1645 s[b]		1095 vs, 625 m
$[Me_3Sb(DMA)]_2O(ClO_4)_2$	1618 s			1116 vs, 625 m
$[Ph_3Sb(DMSO)]_2O(ClO_4)_2$	930 s 935 s[b]	1055[d]	422 m	1095 vs, 625 m
$[Ph_3Sb(DMSO\text{-}d_6)]_2O(ClO_4)_2$	935 s 965–945 s[b]		380 m	1095 vs, 625 m
$[Me_3Sb(DMSO)]_2O(ClO_4)_2$	962 s 955 s[b]		420 m	1090 vs, 625 m
$[Ph_3Sb(DPSO)]_2O(ClO_4)_2$	918 s	1040 s		1090 vs, 625 m
$[Me_3Sb(DPSO)]_2O(ClO_4)_2$	982 s			1100 vs, 625 m
$[Ph_3Sb(pyO)]_2O(ClO_4)_2$	1202, 1192 m	1245 s 1250 s[c]	360–335 b, m	1090 vs, 624 m
$[Me_3Sb(pyO)]_2O(ClO_4)_2$	1212 m 1212 w[c]		330 m	1095 vs, 625 m
$[Ph_3Sb(Ph_3PO)]_2O(ClO_4)_2$	1160 s 1145 m[b]	1190 s 1192 s[b]		1090 vs, 625 m
$[Me_3Sb(Ph_3PO)]_2O(ClO_4)_2$	1150 s 1150 m[b]			1095 vs, 625 m
$[Ph_3Sb(Ph_3AsO)]_2O(ClO_4)$	835 s 845–835 s[b]	880 s 890 s[b]	395 m	1090 vs, 626 m
$[Me_3Sb(Ph_3AsO)]_2O(ClO_4)_2$	855 s 838 s[b]		380 m	1105–1085 vs, 624 m

[a] In solid state unless stated otherwise. Key: b, broad; m, medium; s, strong; vs, very strong. [b] In CH_2Cl_2. [c] In $CDCl_3$. [d] Liquid.

which the ν_3 mode appears as a doublet showing maxima at 1105 and 1085 cm^{-1}. The ν(XO) frequency (X = C, S, N, P, As) in each complex is seen to decrease significantly from that in the free ligand.[13–19] The observed negative shifts of the ν(XO) frequency as well as the changes in the perchlorate frequencies clearly show that these complexes contain the cation $[(R_3SbL)_2O]^{2+}$ in which the antimony atoms are five-coordinate. The ν(CO) and ν(SO) frequencies for the DMA, DMSO, and DPSO complexes occur in the same spectral region as reported for the other O-bonded complexes of these ligands.[15,16,20–23] The ν(NO), ν(PO), and ν(AsO) frequencies are also comparable to those reported for other complexes[18,19,24–27] of these ligands. At the completion of this work, neutral complexes[28] of diorganoantimony trichlorides with DMSO, pyO, and Ph_3PO have also been reported and the ν(SO), ν(NO), and ν(PO) frequencies for these complexes are very similar to those in this work.

For the DMSO, pyO, and Ph_3AsO complexes, an additional band of medium intensity is observed in the low-frequency region which can be assigned to the ν(Sb–O) frequency. In the case of the DMSO complexes the confirmation of this assignment is provided by the negative shift of this frequency in the DMSO-d_6 complex. A similar shift in the ν(M–O) frequency upon deuteration has also been reported for the DMSO complexes[22] of Ga(III) and In(III). The proposed assignments for the ν(Sb–O) frequency are comparable to the reported ν(Sn–O) frequencies for the tin(IV) complexes.[24,26] The assigned ν(Sb–O) frequencies for the DMSO and pyO complexes can also be compared with the recently reported assignments for the diorganoantimony(V) complexes.[28] The spectra of Ph_3PO complexes also show an additional band at *ca.* 400 cm^{-1}. However, similar bands are also observed for the Ph_3PO complexes of organobismuth(V) derivatives which are being currently investigated in our laboratory. Other workers[19,26] have also observed that the ir spectra of the Ph_3PO complexes in the low-frequency region show some additional bands which are not observed in the free ligand. Although the metal–oxygen stretching frequencies for Ph_3PO complexes of antimony trichloride[29] as well as some tin(IV) derivatives[26] have been assigned, in view of the arguments put forward by Deacon and Green[19] these assignments appear to be uncertain. Due to the presence of several ligand bands in the low-frequency region, the ν(Sb–O) frequency for the DMA and DPSO complexes was also not assigned in this work.

The ν(XO) frequencies for the complexes prepared in this study were also determined in dichloromethane or deuterated chloroform and the spectroscopic data are included in Table II. The DPSO complexes as well as the complexes $[Ph_3Sb(pyO)]_2O(ClO_4)_2$ and $[Me_3Sb(DMA)_2]_2O(ClO_4)_2$ are not sufficiently soluble in these solvents. As can be seen from the data in Table II, the ν(XO) frequency for the complexes is not significantly altered in solution. However, the solution spectra for

---

(15) W. F. Currier and J. H. Weber, *Inorg. Chem.*, **6**, 1539 (1967).

(16) P. W. N. M. van Leeuwen and W. L. Groenveld, *Recl. Trav. Chim. Pays-Bas*, **86**, 201 (1967), and references therein.

(17) W. Gerrard, M. F. Lappert, H. Pyszora, and J. W. Wallis, *J. Chem. Soc.*, 2144 (1960).

(18) S. Kida, J. V. Quagliano, J. A. Walmsley, and S. Y. Tyree, *Spectrochim. Acta*, **19**, 189, 201 (1963), and references therein.

(19) G. B. Deacon and J. H. S. Green, *Spectrochim. Acta, Part A*, **24**, 845 (1968); **25**, 355 (1969); and references therein.

(20) N. E. Bull, S. K. Madan, and J. E. Willis, *Inorg. Chem.*, **2**, 303 (1963).

(21) V. G. Kumar Das and W. Kitching, *J. Organometal. Chem.*, **10**, 59 (1967).

(22) A. J. Carty, H. A. Patel, and P. M. Boorman, *Can. J. Chem.*, **48**, 492 (1970).

(23) W. L. Reynolds, *Progr. Inorg. Chem.*, **12**, 1 (1970).

(24) Y. Kawasaki, M. Hori, and K. Uneka, *Bull. Chem. Soc. Jap.*, **40**, 2463 (1967).

(25) G. A. Rodley, D. M. L. Goodgame, and F. A. Cotton, *J. Chem. Soc.*, 1499 (1965).

(26) J. P. Clark, V. M. Langford, and C. J. Wilkins, *J. Chem. Soc. A*, 792 (1967).

(27) V. G. Kumar Das and W. Kitching, *J. Organometal. Chem.*, **13**, 523 (1968).

(28) N. Nishi, Y. Matsumara, and R. Okawara, *ibid.*, **30**, 59 (1971).

(29) S. Milicev and D. Hadzi, *Inorg. Nucl. Chem. Lett.*, **7**, 745 (1971).

the DMA, pyO, and Ph_3PO complexes show $\nu(XO)$ frequencies due to the free ligand as well as due to the coordinated ligand. The spectra of Ph_3AsO complexes in dichloromethane do not indicate the presence of free Ph_3AsO. In the case of DMSO complexes it is difficult to ascertain the presence of free DMSO in solution due to the possible overlap of the $\nu(SO)$ frequency of the free DMSO with the strong perchlorate band at *ca.* 1100 cm^{-1}.

The molar conductances for these complexes in nitromethane and dichloromethane are shown in Table I. The conductance data in nitromethane are comparable to those reported for 1:2 electrolytes.[12] The molar conductance for a 10^{-3} *M* solution of tetraethylammonium perchlorate in dichloromethane was found to be 22.80 $ohm^{-1}\ cm^2\ mol^{-1}$. Therefore, Λ_M values for these complexes in dichloromethane are expected to be $\sim$40 $ohm^{-1}\ cm^2\ mol^{-1}$ or higher. The lower Λ_M values observed for some complexes, particularly for the pyO and Ph_3PO complexes of oxybis(trimethylantimony) diperchlorate, can be explained due to the following equilibrium in solution

$$(R_3SbL)_2O^{2+} + 2ClO_4^- \rightleftharpoons [R_3Sb(ClO_4)]_2O + 2L$$

In view of the ir data there is no doubt regarding the presence of the free ligand in solutions of the complexes of pyO and Ph_3PO. In accordance with the above equilibrium the conductance of dichloromethane solutions of $[Me_3Sb(pyO)]_2O(ClO_4)_2$ and $[Me_3Sb(Ph_3PO)]_2O(ClO_4)_2$ was seen to increase markedly upon addition of pyO or Ph_3PO.

Experimental Section

General Information.—Strictly anhydrous conditions were required for the preparation and handling of the moisture-sensitive compounds. These compounds were therefore manipulated either in a nitrogen-filled drybox or in a conventional vacuum system. Also, the solvents were thoroughly dried and stored under dry nitrogen. Dimethyl sulfoxide, dimethylacetamide, and nitromethane were dried by refluxing over calcium hydride, under reduced pressure, and subsequent distillation. Diethyl ether and methylene chloride were also distilled over calcium hydride under dry nitrogen. Petroleum ether (bp 35–60°) was dried over sodium wire and subsequently distilled. Ethanol was refluxed over magnesium and subsequently distilled. Pyridine *N*-oxide was purified by sublimation *in vacuo*. Trimethyl- and triphenylantimony and oxybis(trimethyl- and triphenylantimony) dichlorides were prepared by the methods described previously.[30] Elemental analyses of moisture-sensitive compounds were performed by Schwarzkopf Microanalytical Laboratory, Woodside, N. Y. Analyses for other compounds were performed in this department. Analytical data are recorded in Table I.

Oxybis(trimethylantimony) Diperchlorate.—In a typical preparation, 3.332 g of oxybis(trimethylantimony) dichloride was added to a solution of silver perchlorate (3.293 g) in ethanol and stirred for about 0.5 hr. The resultant mixture was filtered and the filtrate was concentrated under vacuum when oxybis(trimethylantimony) diperchlorate separated as thick white crystals. The compound was recrystallized from a mixture of acetone and petroleum ether (bp 35–60°).

Oxybis(triphenylantimony) Diperchlorate Dihydrate.—This was also prepared by the above-described method. The product was recrystallized at ∼5° from a mixture of ethanol, diethyl ether, and petroleum ether (bp 35–60°).

Oxybis(triphenylantimony) Diperchlorate (Anhydrous).—Triethyl orthoformate was added to a solution of hydrated oxybis(triphenylantimony) diperchlorate in absolute ethanol. Diethyl ether was then slowly added to the above solution until it became turbid. Upon storing the turbid solution overnight in a refrigerator, crystals of anhydrous oxybis(triphenylantimony) diperchlorate appeared which were collected and dried *in vacuo*.

Preparation of Complexes.—Complexes were prepared by mixing the diperchlorate and the ligand, in 1:2 mole ratio, in absolute alcohol. The solution was allowed to stand overnight. The complexes of DMA, DMSO, DPSO, and pyO were isolated by removing the solvent *in vacuo* until crystals of the complex appeared. The complexes of Ph_3PO and Ph_3AsO were isolated by adding dropwise petroleum ether (bp 35–60°) or diethyl ether to the solution until it became turbid. The turbid solution was refrigerated until crystals of the complex were obtained. The crystals were washed successively with benzene, petroleum ether (bp 35–60°), and diethyl ether and then dried *in vacuo*. Attempts to recrystallize the complexes from various solvents resulted in the partial loss of ligand. Some of the complexes could be recrystallized from absolute alcohol to which ligand had been added.

Physical Measurements.—Infrared spectra were recorded on a Beckman IR-12 double beam spectrophotometer using KRS-5, polyethylene, and silver bromide windows. Solid samples were prepared as mulls in Nujol or Halocarbon oil. NaCl or AgBr cells (0.1-mm path length) were used to obtain spectra in solution. Conductance measurements were made at 25° using a Beckman RC-18 coductivity bridge. Nmr spectra were obtained on a Varian A-60 spectrometer using internal TMS reference. Melting points were determined with a Gallenkamp apparatus and are uncorrected. Thermogravimetric data were obtained at the Uniroyal Research Laboratories, Guelph, Ontario.

Acknowledgment.—This work was supported by a research grant from National Research Council of Canada.

---

[30] R. G. Goel, P. M. Joshi, D. R. Ridley, and R. E. Beaumont, *Can. J. Chem.*, **47**, 1423 (1969), and references therein.