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ORGANOANTIMONY COMPOUNDS

VII*. PREPARATION AND CHARACTERIZATION OF COMPLEX TRIORGANOANTIMONY(V) CATIONS, $R_3SbL_2^{2+}$

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SUMMARY

Pentacoordinate cationic complexes of the type $[R_3SbL_2](ClO_4)_2$, where R = methyl or phenyl, and L = DMSO, DMSO-d_6, DPSO, Ph_3PO or Ph_3AsO, have been isolated and characterized by elemental analysis, infrared and proton NMR spectral and conductance measurements. The Sb–O stretching frequencies for the complex cations containing DMSO, DMSO-d_6 and Ph_3AsO occur in the 475 to 400 cm^{-1} region. For the complexes containing DPSO or Ph_3PO, definite assignments cannot be made for this frequency. All the complexes behave as 1/2 electrolytes in nitromethane. The infrared spectral measurements in dichloromethane or nitromethane indicate no dissociation of the complex cations in these solvents.

INTRODUCTION

There has been considerable interest in the coordination chemistry of organometallic cations of main Group III and IV elements[1-6]. However, complex organometallic cations of Group V elements have received little attention. In an earlier study[7] the Raman spectra of aqueous solutions of $Me_3Sb(NO_3)_2$ and $Me_3Sb(ClO_4)_2$ have been interpreted in terms of planar Me_3Sb^{2+} cations. Very recently it has been shown that organoantimony perchlorates[8] of the type $[R_3Sb(OClO_3)]_2O$, where R = methyl or phenyl, react with neutral oxygen-donor ligands to form pentacoordinate cationic complexes of the type $[(R_3SbL)_2O](ClO_4)_2$. An aquo complex $[Ph_3Sb(H_2O)]_2O(ClO_4)_2$ has also been isolated[8]. In the present work complex triorganoantimony cations of the type $R_3SbL_2^{2+}$ have been prepared and characterized. Similar organobismuth complexes have been reported[9] elsewhere.

RESULTS AND DISCUSSION

The $R_3SbL_2^{2+}$ cations like the analogous bismuth cations are accessible by the following reaction in benzene:

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* For Part VI, see ref. 8.

$$R_3SbCl_2 + 2L + 2AgClO_4 \rightarrow [R_3SbL_2](ClO_4)_2 + 2AgCl$$

In contrast to the $Ph_3BiL_2^{2+}$ cations, which are unaffected by moisture, the $R_3SbL_2^{2+}$ cations are readily hydrolyzed to form the oxygen bridged $(R_3SbL)_2O^{2+}$ cations, and as such, they are much more difficult to isolate. The complexes isolated in this study are listed in Table 1. Attempts to isolate complexes of other O-donor ligands such as

TABLE 1

ANALYTICAL AND CONDUCTANCE DATA AND MELTING POINTS

Compound[a]	*C (%)*		*H (%)*		*M.p. (°C)*	*Molarconductance*[b]	
	Calcd.	*Found*	*Calcd.*	*Found*		*Concn., M*	Λ_M[c]
$[Ph_3Sb(DMSO)_2](ClO_4)_2$	37.71	37.29	3.84	3.97	207–8	1.19×10^{-3}	178.1
$[Ph_3Sb(DMSO\text{-}d_6)_2](ClO_4)_2$	36.68	36.95	3.77	3.91	204	1.57×10^{-3}	156.8
$[Me_3Sb(DMSO)_2](ClO_4)_2$	16.10	16.54	4.05	4.33	109–128[d]	0.95×10^{-3}	183.0
$[Ph_3Sb(DPSO)_2](ClO_4)_2$	52.73	52.99	3.68	4.18	197–199	1.24×10^{-3}	171.6
$[Ph_3Sb(Ph_3PO)_2](ClO_4)_2$	58.50	58.73	4.09	4.29	257	1.64×10^{-3}	150.0
$[Me_3Sb(Ph_3PO)_2](ClO_4)_2$	50.78	50.47	4.26	4.24	114–119[d]	1.17×10^{-3}	167.3
$[Ph_3Sb(Ph_3AsO)_2](ClO_4)_2$	54.21	53.98	3.79	3.84	190	0.70×10^{-3}	173.6
$[Me_3Sb(Ph_3AsO)_2](ClO_4)_2$	46.37	46.30	3.89	4.04	122–126[d]	1.25×10^{-3}	173.1

[a] DMSO = dimethyl sulfoxide; DPSO = diphenyl sulfoxide. [b] In $ohm^{-1} \cdot cm^2 \cdot mol^{-1}$. [c] In nitromethane at 25°. [d] Decomposed without melting.

TABLE 2

INFRARED[a] AND ¹H NMR DATA

Compound	*ν(XO)*[b]		*ν(Sb–O)*	*Anion frequencies*	*δ*[c,d]
	Complex	*Free ligand*			
$[Ph_3Sb(DMSO)_2](ClO_4)_2$	875 s 910[d]	1055 s[e]	476 m	1095 vs, 625 s	2.85 (DMSO)
$[Ph_3Sb(DMSO\text{-}d_6)]_2(ClO_4)_2$	870 ms 890 ms[d]		461 m	1100 vs, 625 s	
$[Me_3Sb(DMSO)_2](ClO_4)_2$	939 s 950 ms[d]		454 ms	1085 vs, 623 s	3.06 (DMSO) 2.31 ($SbCH_3$)
$[Me_3Sb(DMSO\text{-}d_6)_2](ClO_4)_2$	950 ms		435 m	1100 vs, 625 m	
$[Ph_3Sb(DPSO)_2](ClO_4)_2$	877 s 890 s[f], 880 s[d]	1044 s		1090 vs, 625 m	
$[Ph_3Sb(Ph_3PO)_2](ClO_4)_2$	1125 s 1124 s[f]	1190 s 1192 s[f]		1090 vs, 625 m 1100 vs[f]	
$[Me_3Sb(Ph_3PO)_2](ClO_4)_2$	1127 s 1127 s[f]			1090 vs, 625 m	2.20 ($SbCH_3$)
$[Ph_3Sb(Ph_3AsO)_2](ClO_4)_2$	802 ms 800 m[f], 800 ms[d]	880 s 890 s[f]	410 m	1090 vs, 625 m 1100 vs[f]	
$[Me_2Sb(Ph_3AsO)_2](ClO_4)_2$	800 ms 808 ms[f], 805 s[d]		405 m	1090 vs, 625 m 1100 vs[f]	1.96 ($SbCH_3$)

[a] In cm^{-1}; in the solid state unless stated otherwise. [b] X = S, P or As. [c] In ppm relative to internal TMS. [d] In nitromethane. [e] Liquid. [f] In dichloromethane.

pyridine *N*-oxide and *N,N*-dimethylacetamide were unsuccessful due to their hydrolytic instability.

All the complexes, listed in Table 1, were characterized in the solid state by their infrared spectra in the 4000 to 200 cm^{-1} region. The important infrared frequencies, together with their assignments, are listed in Table 2. As shown in Table 2, the $\nu(SO)$[10–13], $\nu(PO)$[14–15] or the $\nu(AsO)$[15–17] frequencies for these complexes are considerably lower than those for the free ligands. The perchlorate frequencies, for each complex, correspond to those reported for the free anion[18]. Therefore, it is clear that all the complexes, prepared in this work, contain the pentacoordinate cation $R_3SbL_2^{2+}$. The infrared spectra of the $R_3Sb(DMSO)_2^{2+}$ cations show a band of medium intensity in the ca. 475 to 430 cm^{-1} region which can be assigned to the Sb–O stretching frequency. As expected, this band is shifted to a lower frequency in the $R_3Sb(DMSO\text{-}d_6)_2^{2+}$ cations. The ratio of the frequencies $\nu(Sb{-}O)_{DMSO}/\nu(Sb{-}O)_{DMSO-d_6}$ for the phenyl as well as the methyl complexes is very close to the calculated ratio of 1.035[*]. In the spectra of the $R_3Sb(Ph_3AsO)_2^{2+}$ cations, a band of medium intensity at ca. 410–405 cm^{-1} can also be assigned to the Sb–O stretching frequency. The $\nu(Sb{-}O)$ frequencies for the DMSO as well as for the Ph_3AsO complexes are quite consistent with the $\nu(Bi{-}O)$ frequencies for the analogous triorganobismuth(V) complexes. This provides some confirmation for the validity of the proposed assignments. As discussed previously[8,9], reliable assignments cannot be made for the metal–oxygen stretching frequencies for the DPSO and Ph_3PO complexes.

The $\nu(Sb{-}O)$ frequencies for the $R_3SbL_2^{+}$ cations are higher than those for the corresponding $(R_3SbL)_2O^{2+}$ cations[8]. The shifts in the $\nu(XO)$ frequencies, $\Delta\nu(XO)$ $[\Delta\nu(XO) = \nu(XO)_{\text{free ligand}} - \nu(XO)_{\text{complex}}$; X = S, P or As], for the former cations are also considerably larger than those for the latter cations. Therefore the R_3Sb^{2+} cations are better electron pair acceptors than the $(R_3Sb)_2O^{2+}$ cations. The shifts in the $\nu(XO)$ frequencies for the $Ph_3SbL_2^{2+}$ and $Ph_3BiL_2^{2+}$ cation are comparable[9].

X-ray diffraction[19–21] and infrared and Raman spectroscopic[22,23] studies have shown that at least in the solid state the neutral R_3SbX_2 derivatives, where X is an anionic group, adopt a trigonal bipyramidal structure with the X groups in the apical positions. The infrared spectra of the $Me_3SbL_2^{2+}$ cations are also in accord with a similar structure as shown by the observation of single $Sb{-}CH_3$[**] and Sb–O stretching frequencies which can be assigned to the antisymmetric stretching modes. In the case of the $Me_3Sb(Ph_3PO)_2^{2+}$ cation, bands due to the Ph_3PO appear in the region of the symmetric $Sb{-}CH_3$ frequency but no bands are observed in this region in the spectra of the $Me_3Sb(DMSO)_2^{2+}$, $Me_3Sb(DMSO\text{-}d_6)_2^{2+}$ and $Me_3Sb(Ph_3AsO)_2^{2+}$ cations. Although the configuration of the phenyl groups bonded to antimony cannot be determined from the infrared spectra of the $Ph_3SbL_2^{2+}$ cations, the spectra of these cations also show a single Sb–O stretching frequency. Therefore, it is very likely that the $Ph_3SbL_2^{2+}$ cations are structurally similar to the $Me_3SbL_2^{2+}$ cations.

The behaviour of the $R_3SbL_2^{2+}$ cations in solution, in nitromethane or dichloromethane, was examined by conductance and infrared and proton NMR measure-

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[*] Based on a simple harmonic oscillator approximation assuming the $(CH_3)_2SO$ group as a single unit of mass.

[**] The antisymmetric $Sb{-}CH_3$ stretching frequency was observed at *ca.* 580 cm^{-1} which is similar to that observed for the Me_3SbX_2 derivatives.

ments. In either solvent the ν(XO) frequencies for the complex cations were not significantly altered from the solid state values. In no case was infrared spectral evidence found for the presence of the free ligand in solution. As shown in Table 1, the molar conductances for all the complexes, in nitromethane, correspond to those for 1/2 electrolytes[14]. The chemical shifts for the $SbCH_3$ and DMSO protons for the complex cations are recorded in Table 2. As expected, single sharp resonance signals were observed for both the $SbCH_3$ and DMSO protons. The signals for the DMSO protons for the cations containing DMSO are shifted considerably down field from the value for free DMSO. The resonances due to the methyl groups bonded to antimony also show marked dependence upon the nature of the ligand L; the shielding of the $SbCH_3$ protons increasing in the order DMSO$<$ $Ph_3PO$$<$ Ph_3AsO.

EXPERIMENTAL

Caution

A violent explosion occurred during the preparation of $[Me_3Sb(DMSO\text{-}d_6)_2](ClO_4)_2$. Other complexes should also be considered as potentially explosive.

General

Anhydrous silver perchlorate was obtained from G. Frederick Smith Chemical Company and was used without further purification. Dimethyl sulfoxide and nitromethane were dried by refluxing over calcium hydride, under reduced pressure, and subsequent distillation. Diethyl ether and dichloromethane were also distilled over calcium hydride, under dry nitrogen. Petroleum ether (b.p. 35–60°) and benzene were dried over sodium wire and subsequently distilled. Ethanol was refluxed over magnesium and subsequently distilled. Trimethyl- and triphenylantimony dichlorides were prepared by the methods described previously[25,26]. Other chemicals were reagent grade and were used without further purification. All the compounds prepared in this study were manipulated either in a nitrogen-filled drybox or in a glass vacuum system. Elemental analyses were performed either by Schwarzkopf Microanalytical Laboratory, Woodside, New York, or by M.H.W. Laboratories, Garden City, Michigan. Analytical data are recorded in Table 1.

Preparation of complexes

In a typical preparation triorganoantimony dichloride and the neutral ligand, in 1/2 mole ratio, were dissolved in benzene and two equivalent of silver perchlorate were added to this solution. After stirring the mixture for about 2 h a mixture of silver chloride and the desired complex was precipitated. It was filtered and washed thoroughly with benzene and then the complex was dissolved in ethanol. The complexes $[R_3Sb(Ph_3PO)_2](ClO_4)_2$ and $[R_3Sb(Ph_3AsO)_2](ClO_4)_2$ were isolated as white crystalline solids upon concentrating the ethanol solutions. In the case of $[R_3Sb(DMSO)_2](ClO_4)_2$ and $[R_3Sb(DPSO)_2](ClO_4)_2$ complexes, a glue-like material was obtained upon evaporating the ethanol solution. Complexes were isolated as white solids upon treating the glue-like material with a mixture of diethyl ether and petroleum ether (b.p. 35–60°). All the complexes were washed successively with benzene, diethyl ether and petroleum (b.p. 35–60°). Finally they were dried under vacuum.

Physical measurements

The infrared spectra were recorded on a Beckman IR-12 double beam spectrophotometer using KRS-5, polyethylene or sodium chloride windows. Solid samples were prepared as mulls in Nujol. Solution spectra were obtained using 0.1 mm pathlength sealed sodium chloride cells. Conductance measurements were made at 25° using a Beckman RC-18 conductivity bridge. The 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.

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REFERENCES

1 R. C. Poller, *The Chemistry of Organotin Compounds*, Logos Press, London, 1970, p. 185, and references therein.
2 H. Shapiro and F. W. Frey, *The Organic Compounds of Lead*, Interscience, New York, 1969, p. 298, and references therein.
3 H. Kurosawa and R. Okawara, *Organometal. Chem. Rev., Sect. A*, 6 (1970) 65, and references therein.
4 H. C. Clark and A. L. Pickard, *J. Organometal. Chem.*, 13 (1968) 61.
5 G. E. Glass, W. B. Schwabacher and R. S. Tobias, *Inorg. Chem.*, 7 (1968) 2471.
6 R. S. Tobias, M. J. Sprague and G. E. Glass, *Inorg. Chem.*, 7 (1968) 1714.
7 A. J. Downs and I. A. Steer, *J. Organometal. Chem.*, 8 (1967) p 23.
8 R. G. Goel and H. S. Prasad, *Inorg. Chem.*, 11 (1972) 2141.
9 R. E. Beaumont, R. G. Goel and H. S. Prasad, *Inorg. Chem.*, 12 (1973) 944.
10 W. D. Horrocks Jr. and F. A. Cotton, *Spectrochim. Acta*, 17 (1961) 134.
11 W. F. Currier and J. H. Webber, *Inorg. Chem.*, 6 (1967) 1539.
12 P. W. N. M. van Leeuwen and W. L. Groenveld, *Recl. Trav. Chim., Pays-Bas* 86 (1967) 201.
13 M. T. Forel and M. Tranguille, *Spectrochim. Acta, Part A*, 26 (1970) 1023.
14 F. A. Cotton, R. D. Barnes, and E. Bannister, *J. Chem. Soc.*, (1960) 2199.
15 G. B. Deacon and J. H. S. Green, *Spectrochim. Acta, Part A*, 24 (1968) 845; 25A (1969) 355.
16 D. J. Phillips and S. Y. Tyree, *J. Amer. Chem. Soc.*, 83 (1961) 1806.
17 G. A. Rodley, D. M. L. Goodgame and F. A. Cotton, *J. Chem. Soc.* (1965) 1499.
18 K. Nakamoto, *Infrared Spectra of Inorganic and Coordination Compounds*, Wiley, New York, 1970, p. 98.
19 A. F. Wells, *Z. Kristallogr.*, 99 (1938) 367.
20 T. N. Polynova and M. A. Porai-Koshits, *J. Struct. Chem.* (*USSR*), 7 (1960) 146.
21 K-W. Shen, N. E. McEwen, S. J. LaPlaca, W. C. Hamilton and A. P. Wolf, *J. Amer. Chem. Soc.*, 90 (1968) 1718.
22 R. G. Goel, E. Maslowsky Jr. and C. V. Senoff, *Inorg. Chem.*, 10 (1971) 2572.
23 C. Woods and G. G. Long, *J. Mol. Spectrosc.*, 38 (1971) 387.
24 W. J. Geary, *Coord. Chem. Rev.*, 7 (1971) 81.
25 H. C. Clark and R. G. Goel, *Inorg. Chem.*, 5 (1966) 998.
26 R. G. Goel, P. N. Joshi, D. R. Ridley and R. E. Beaumont, *Can. J. Chem.*, 47 (1969) 1423.