

Complexes of 2,2,2-Trichloroethoxytetrachloroantimony(V) with Nitrogen & Oxygen Donors

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Complexes of 2,2,2-trichloroethoxytetrachloroantimony(V) $[Sb(OCH_2CCl_3)Cl_4]$ with pyridine and its N-oxide, morpholine, 8-hydroxyquinoline and its N-oxide, α,α' -dipyridyl and its dioxide, 1,10-phenanthroline, 2-, 3- and 4-picoline-N-oxides, hexamethylphosphoramide, triphenylphosphine oxide, and phosphoryloxytrichloride, having the general formulae $Sb(OCH_2CCl_3)Cl_4 \cdot L$ and $[Sb(OCH_2CCl_3)Cl_4]_2 \cdot L'$ (where L and L' are monodentate and bidentate ligands respectively) have been prepared. The new complexes have been characterized by elemental analyses, molar conductance, molecular weights and infrared data.

METHOXY- and ethoxy-tetrachloroantimony(V) have an octahedral geometry around central metal ion, involving alkoxy bridging^{1,2}. 2-Chloroethoxytetrachloroantimony(V) has also been found to be dimeric³ although it contains one electron-withdrawing chlorine atom in the ethoxy group. However, 2,2,2-trichloroethoxytetrachloroantimony(V) has been found to exist as monomer in benzene⁴ like $SbCl_5$.

In earlier publications^{3,4} from our laboratory the acceptor properties of methoxy-, ethoxy- and 2-chloroethoxy-tetrachloroantimony(V) were reported. The formation of the complexes involved the breakdown of the alkoxy bridging of the pure alkoxide and then coordination of the ligand molecule to antimony. 2,2,2-Trichloroethoxytetrachloroantimony(V) does not involve alkoxy bridging. It is, therefore, expected to form addition compounds, the preparation and characterization of which are reported in this paper. The ligands employed were pyridine-N-oxide, 2-, 3- and 4-picoline-N-oxides, 8-hydroxyquinoline-N-oxide, α,α' -dipyridyl-N-N'-dioxide, hexamethylphosphoramide, triphenylphosphine oxide, phosphoryloxytrichloride, pyridine, morpholine, 8-hydroxyquinoline, α,α' -dipyridyl and 1,10-phenanthroline.

Materials and Methods

2,2,2-Trichloroethoxytetrachloroantimony(V) $[Sb(OCH_2CCl_3)Cl_4]$ was prepared by treating 2,2,2-trichloroethyl sulphite with an equimolar amount of antimony(V) chloride⁵. The yellowish brown solid obtained was filtered, washed repeatedly with carbon tetrachloride and dried in a vacuum desiccator. Its purity was checked by its m.p., analysis and IR spectrum⁴.

Complexes of $Sb(OCH_2CCl_3)Cl_4$ with various ligands were prepared by mixing a cold solution, the former in chloroform with liquid ligands or a solution of the solid ligand in carbon tetrachloride, acetone or benzene in nearly equimolar amounts. The reactions have been found to be exothermic.

The complexes were precipitated by adding an excess of dry ether. In the case of complexes of α,α' -dipyridyl dioxide and 8-hydroxyquinoline-N-oxide, the mixture was refluxed on water-bath for 1 hr, when the solid product precipitated out. The complexes were filtered under anhydrous condition, repeatedly washed with chloroform and ether and dried *in vacuo*.

Chlorine and antimony were estimated by the methods reported earlier^{3,4}. Molecular weights of $10^{-2}M$ solutions of the complexes were determined cryoscopically in nitrobenzene. Molar conductances of $10^{-3}M$ solutions of the complexes were also measured out in nitrobenzene. Infrared spectra of the complexes were recorded on a Perkin-Elmer 337 and 521 infrared spectrophotometers.

Results and Discussion

The analytical data (Table 1) indicate that the complexes with monodentate ligands have 1:1 stoichiometry while with bidentate ligands, the complexes have 2:1 stoichiometry $[Sb(OR)Cl_4 \cdot \text{ligand}]$. The complexes are slightly moisture sensitive and insoluble in most of common organic solvents except nitrobenzene. The complexes of hexamethylphosphoramide and 4-picoline-N-oxide are very soluble in nitrobenzene. The molar conductances of solutions of these complexes are far below than that required for the uni-univalent electrolytes, except for α,α' -dipyridyl dioxide complex which has the values 11.9 and 14.3 $cm^2 \text{ ohm}^{-1} \text{ mole}^{-1}$ at two different concentrations. These values point to the possibility of existence of this complex in an ionic form (I) along with the non-ionic one (II).

The molecular weights of the complexes indicate them to be monomers in nitrobenzene.

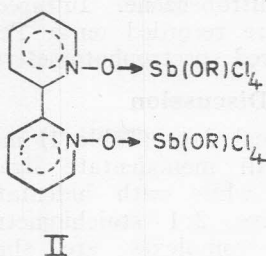
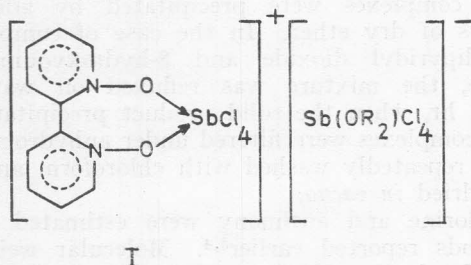
Infrared spectra* of the complexes compare well with the previously reported complexes of these ligands with some other acceptors⁶⁻¹². The direction of shift of major vibrations are in agreement with the

*Detailed IR data can be had from the authors on request.

TABLE 1 — COMPLEXES OF 2,2,2-TRICHLOROETHOXYTETRACHLOROANTIMONY(V) WITH SOME OXYGEN AND NITROGEN DONOR LIGANDS

| Complex | Colour | m.p. (°C) | Cl (%) | | Sb (%) | |
|---|-------------------------|--------------|--------|-------|--------|-------|
| | | | Found | Calc. | Found | Calc. |
| Sb(OCH ₂ CCl ₃)Cl ₄ (A) | Light brown | 63-64 | 61.0 | 60.24 | 30.1 | 29.57 |
| A.Py-O | Orange-brown semi-solid | — | 47.2 | 48.96 | 23.2 | 24.04 |
| A.2Pic-O | Pale yellow | 98-99 | 47.0 | 47.65 | 23.6 | 23.39 |
| A.3Pic-O | Orange-brown semi-solid | — | 46.9 | 47.65 | 22.9 | 23.39 |
| A.4Pic-O | White | 179-80 | 47.0 | 47.65 | 22.9 | 23.39 |
| A.8HQ-O | do | 310 | 40.0 | 40.80 | 20.7 | 20.03 |
| 2A.Dipy-O ₂ | Dirty white | 135d | 48.4 | 49.06 | 24.2 | 24.08 |
| A.HMPA | Yellow | 168-70 | 41.6 | 42.01 | 20.3 | 20.62 |
| A.TPPO | White | 206-7 | 34.6 | 35.98 | 17.6 | 17.66 |
| A.POCl ₃ | do | 125d | 62.2 | 62.83 | 21.9 | 21.55 |
| A.pyridine | do | 94-96 | 49.3 | 50.56 | 24.4 | 24.82 |
| A.8HQ | Yellow | 181-83 | 41.2 | 42.50 | 20.0 | 20.55 |
| A.morpholine | Orange | 165-67 | 49.1 | 50.56 | 24.0 | 24.82 |
| 2A.dipy | White | 298d | 51.6 | 50.66 | 25.2 | 24.87 |
| 2A.phen | Pale yellow | 260d | 48.0 | 49.70 | 25.0 | 24.27 |

Py-O = pyridine-N-oxide; Pic-O = picoline-N-oxide; 8HQ-O = 8-hydroxyquinoline-N-oxide; dipy-O₂ = α,α' -dipyridyl dioxide; HMPA = hexamethylphosphoramide, TPPO = triphenylphosphine oxide, 8HQ = 8-hydroxyquinoline; dipy = α,α' -dipyridyl, and phen = 1,10-phenanthroline.



coordination of the amine-oxide^{6,7} and phosphoryl^{8,9} ligands through their oxygen atoms to antimony. Spectra of the complexes of α,α' -dipyridyl dioxide¹⁰, α,α' -dipyridyl¹¹ and 1,10-phenanthroline¹² show the absence of bands arising from the pure ligands and this observation supports their bidentate donor character in these complexes.

The C—O vibration of the Sb—O—R group is either present at the same frequency as for the pure alkoxide (ν C—O at 1020 cm⁻¹) or is shifted to higher spectral region (1030-1090 cm⁻¹). The O—Sb stretch in the pure alkoxide⁴ at 675 and 570 cm⁻¹ shift to lower frequency region (610-663 and 533-550 cm⁻¹) in the spectra of the complexes. Such a change may be due to the change in the coordination number of antimony from five in the pure alkoxide to six in the complexes. The bands at 340-350 cm⁻¹ in the spectra of the complexes

have been assigned^{13,14} to ν Sb—Cl [ν (Sb—Cl) of SbCl₆ absorbs at 340 cm⁻¹]¹³.

The complexes with 2-, 3- and 4-picoline-N-oxides, α,α' -dipyridyl dioxide, hexamethylphosphoramide, triphenylphosphine-oxide and phosphoryl(V) oxytrichloride show an additional band of medium intensity around 402-450 cm⁻¹ which can be assigned to ν (O→Sb)^{3,4,15,16}.

The complexes [Sb(OCH₂CCl₃)Cl₄]₂.dipyridyl or 1,10-phenanthroline might exist as ion-pair structure in the ionic along with non-ionic form similar to those shown for the bipyridyl dioxide complex. Although the complex 2SbCl₅.phenanthroline has been shown to exist as uni-univalent compound¹⁷, the structural features for the analogous complexes with Sb(OCH₂CCl₃)Cl₄ cannot be understood with definiteness due to the absence of molar conductance or molecular weight data. The dipyridyl dioxide complex exhibits a band at 366 cm⁻¹ which compares well with 369 cm⁻¹ band assigned to (SbCl₄)⁺ ion in the complex [SbCl₄(CH₃CN)₂]⁺SbCl₆⁻ (ref. 18). The corresponding bipyridyl and 1,10-phenanthroline complexes do not exhibit any band in this region.

Thus it is seen that the introduction of three chlorine atoms in the alkoxy group induces the compound to become monomeric by withdrawing the electron cloud on oxygen atom. This does not happen with the introduction of one chlorine atom, as in the case 2-chloroethoxytetrachloroantimony(V). In the present complexes antimony(V) acquires a more stable configuration by attaining its favoured coordination number six.

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The spectra of Co(II) and Ni(II) bisphosphonates with 2,2,2-trichloroethoxy-4,4,4-trichloropentane-1,1-diol and 2,2,2-trichloroethoxy-4,4,4-trichloropentane-1,1-diol-3-ylidene have been characterized on the basis of their electronic and IR spectra and magnetic moment data. The results reveal that whereas Ni(II) is able to form both pentacoordinated 1:1 and hexacoordinated 1:2 adducts depending on the nature of ligands, Co(II) forms only pentacoordinated 1:1 adduct with both the ligands. The studies further reveal a change in adduct-forming ability of the metallic bisphosphonate as the organic moiety on phosphorus atom changes from phenyl to p-tolyl. Steric effect is thus a major factor controlling the reaction of the metallic bisphosphonate, MX_2 , where $M = Co(II)$ or $Ni(II)$ and $X = diphenylphosphinate$ (dip) or p-tolyl analogue (Mtdip), with nitrogen heterocycles.

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TABLE I — Coordination Number and Molecular Data of Co(II) and Ni(II) Derivatives of Bisphosphonates
 The table lists coordination numbers (CN) and molecular weights (M) for various complexes of Co(II) and Ni(II) with different bisphosphonate ligands. The data is organized into columns for Co(II) and Ni(II) complexes, and rows for different ligands.

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Table I — Coordination Number and Molecular Data of Co(II) and Ni(II) Complexes

| Complex | Co(II) | | Ni(II) | |
|---|--------|-----|--------|-----|
| | CN | M | CN | M |
| Co(II) with diphenylphosphinate | 5 | 287 | 5 | 287 |
| Ni(II) with diphenylphosphinate | 5 | 287 | 5 | 287 |
| Co(II) with p-tolylphosphinate | 5 | 287 | 5 | 287 |
| Ni(II) with p-tolylphosphinate | 5 | 287 | 5 | 287 |
| Co(II) with 2,2,2-trichloroethoxy-4,4,4-trichloropentane-1,1-diol | 5 | 487 | 5 | 487 |
| Ni(II) with 2,2,2-trichloroethoxy-4,4,4-trichloropentane-1,1-diol | 5 | 487 | 5 | 487 |
| Co(II) with 2,2,2-trichloroethoxy-4,4,4-trichloropentane-1,1-diol-3-ylidene | 5 | 687 | 5 | 687 |
| Ni(II) with 2,2,2-trichloroethoxy-4,4,4-trichloropentane-1,1-diol-3-ylidene | 5 | 687 | 5 | 687 |