

## Synthesis & Characterization of Some Complexes of Antimony(III) with Polyhydric Phenols, Acid Amides & Indene

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Received 18 January 1985; revised and accepted 16 October 1985

Reactions of antimony trichloride with polyhydric phenols (catechol, resorcinol, quinol, pyrogallol, and phloroglucinol) in 1:2 ratio in presence of amides (formamide, dimethylformamide, and urea) give complexes of the type  $Sb(OPh)_2(A)_2Cl$ . Treatment of these complexes with sodium indenide in THF yields indenyl derivatives of the type  $Sb(OPh)_2(A)_2In$  (A = amide, In = indenyl). These compounds on slow heating lose the amide molecules to give complexes of the type  $Sb(OPh)_2In$ . The complexes have been characterized by their elemental analyses, molecular weight determination, conductivity measurements, magnetic susceptibility measurements, and IR and electronic spectral data.

This work is in continuation of our earlier work on the phenoxy derivatives of antimony(III), titanium(IV), niobium(V), and tungsten(VI) containing cyclopentadienyl or indenyl groups<sup>1</sup>. No work has been reported on the mixed ligand complexes of antimony(III) involving polyhydric phenols, acid-amides, and indene as ligands. Only a few cyclopentadienyl derivatives of antimony(III) are reported<sup>2</sup>, but no indenyl derivatives of antimony(III) are reported.

All the reactions were carried out in non-aqueous medium in a dry atmosphere. The solvents and the reactants were dried before use. Antimony trichloride, the phenols, and the amides (BDH or E Merck) of AR or equivalent grade were used. Antimony was estimated iodometrically; carbon, hydrogen, and nitrogen were estimated semimicroanalytically.

### *Preparation of di(formamide)di(phenoxy)-antimony(III) chlorides*

Antimony trichloride and the respective phenols were taken in 1:2 molar ratio and stirred with 10 ml of formamide in 40 ml of benzene. The reaction mixtures were gently refluxed for 6 hr. After cooling, the solutions were filtered and the clear filtrates were concentrated by evaporation *in vacuo*. On keeping overnight, light coloured solids were obtained which were suction filtered. They were washed well with petroleum ether and dried and finally recrystallized from formamide-THF mixture (1:3).

### *Preparation of bis(dimethylformamide)di(phenoxy)-antimony(III) chlorides*

Di(formamide)di(phenoxy)antimony(III) chlorides were stirred well in 15 ml of dimethylformamide and kept for 24 hr at room temperature. The light coloured solids thus obtained were filtered by suction and washed 2-3 times with small amounts of dimethylformamide and suction dried. The solids were recrystallized from a dimethylformamide-THF mixture (1:3). The crystals were washed well with petroleum ether and dried.

### *Preparation of di(urea)di(phenoxy)-antimony(III) chlorides*

The di(formamide)di(phenoxy)antimony(III) chlorides and urea were taken in 1:2 molar ratio and shaken in 30 ml of dry ethanol; the reaction mixtures were gently refluxed till all urea had disappeared (3-4 hr). The solutions were then filtered hot and after evaporation were kept for crystallization. The light coloured solids so obtained were filtered and washed with benzene and dried. They were recrystallized from ethanol-THF (1:1) mixture.

The analytical data of all these complexes are given in Table 1.

### *Preparation of (indenyl)di(amide)-di(phenoxy)antimony(III)*

The respective di(amide)di(phenoxy)antimony(III) chlorides were dissolved in 30 ml of THF and a solution of sodium indenide in THF was added in 1:1 molar ratio with stirring. The reaction mixtures were refluxed for 2 hr, cooled and filtered. The clear dark coloured filtrates were evaporated to small volumes under reduced pressure and cooled. They were then treated with excess of petroleum ether when brownish solids separated out. They were filtered and recrystallized from an ether-THF mixture (2:1). They were washed well with petroleum ether and dried.

### *Preparation of (indenyl)di(phenoxy)antimony(III)*

The respective (indenyl)di(amide)di(phenoxy)antimony(III) complexes were kept at  $\sim 50^\circ C$  under reduced pressure for about 12 hr. The residues were cooled and washed well with petroleum ether. The brownish solids so obtained were recrystallized from ether-THF mixture (5:1).

Some characteristics and analytical data of the indenyl derivatives are given in Tables 2 and 3 respectively.

Table 1—Characterisation Data of Di(amide)di(phenoxy)antimony(III) Chlorides

Compound	Colour (Dec.temp. °C)	Mol.wt. Calc. (found)	Cal. (found), %		
			Sb	Cl	N
Sb(O <sub>2</sub> C <sub>6</sub> H <sub>5</sub> ) <sub>2</sub> {HCON(CH <sub>3</sub> ) <sub>2</sub> } <sub>2</sub> Cl (catechoxy)	Dull yellow (91)	521.2 (522.7)	23.34 (23.23)	6.81 (6.93)	5.37 (5.22)
Sb(O <sub>2</sub> C <sub>6</sub> H <sub>5</sub> ) <sub>2</sub> {HCON(CH <sub>3</sub> ) <sub>2</sub> } <sub>2</sub> Cl (resorcinoxy)	Dirty white (92)	521.2 (532.5)	23.34 (23.61)	6.81 (6.73)	5.37 (5.31)
Sb(O <sub>2</sub> C <sub>6</sub> H <sub>5</sub> ) <sub>2</sub> {HCON(CH <sub>3</sub> ) <sub>2</sub> } <sub>2</sub> Cl (quinoxy)	Pale yellow (89)	521.2 (529.3)	23.34 (23.54)	6.81 (6.87)	5.37 (5.28)
Sb(O <sub>3</sub> C <sub>6</sub> H <sub>5</sub> ) <sub>2</sub> {HCON(CH <sub>3</sub> ) <sub>2</sub> } <sub>2</sub> Cl (pyrogalloxy)	Light brown (93)	553.2 (562.7)	21.99 (21.83)	6.41 (6.37)	5.06 (5.14)
Sb(O <sub>3</sub> C <sub>6</sub> H <sub>5</sub> ) <sub>2</sub> {HCON(CH <sub>3</sub> ) <sub>2</sub> }Cl (phloroglucinoxy)	Dull grey (92)	553.2 (565.9)	21.99 (21.14)	6.41 (6.53)	5.06 (5.01)
Sb(O <sub>2</sub> C <sub>6</sub> H <sub>5</sub> ) <sub>2</sub> (HCONH <sub>2</sub> ) <sub>2</sub> Cl (catechoxy)	Ash grey (91)	465.2 (472.3)	26.16 (26.35)	7.63 (7.56)	6.01 (6.20)
Sb(O <sub>2</sub> C <sub>6</sub> H <sub>5</sub> ) <sub>2</sub> (HCONH <sub>2</sub> ) <sub>2</sub> Cl (resorcinoxy)	Light brown (89)	465.2 (477.5)	26.16 (26.43)	7.63 (7.73)	6.01 (6.18)
Sb(O <sub>2</sub> C <sub>6</sub> H <sub>5</sub> ) <sub>2</sub> (HCONH <sub>2</sub> ) <sub>2</sub> Cl (quinoxy)	Pale yellow (88)	465.2 (468.9)	26.16 (25.95)	7.63 (7.58)	6.01 (6.15)
Sb(O <sub>3</sub> C <sub>6</sub> H <sub>5</sub> ) <sub>2</sub> (HCONH <sub>2</sub> ) <sub>2</sub> Cl (pyrogalloxy)	Dirty white (93)	497.2 (503.4)	24.47 (24.53)	7.13 (7.02)	5.63 (5.71)
Sb(O <sub>3</sub> C <sub>6</sub> H <sub>5</sub> ) <sub>2</sub> (HCONH <sub>2</sub> ) <sub>2</sub> Cl (phloroglucinoxy)	Ash grey (90)	497.2 (507.6)	24.47 (24.62)	7.13 (7.25)	5.63 (5.78)
Sb(O <sub>2</sub> C <sub>6</sub> H <sub>5</sub> ) <sub>2</sub> (NH <sub>2</sub> CONH <sub>2</sub> ) <sub>2</sub> Cl (catechoxy)	Grey (90)	495.2 (503.4)	24.57 (24.32)	7.16 (7.23)	11.30 (11.19)
Sb(O <sub>2</sub> C <sub>6</sub> H <sub>5</sub> ) <sub>2</sub> (NH <sub>2</sub> CONH <sub>2</sub> ) <sub>2</sub> Cl (resorcinoxy)	Light brown (88)	495.2 (501.7)	24.57 (24.41)	7.16 (7.25)	11.30 (11.20)
Sb(O <sub>2</sub> C <sub>6</sub> H <sub>5</sub> ) <sub>2</sub> (NH <sub>2</sub> CONH <sub>2</sub> ) <sub>2</sub> Cl (quinoxy)	Dirty pink (87)	495.2 (506.8)	24.57 (24.68)	7.16 (7.19)	11.30 (11.48)
Sb(O <sub>3</sub> C <sub>6</sub> H <sub>5</sub> ) <sub>2</sub> (NH <sub>2</sub> CONH <sub>2</sub> ) <sub>2</sub> Cl (pyrogalloxy)	Light brown (87)	527.2 (530.3)	23.08 (22.88)	6.73 (6.81)	10.62 (10.72)
Sb(O <sub>3</sub> C <sub>6</sub> H <sub>5</sub> ) <sub>2</sub> (NH <sub>2</sub> CONH <sub>2</sub> ) <sub>2</sub> Cl (phloroglucinoxy)	Light brown (89)	527.2 (533.7)	23.08 (22.91)	6.73 (6.87)	10.62 (10.76)

The di(amide)di(phenoxy)antimony(III) chlorides are light coloured solids, while the indenyl derivatives are darker in colour, ranging from red to dark brown. The complexes are soluble in THF but are insoluble in water, benzene, and chloroform. They are readily hydrolysed by hot water, hot dilute mineral acids and alkalis. They decompose on heating without melting. Their suspensions in ethanol change to gelatinous mass on keeping.

Molecular weights of all the complexes determined by cryoscopic method suggest that they are monomeric. Conductance studies ( $\Lambda_M \sim 0.6 \text{ ohm}^{-1}$

$\text{cm}^2 \text{ mol}^{-1}$  in dimethylformamide) show that they are non-electrolytes. The magnetic moments of the complexes are very low ( $\sim 0.02 \text{ B.M.}$ ) indicating that they are diamagnetic. The electronic spectra of the complexes show a single band in the region  $25000\text{--}24000 \text{ cm}^{-1}$  ( $\epsilon_{\text{max}} \sim 11000$ ). The band could be assigned to charge transfer<sup>3</sup>.

The attachment of two amide molecules and two phenoxy groups to the antimony atom weakens the remaining Sb-Cl bond and this chlorine is easily replaced by the indenyl group. In all the thermal dissociation reactions under study the volatile

Table 2—Characterisation Data of (Indenyl)di(amide)di(phenoxy)antimony(III) Complexes

Compound	Colour (Dec. temp. °C)	Mol. wt. Calc. (found)	Calc. (found), %		
			Sb	C	H
Sb(O <sub>2</sub> C <sub>6</sub> H <sub>5</sub> ) <sub>2</sub> {HCON(CH <sub>3</sub> ) <sub>2</sub> } <sub>2</sub> (C <sub>9</sub> H <sub>7</sub> ) (catechoxy)	Brown (64)	600.7 (607.3)	20.25 (20.13)	53.93 (53.59)	5.16 (5.19)
Sb(O <sub>2</sub> C <sub>6</sub> H <sub>5</sub> ) <sub>2</sub> {HCON(CH <sub>3</sub> ) <sub>2</sub> } <sub>2</sub> (C <sub>9</sub> H <sub>7</sub> ) (resorcinoxy)	Red brown (61)	600.7 (612.9)	20.25 (20.29)	53.93 (53.76)	5.16 (5.21)
Sb(O <sub>2</sub> C <sub>6</sub> H <sub>5</sub> ) <sub>2</sub> {HCON(CH <sub>3</sub> ) <sub>2</sub> } <sub>2</sub> (C <sub>9</sub> H <sub>7</sub> ) (quinoxy)	Orange brown (59)	600.7 (619.1)	20.25 (20.34)	53.93 (54.23)	5.16 (5.08)
Sb(O <sub>3</sub> C <sub>6</sub> H <sub>3</sub> ) <sub>2</sub> {HCON(CH <sub>3</sub> ) <sub>2</sub> } <sub>2</sub> (C <sub>9</sub> H <sub>7</sub> ) (pyrogalloxy)	Brown (62)	632.7 (641.3)	19.23 (19.59)	51.20 (51.42)	4.89 (4.91)
Sb(O <sub>3</sub> C <sub>6</sub> H <sub>3</sub> ) <sub>2</sub> {HCON(CH <sub>3</sub> ) <sub>2</sub> } <sub>2</sub> (C <sub>9</sub> H <sub>7</sub> ) (phloroglucinoxy)	Dark red (60)	632.7 (644.2)	19.23 (19.09)	51.20 (51.11)	4.89 (4.73)
Sb(O <sub>2</sub> C <sub>6</sub> H <sub>5</sub> ) <sub>2</sub> (HCONH <sub>2</sub> ) <sub>2</sub> (C <sub>9</sub> H <sub>7</sub> ) (catechoxy)	Red brown (66)	544.7 (552.3)	22.34 (22.26)	50.67 (50.87)	4.22 (4.13)
Sb(O <sub>2</sub> C <sub>6</sub> H <sub>5</sub> ) <sub>2</sub> (HCONH <sub>2</sub> ) <sub>2</sub> (C <sub>9</sub> H <sub>7</sub> ) (resorcinoxy)	Brick red (60)	544.7 (556.7)	22.34 (22.23)	50.67 (50.48)	4.22 (4.31)
Sb(O <sub>2</sub> C <sub>6</sub> H <sub>5</sub> ) <sub>2</sub> (HCONH <sub>2</sub> ) <sub>2</sub> (C <sub>9</sub> H <sub>7</sub> ) (quinoxy)	Grey brown (58)	544.7 (560.4)	22.34 (22.27)	50.67 (50.73)	4.22 (4.31)
Sb(O <sub>3</sub> C <sub>6</sub> H <sub>3</sub> ) <sub>2</sub> (HCONH <sub>2</sub> ) <sub>2</sub> (C <sub>9</sub> H <sub>7</sub> ) (pyrogalloxy)	Brown (64)	576.7 (583.6)	21.10 (21.23)	47.85 (47.67)	3.98 (3.96)
Sb(O <sub>3</sub> C <sub>6</sub> H <sub>3</sub> ) <sub>2</sub> (HCONH <sub>2</sub> ) <sub>2</sub> (C <sub>9</sub> H <sub>7</sub> ) (phloroglucinoxy)	Red brown (60)	576.7 (587.2)	21.10 (21.37)	47.85 (47.75)	3.98 (3.93)
Sb(O <sub>2</sub> C <sub>6</sub> H <sub>5</sub> ) <sub>2</sub> (NH <sub>2</sub> CONH <sub>2</sub> ) <sub>2</sub> (C <sub>9</sub> H <sub>7</sub> ) (catechoxy)	Grey brown (63)	574.7 (583.4)	21.17 (21.03)	48.02 (48.14)	4.35 (4.27)
Sb(O <sub>2</sub> C <sub>6</sub> H <sub>5</sub> ) <sub>2</sub> (NH <sub>2</sub> CONH <sub>2</sub> ) <sub>2</sub> (C <sub>9</sub> H <sub>7</sub> ) (resorcinoxy)	Brown (59)	574.7 (588.3)	21.17 (21.23)	48.02 (48.25)	4.35 (4.29)
Sb(O <sub>2</sub> C <sub>6</sub> H <sub>5</sub> ) <sub>2</sub> (NH <sub>2</sub> CONH <sub>2</sub> ) <sub>2</sub> (C <sub>9</sub> H <sub>7</sub> ) (quinoxy)	Red brown (56)	574.7 (580.1)	21.17 (21.09)	48.02 (48.22)	4.35 (4.41)
Sb(O <sub>3</sub> C <sub>6</sub> H <sub>3</sub> ) <sub>2</sub> (NH <sub>2</sub> CONH <sub>2</sub> ) <sub>2</sub> (C <sub>9</sub> H <sub>7</sub> ) (pyrogalloxy)	Dark brown (61)	606.7 (612.3)	20.05 (20.17)	45.49 (45.33)	4.12 (4.17)
Sb(O <sub>3</sub> C <sub>6</sub> H <sub>3</sub> ) <sub>2</sub> (NH <sub>2</sub> CONH <sub>2</sub> ) <sub>2</sub> (C <sub>9</sub> H <sub>7</sub> ) (phloroglucinoxy)	Red brown (58)	606.7 (619.4)	20.05 (20.21)	45.49 (45.58)	4.12 (4.16)

products were identified qualitatively and by their IR spectra.

All the complexes showed sharp bands at  $\sim 3450$  and  $1150 \text{ cm}^{-1}$  which may be assigned to the O—H stretching and bending respectively of the uncoordinated phenolic OH group<sup>4</sup>. The N—H stretching frequency of the amide group in the formamide and urea complexes appearing at  $\sim 3440 \text{ cm}^{-1}$  overlaps with the O—H stretching frequency, but the broad bands at  $\sim 3340$  and  $3200 \text{ cm}^{-1}$  may be assigned to the N—H stretching mode. These bands are not present in the IR spectra of the dimethylformamide complexes. The band at  $\sim 1640$

$\text{cm}^{-1}$  is probably the NH<sub>2</sub> deformation mode and is not observed in dimethylformamide complexes. This may be regarded as the amide II band. There are also bands in the range  $1340\text{--}1440 \text{ cm}^{-1}$ , the origin of which is not clear<sup>5</sup>. The lowering of the C=O stretching frequency (amide I band) to  $\sim 1500 \text{ cm}^{-1}$  of the complexes as compared to that of free amides ( $1685 \text{ cm}^{-1}$  for urea,  $1725 \text{ cm}^{-1}$  for formamide, and  $1650 \text{ cm}^{-1}$  for dimethylformamide) indicates that the amide ligands are coordinated to the antimony through oxygen atom<sup>6</sup>. There occurs no appreciable change in the N—H stretching frequency ruling out coordination through amide nitrogen atom. A group of

Table 3—Characterisation Data of (Indenyl)di(phenoxy)antimony(III) Complexes

Compound	Colour (Dec. temp. °C)	Mol. wt. Calc. (found)	Calc. (found), %		
			Sb	C	H
Sb(O <sub>2</sub> C <sub>6</sub> H <sub>5</sub> ) <sub>2</sub> (C <sub>9</sub> H <sub>7</sub> )* (catechoxy)	Red brown (70)	454.7 (461.2)	26.76 (26.57)	55.42 (55.21)	3.73 (3.80)
Sb(O <sub>2</sub> C <sub>6</sub> H <sub>5</sub> ) <sub>2</sub> (C <sub>9</sub> H <sub>7</sub> ) (resorcinoxy)	Orange brown (67)	454.7 (465.3)	26.76 (26.85)	55.42 (55.53)	3.73 (3.68)
Sb(O <sub>2</sub> C <sub>6</sub> H <sub>5</sub> ) <sub>2</sub> (C <sub>9</sub> H <sub>7</sub> ) (quinoxy)	Brick red (65)	454.7 (464.3)	26.76 (26.66)	55.42 (55.33)	3.73 (3.80)
Sb(O <sub>3</sub> C <sub>6</sub> H <sub>5</sub> ) <sub>2</sub> (C <sub>9</sub> H <sub>7</sub> ) (pyrogalloxy)	Dark brown (69)	486.7 (493.2)	25.00 (24.83)	51.77 (51.41)	3.49 (3.45)
Sb(O <sub>3</sub> C <sub>6</sub> H <sub>5</sub> ) <sub>2</sub> (C <sub>9</sub> H <sub>7</sub> ) (phloroglucinoxy)	Red brown (66)	486.7 (497.3)	25.00 (25.14)	51.77 (51.48)	3.49 (3.46)

\*Products obtained by heating different amide complexes gave similar analytical results

frequencies are observed in the range 1100-1400 cm<sup>-1</sup> which may be regarded as composite of the O-H deformation, C-C skeletal mode, C-H in-plane deformation,  $\nu$  M-O (phenoxide), and C-N stretching. Only one Sb-Cl stretching frequency appears in the IR spectra of the di(amide)di(phenoxy)antimony(III) chlorides at ~310 cm<sup>-1</sup> (ref.8). The IR spectra of the (indenyl)di(amide)di(phenoxy)antimony(III) are comparable to the spectra of indene with respect to the absorption of the indenyl group. Hence, it appears that the indenyl group is  $\sigma$ -bonded to the antimony atom. The presence of weak to medium bands in the range 2950-2980 cm<sup>-1</sup> due to C-H asymmetric stretching, a weak to medium band at ~1625 cm<sup>-1</sup> due to C=C stretching, and a strong band at ~755 cm<sup>-1</sup> due to C-H deformation support this contention<sup>2,10</sup>.

The IR spectra of the (indenyl)-di(phenoxy)antimony(III) complexes are slightly different from those of the indenyl di(amide)-di(phenoxy)antimony(III) complexes. Bands due to NH<sub>2</sub> and CO moieties of the amide group are absent but those due to phenoxy moiety are present.  $\nu$ OH and  $\delta$ OH appear at ~3450 and ~1160 cm<sup>-1</sup>. Hence, it appears that the indenyl group is  $\sigma$ -as well as  $\pi$ -bonded to the antimony atom or there occurs a transition between the two types. This may be understood if the structure of the complexes is assumed to have a distorted pyramidal geometry with sp<sup>3</sup> hybridized antimony atom as in antimony trichloride. Both the phenyl rings of the two phenoxy groups and the indenyl ring tend to accept back the

lone pair on antimony introducing a  $\pi$ -bond character in the metal-ring bonding. Further, there appears to be a transition of  $\pi$ -electrons from the indenyl ring to the phenoxy ring or vice versa through the vacant *d*-orbitals of the antimony atom providing stability to the bonds and helping in the removal of the amide molecules from the diamidediphenoxyindenyl derivatives. This suggestion is supported by the electronic spectra of the complexes which show two bands in the range 28400-28000 cm<sup>-1</sup> ( $\epsilon_{\max}$  ~9500) probably due to intraligand electronic transitions<sup>12</sup>. Intense colour of the complexes may be due to conjugation over the entire molecule and due to charge transfer.

## References

- Sharma R C & Rastogi M K, *Indian J Chem*, **23A** (1984) 431; Rastogi M K & Multani R K, *J Chinese chem Soc*, **24** (1977) 175; Rastogi M K & Nigam S N, *J Chinese chem Soc*, **28** (1981) 111; Rastogi M K, *Curr Sci*, **47** (1978) 343; **51** (1982) 924.
- Deubzer B, Elian M, Fischer E O & Fritz H P, *Chem Ber*, **103** (1974) 797; Fischer E O & Schreiner S, *Chem Ber*, **93** (1960) 1417; Kronmes P & Lorberth J, *J organometal Chem*, **88** (1975) 329; Jutzi P, Kuhn M & Herzog F, *Chem Ber*, **108** (1975) 2493; Rastogi M K & Sharma R C, *Curr Sci*, **18** (1983) 862.
- Hulme R, Mullen D & Scrutton J C, *Acta Crystallogr*, **A25** (1969) 5171.
- Kuhn L P, *J Am chem Soc*, **74** (1952) 2492.
- Richards R E & Thomson H M, *J chem Soc*, (1947) 1248; Randall H M, Fowler R G, Fuson N & Dangle J R, *Infrared*

NOTES

- determination of organic structures* (Von Nostrand, Princeton, New Jersey) 1949.
- 6 Penland R B, Mizushima S, Curran C & Quagliano J V, *J Am chem Soc*, 79 (1957) 1575.
- 7 Balahura R J & Jordan R B, *J Am chem Soc*, 92 (1970) 1533.
- 8 Cazzoli G & Caminati W, *J molec Spectrosc*, 62 (1976) 1.
- 9 Nakanishi K, *Infrared absorption spectroscopy—practical* (Nankodo Co Ltd, Tokyo) 1962; Rao C N R, *Chemical applications of infrared spectroscopy* (Academic Press, New York & London) 1963.
- 10 Fritz H P, *Adv organomet Chem*, 1 (1964) 279.
- 11 Scharf G W & Brown R K, *Can J Chem*, 38 (1960) 697.
- 12 Narang K K & Lal R A, *Transition Met Chem*, 3 (1978) 272.