

## Reactions of Bidentate Oxime and Quinoline Ligands with Antimony Trichloride Adducts with N-donors.

M.K. RASTOGI\*

Department of Chemistry  
Hindu College, Delhi-110 007, India

Some nitrogen donor molecules form stable adducts with antimony trichloride. These adducts are allowed to react with dioximes, salicylaloxime and 8-hydroxy quinoline in molar ratios 1 : 2 in cold and in hot in THF solvent. Different products are obtained under two different conditions. In cold the oximes and 8-hydroxy-quinoline simply behave as mono acid ligands (except  $\gamma$ -benzil-dioxime) and replace two of the chlorine atoms in the antimony trichloride adducts. But in hot, one of the dioxime molecules behaves as diacid ligand while the other molecule as monoacid ligand and replacement of all the three chlorine atoms takes place. Their structures are concluded from physical measurements and analytical data.

### INTRODUCTION

We have seen that dioximes form stable complexes with a number of metals. This study is in continuation of our previous work where adducts of oxygen donor molecules were used.<sup>1</sup> Nitrogen donor molecule adducts of antimony trichloride behave differently in hot solutions probably due to the ligands being also coordinating through oxime nitrogen atom, a case of symbiosis. There is no reference of such a study with antimony trichloride adducts in the chemical literature. Thus, it is worthwhile to study the antimony trichloride adducts with N-donors. All the reactions were carried out in dry atmosphere and dry THF. The chemicals used were of high purity or purified and dried before use. The antimony trichloride adducts were prepared as reported earlier.<sup>2</sup> Although a large number of such compounds were prepared, but only those that are best confirmed are reported.

### EXPERIMENTAL

#### Preparation of chlorobis (dimethylglyoximate) aniline antimony(III) (Complexes No. I)

1 g of antimony trichloride adduct with aniline was dissolved in 100 mL of THF and dimethyl glyoxime (molar ratio 1 : 2) was added to this solution. The

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\*Address of Correspondence: 66 UB, Jawahar Nagar, Delhi-110 007, India.

reaction mixture was stirred for *ca.* 12 h and then filtered through a G-4 sintered glass disc. The clear coloured mother liquor was evaporated to dryness under reduced pressure very slowly. The yellowish orange residue was washed with petroleum ether and recrystallised with THF-petroleum ether mixture.

Reactions with other adducts and oximes were carried out in a similar way.

#### **Preparation of chloro $\gamma$ -benzildioximato dipyridine antimony(III) (Complex No. II)**

A mixture of 1 g antimony trichloride-pyridine adduct and  $\gamma$ -benzildioxime (molar ratio 1 : 1) in 100 mL of THF was stirred for *ca.* 12 h at *ca.* 35°C. The reaction mixture was then filtered and the clear filtrate was evaporated to dryness under reduced pressure. The orange brown residue was repeatedly washed with petroleum ether and dried. It was recrystallized from THF-ether mixture.

#### **Preparation of bis (salicyloximato) nitrilo antimony(III) (Complex No. III)**

1 g of antimony trichloride-methyl cyanide adduct was taken with 100 mL of THF and salicylaloxime (molar ratio 1 : 2) was added to it. The reaction mixture was refluxed for 18 h and filtered hot. The clear filtrate was evaporated to dryness under reduced pressure. The residue was washed with petroleum ether and the reddish brown solid was recrystallised from THF-ether mixture.

#### **Preparation of bis ( $\gamma$ -benzildioximato) bis (2,3-dihydroxy) pyridine antimony(III) (Complex No. IV)**

1 g of antimony trichloride adduct with 2,3-dihydroxy pyridine,  $\gamma$ -benzildioxime (in 1 : 2 molar ratio) and 100 mL of THF were well shaken in a flask. The reaction mixture was refluxed for 12 h and filtered. The clear mother liquor was evaporated to dryness under reduced pressure and the solid residue was well washed with petroleum ether. The orange red solid was recrystallised from THF-ether mixture.

### **RESULTS AND DISCUSSION**

The effective magnetic moments of all the complexes are low (0.26–0.51 BM) indicating them to be diamagnetic with some orbital contribution to the magnetic moment. The molar conductance of the complexes are also low (0.25–0.75  $\text{ohm}^{-1} \text{cm}^{-1} \text{mol}^{-1}$ ) indicating their non-ionic nature. Cryoscopically determined molecular weight confirms their monomeric nature. The IR spectra of complex no. I (except those of  $\gamma$ -benzildioximato) showed<sup>3,4</sup>  $\nu(\text{O—H})$  at *ca.* 3000  $\text{cm}^{-1}$  and 2400  $\text{cm}^{-1}$ ; the split in  $\nu(\text{O—H})$  is due to the unsymmetrical H-bonded OH groups. The  $\delta(\text{O—H})$  (in-plane and out-of-plane) are assigned at *ca.* 1710 and 840  $\text{cm}^{-1}$ . The  $\nu(\text{C}=\text{N})$  is assigned at *ca.* 1480  $\text{cm}^{-1}$ ; the lowering of this frequency suggests the coordination of azomethine nitrogen to antimony. The two bands at *ca.* 1260 and 1190  $\text{cm}^{-1}$  are assigned to  $\nu(\text{N—O})$ . This split in  $\nu(\text{N—O})$  indicates that the two N—O linkages are not equal.<sup>3</sup> These results on comparing the complexes with these of nickel, palladium<sup>5</sup>, tungsten<sup>6</sup>, niobium<sup>3,7</sup> suggest the bis-dioxime part to be planar. The  $\nu(\text{Sb—N})$  appears in the form of two-three

TABLE-1  
 PHYSICAL AND ANALYTICAL DATA OF QUINOLINATO AND OXIMATO DERIVATIVES OF  
 ANTIMONY TRICHLORIDE ADDUCTS WITH N-DONORS

Compound	Colour (Dec. Temp.) °C	m.w. Found (calcd.)	Found (Calcd.) %			Conductivity ohm <sup>-1</sup> cm <sup>2</sup> mol <sup>-1</sup>	$\mu_{\text{eff}}$ (B.M.)
			Sb	Cl	N		
(C <sub>4</sub> H <sub>7</sub> N <sub>2</sub> O <sub>2</sub> ) <sub>2</sub> SbCl·C <sub>6</sub> H <sub>5</sub> NH <sub>2</sub>	yellow-orange (129)	498.6 (480.2)	25.53 (25.34)	7.43 (7.39)	14.34 (14.57)	0.71	0.27
Aniline, dimethylglyoxime (cold) (1 : 2)							
(C <sub>14</sub> H <sub>10</sub> N <sub>2</sub> O <sub>2</sub> )(C <sub>14</sub> H <sub>11</sub> N <sub>2</sub> O <sub>2</sub> )Sb·CH <sub>3</sub> C <sub>6</sub> H <sub>4</sub> NH <sub>2</sub>	red-brown (133)	695.2 (705.7)	17.41 (17.24)	—	10.13 (9.92)	0.32	0.43
<i>o</i> -toluidine, $\gamma$ -benzildioxime (hot) (1 : 2)							
(C <sub>9</sub> H <sub>6</sub> NO) <sub>2</sub> SbCl·CH <sub>3</sub> OC <sub>6</sub> H <sub>4</sub> NH <sub>2</sub>	yellow-brown (140)	575.3 (568.2)	21.28 (21.42)	6.32 (6.24)	7.45 (7.39)	0.63	0.38
<i>p</i> -anisidine, 8-hydroxyquinoline (cold) (1 : 2)							
(C <sub>14</sub> H <sub>11</sub> N <sub>2</sub> O <sub>2</sub> )(C <sub>14</sub> H <sub>10</sub> N <sub>2</sub> O <sub>2</sub> )Sb·C <sub>6</sub> H <sub>5</sub> N(CH <sub>3</sub> ) <sub>2</sub>	orange brown (110)	703.2 (719.7)	16.76 (16.91)	—	9.64 (9.72)	0.26	0.23
dimethyl aniline, $\alpha$ -benzildioxime (hot) (1 : 2)							
(C <sub>4</sub> H <sub>7</sub> N <sub>2</sub> O <sub>2</sub> )(C <sub>4</sub> H <sub>6</sub> N <sub>2</sub> O <sub>2</sub> )Sb·NO <sub>2</sub> C <sub>6</sub> H <sub>4</sub> NH <sub>2</sub>	brownish red (113)	497.8 (488.7)	24.63 (24.90)	—	17.32 (17.19)	0.43	0.29
<i>p</i> -nitroaniline, dimethylglyoxime (hot) (1 : 2)							
(C <sub>14</sub> H <sub>10</sub> N <sub>2</sub> O <sub>2</sub> )SbCl·2C <sub>5</sub> H <sub>5</sub> N	orange-brown (127)	570.3 (553.2)	22.31 (22.00)	6.53 (6.41)	10.23 (10.12)	0.58	0.34
pyridine, $\gamma$ -benzildioxime (cold) (1 : 1)							
(C <sub>4</sub> H <sub>7</sub> N <sub>2</sub> O <sub>2</sub> )(C <sub>4</sub> H <sub>6</sub> N <sub>2</sub> O <sub>2</sub> )Sb·C <sub>10</sub> H <sub>8</sub> N <sub>2</sub>	red-brown (121)	499.6 (506.7)	24.37 (24.02)	—	16.34 (16.58)	0.41	0.47
bipyridyl, dimethylglyoxime (hot) (1 : 2)							
(C <sub>7</sub> H <sub>6</sub> O <sub>2</sub> N)SbCl·C <sub>12</sub> H <sub>8</sub> N <sub>2</sub>	dark red (119)	595.4 (609.2)	20.18 (19.97)	6.01 (5.82)	9.23 (9.19)	0.57	0.26
1,10-phenanthroline, salicylaloxime (cold) (1 : 2)							
(C <sub>14</sub> H <sub>10</sub> N <sub>2</sub> O <sub>2</sub> )(C <sub>14</sub> H <sub>11</sub> N <sub>2</sub> O <sub>2</sub> )Sb·2C <sub>5</sub> H <sub>3</sub> (OH) <sub>2</sub> N	orange red (136)	833.6 (820.7)	14.75 (14.83)	—	10.17 (10.23)	0.37	0.37
2,3-dihydroxy pyridine, $\gamma$ -benzildioxime (hot) (1 : 2)							
(C <sub>14</sub> H <sub>11</sub> N <sub>2</sub> O <sub>2</sub> )(C <sub>14</sub> H <sub>10</sub> N <sub>2</sub> O <sub>2</sub> )Sb·2C <sub>5</sub> H <sub>3</sub> (OH)(NH <sub>2</sub> )N	yellowish red (114)	835.2 (818.7)	14.97 (14.86)	—	13.75 (13.68)	0.40	0.31
2-amino, 3-hydroxy pyridine $\alpha$ -benzildioxime (hot) (1 : 2)							
(C <sub>14</sub> H <sub>11</sub> N <sub>2</sub> O <sub>2</sub> ) <sub>2</sub> SbCl·2N(C <sub>2</sub> H <sub>5</sub> ) <sub>3</sub>	dark orange (105)	823.7 (837.2)	14.41 (14.53)	4.31 (4.24)	10.19 (10.03)	0.68	0.42
triethylamine, $\alpha$ -benzildioxime (cold) (1 : 2)							
(C <sub>7</sub> H <sub>6</sub> O <sub>2</sub> N)(C <sub>7</sub> H <sub>5</sub> O <sub>2</sub> N)Sb·CH <sub>3</sub> CN	reddish brown (123)	445.3 (433.7)	28.23 (28.06)	—	9.51 (9.68)	0.49	0.51
methyl cyanide salicylaloxime (hot) (1 : 2)							

bands in the range 570–530  $\text{cm}^{-1}$  which may be due to a combination of the  $\nu(\text{Sb—N})$  oxime linkage and  $\nu(\text{Sb—N})$  of the nitrogen donor adduct. The  $\nu(\text{Sb—Cl})$  appears at *ca.* 300  $\text{cm}^{-1}$  in these complexes.

The IR spectra of complex no. II show no  $\nu(\text{O—H})$  band indicating the absence of OH group and implies the participation of both the groups in bonding;  $\gamma$ -benzildioxime acting as a diacid ligand. The two bands assigned to  $\nu(\text{N—O})$  are at *ca.* 1230 and 1075  $\text{cm}^{-1}$  indicating the inequality of the two N—O linkages. This suggests that one oxime group is attached to antimony through nitrogen and the other through oxygen atom forming a six-membered ring.<sup>6,7</sup>

The IR spectra of complexes no. III show a band at 3000  $\text{cm}^{-1}$  which may be assigned to  $\nu(\text{O—H})$  hydrogen bonded. The  $\delta(\text{O—H})$  (in-plane and out-of-plane) appear at *ca.* 1700 and 850  $\text{cm}^{-1}$  indicating the hydrogen bonding to be unsymmetrical. It appears that one of the O—H bonds of the oxime group is ruptured and reacts with the third chlorine atom. This fact has been observed in bimetallic complexes reported by us.<sup>8</sup> This is supported by the fact that no chlorine is present in these complexes. The  $\nu(\text{C=N})$  is as assigned at *ca.* 1500  $\text{cm}^{-1}$  which is lower than that of the free ligands, suggesting coordination of the oximato nitrogen to antimony. This is favoured due to the presence of ligands which are all nitrogen bonded (symbiosis). The two  $\nu(\text{N—O})$  are assigned at *ca.* 1275 and 1170  $\text{cm}^{-1}$  indicating a split and non-equality of the two N—O linkages. The  $\nu(\text{Sb—N})$  appears as a group of bands between 560–500  $\text{cm}^{-1}$  which are due to oximato and adduct nitrogen linkage to antimony.

Complexes of the type IV show  $\nu(\text{O—H})$  at *ca.* 2950  $\text{cm}^{-1}$  and  $\delta(\text{OH})$  (in-plane and out-of-plane) at *ca.* 1650 and 875  $\text{cm}^{-1}$  indicating the presence of one unsymmetrically hydrogen bonded hydroxyl group. The lowering of  $\nu(\text{C=N})$  to 1490  $\text{cm}^{-1}$  suggests coordination of  $\gamma$ -benzildioximato nitrogen to antimony. The split in the  $\nu(\text{N—O})$  at 1250 and 1180  $\text{cm}^{-1}$  indicates the inequality of the two N—O linkages. The  $\nu(\text{Sb—N})$  appears as a group of bands in the range 550–500  $\text{cm}^{-1}$  indicating different nitrogen atoms coordinating to antimony.

The UV spectra of the complexes show bands in three main regions: 250 nm, 300 nm and 350 nm. The bands between 250 and 300 nm are probably due intra-ligand transitions. The splitting and red shift of intraligand bands are good evidence for chelation. The bands *ca.* 350 nm may be due to ligand to metal charge transfer transitions.<sup>3</sup>

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