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Reactions of Some Bidentate Ligands with Antimony Trichloride Adducts with Oxygen Donors-I

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Stable adducts of antimony trichloride with oxgen donor molecules (urea, formamide, acetamide, dimethyl formamide, benzamide, acetanilide, benzanilide, and DMSO) on treatment with bidentate ligands (8-hydroxy quinoline, dimethyl glyoxime, α-benzildioxime, γ-benzildioxime and salicylaldoxime) in chloroform in 1 : 2 molar ratio (except γ-benzildioxime, 1 : 1 ratio) produce stable complexes by replacing 2 chlorine atoms of the antimony trichloride molecule. Some physical characteristics of the products are reported and conclusions about their structural mode.

INTRODUCTION

A number of dioximes form stable chelates with metals either by replacement of hydrogen or by coordinating with antidioximes involves the formation of five membered rings whereas amphidioximes form chelates with six-membered rings.[1] There has been a continuing interest in metal oximates because of their analytical, biochemical and structural importance. There is no reference in chemical literature about the oximato derivatives of antimony trichloride adducts. All the reactions were carried out in dry atmosphere. All the chemicals used were either of A.R. quality or well purified and dried before use. The adducts of antimony trichloride were obtained as reported earlier.[2]

EXPERIMENTAL

Preparation of 8-hydroxyquinolinato/salicylaldoximato derivative of antimony trichloride adducts

1.0 g of the $SbCl_3$ adduct was dissolved in 100 mL of hot chloroform. 8-hydroxyquinoline/salicylaldoxime (molar ratio 1 : 2) was added and the mixture was refluxed till evolution of HCl fumes ceased. The reaction mixture was cooled and filtered through a G-4 sintered glass disc. The clear mother liquor was evaporated to dryness under reduced pressure. The residue was well washed with petroleum ether and recrystallised from THF-ether mixture.

Preparation of dioximato derivative of antimony trichloride adducts

1 g of the pure adduct was gently refluxed with the oximes in molar ratio 1:2 for about 3 h in chloroform. The reaction mixture was cooled and filtered. The clear mother liquor on evaporation gave stable solid residues which were well washed with benzene and then with ether and dried. The complexes were recrystallised from THF-ether mixture.

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Preparation of γ-benzildioximato derivatives of antimony trichloride adducts

These complexes were similarly prepared except that the reactants were taken in 1 : 1 molar ratio. They were recrystallised from THF-$CHCl_3$ mixture.

The analytical and other physical data are summarized in Table-1.

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

Compound	Colour (Dec. Temp) °C	Mol. wt. Found (Calcd.)	Found (Calcd.) % Sb	Cl	N
$(C_9H_6NO)_2SbCl{\cdot}NH_2CONH_2$ (Urea, quinolinato)	dirty green (127)	521.3 (505.2)	23.92 (24.09)	7.15 (7.02)	11.23 (11.08)
$(C_7H_5O_2N)SbCl{\cdot}2(CH_3)_2SO$ (DMSO, salicylaldioximato)	red (115)	440.9 (448.2)	27.31 (27.15)	7.81 (7.92)	18.95 (18.74)
$(C_{14}H_{11}N_2O_2)_2SbCl{\cdot}NH_2CONH_2$ (Urea, α-benzildoximato)	orange red (129)	680.7 (695.2)	17.71 (17.50)	5.23 (5.10)	8.14 (8.05)
$(C_{14}H_{10}N_2O_2)SbCl{\cdot}C_6H_5NHCOCH_3$ (Acetanilide, γ-benzildioximato)	red brown (118)	539.4 (530.2)	23.22 (22.95)	6.73 (6.69)	7.80 (7.92)
$(C_4H_7N_2O_2)_2SbCl{\cdot}(CH_3)_2SO$ (DMSO, dimethylglyoximato)	orange brown (120)	473.8 (465.2)	26.03 (26.16)	7.81 (7.63)	12.21 (12.03)
$(C_9H_6NO_2)SbCl{\cdot}HCONH_2$ (Formamide, quinolinato)	greenish brown (113)	481.7 (490.2)	24.71 (24.82)	7.11 (7.24)	8.38 (8.56)
$(C_7H_5O_2N)SbCl{\cdot}CH_3CONH_2$ (Acetamide, salicylaldoximato)	red brown (122)	362.2 (351.2)	34.54 (34.65)	10.23 (10.11)	7.81 (7.97)
$(C_{14}H_{11}N_2O_2)_2SbCl{\cdot}HCON(CH_3)_2$ (DMF, α-benzildioximato)	red (125)	701.3 (708.2)	17.27 (17.18)	5.12 (5.01)	9.69 (9.88)
$(C_{14}H_{10}N_2O_2)SbCl{\cdot}HCON(CH_3)_2$ (Dimethyl formamide, γ benzildioximato)	brown (122)	456.8 (468.2)	26.13 (25.99)	7.63 (7.58)	8.81 (8.97)
$(C_4H_7N_2O_2)_2SbCl{\cdot}CH_3CONH_2$ (Acetamide, dimethylglyoximato)	brownish red (114)	440.9 (446.2)	27.12 (27.27)	7.98 (7.95)	15.73 (15.60)
$(C_9H_6NO)_2SbCl{\cdot}C_6H_5NHCOCH_3$ (Acetanilide, quinolinato)	brown (119)	512.7 (504.2)	24.28 (24.13)	7.18 (7.04)	8.25 (8.33)
$(C_7H_5O_2N)SbCl{\cdot}2C_6H_5CONH_2$ (Benzamide, salicylaldoximato)	orange brown (103)	543.3 (534.2)	22.93 (22.78)	6.73 (6.64)	7.99 (7.86)
$(C_{14}H_{11}N_2O_2)_2SbCl{\cdot}C_6H_5NHCOC_6H_5$ (Benzanilide, α-benzildioximato)	orange red (120)	824.6 (833.2)	14.82 (14.60)	4.31 (4.26)	8.27 (8.40)
$(C_{14}H_{10}N_2O_2)SbCl{\cdot}2C_6H_5CONH_2$ (Benzamide, γ-benzildioximato)	brown red (112)	509.8 (516.2)	23.73 (23.57)	6.98 (6.87)	10.68 (10.85)
$(C_4H_7N_2O_2)_2SbCl{\cdot}C_6H_5NHCOC_6H_5$ (benzanilide, dimethylglyoximato)	brown (110)	595.3 (584.2)	20.72 (20.83)	6.15 (6.07)	11.77 (11.98)

RESULTS AND DISCUSSIONS

The measured magnetic susceptibilities of the complexes are low (0.22–0.34 B.M.) indicating all electrons are paired up. The molar conductance, measured on Northup type conductivity bridge, are very low (*ca.* 0.50–1.5 ohm^{-1} cm^2 mol^{-1}) indicating their non-ionic nature. The observed molecular weights are tallying with their monomeric nature.

The structural assignments of IR peaks are as follows: The presence of formamide, acetamide, benzamide, acetanilide, benzanilide and urea molecules in the complexes are indicated by the IR bands at *ca.* 3400 and 3300 cm^{-1} which may be assigned to ν_{asym}(N—M) and ν_{sym}(N—H) respectively. The band at 1600 cm^{-1} may be due to δ(N—H). The IR spectra of dimethyl formamide compound do not show these bands. The ν(C=O) band is assigned at *ca.* 1450 cm^{-1}; the lowering of this band indicates that all the amides and anilides are coordinated to antimony through oxygen atom.[2] The band *ca.*1400 cm^{-1} is assigned to ν(C—N), but in acetanilide and benzanilide complexes it appears *ca.* 1310 cm^{-1} and may be considered as mixed band due to ν(C—N), δ(N—H), $\nu(CH_3—C)$ and $\nu(C_6H_5—C)$.[3] The IR spectra of the DMSO compound showed a band at 980 cm^{-1} which is assigned to ν(S=O) and is lower than that in free DMSO indicating its coordinatioin to antimony through oxygen.[4] The ν(Sb—O) is assigned in the range 450–400 cm^{-1} which overlaps with the ν(Sb—N) of the oxime group in the complexes.

The oximato group in the prepared dimethylglyoximato and α-benzildioximato complexes is indicated by a band at *ca* 2380 cm^{-1} and 2900 cm^{-1} respectively assigned to ν(O—H) lowered due to hydrogen bondings and band at *ca.* 1720 cm^{-1} due to δ(O—H) (in-plane). The broad medium band at 1590 cm^{-1} in the oxime ligands shifts to lower frequency at *ca.* 1510 cm^{-1} and may thus be assigned to ν(C=N). The lowering of this frequency suggests coordination of azomethine nitrogen to antimony[1]. Bands *ca.* 540 cm^{-1} and 420 cm^{-1} are perhaps due to ν(Sb—N) and ν(Sb—O) respectively. The two bands at *ca.* 1250 and 1175 cm^{-1} are assigned to ν(N—O) which indicates them to be probably unequal. This is because in dimethylglyoximato and α-benzildioximato complexes one unionized O—H group is present making the two N—O linkages unequal; but in γ-benzildioximato complexes both the O—H groups are ionized, but the metal antimony appears to be attached to one group through nitrogen atom and to the other through oxygen atom making the two N—O linkages unequal and forming a 6-membered ring. γ-Benzildioximato complexes show no bands due to free O—H or hydrogen bonded OH group which implies that both the OH groups have taken part in bond formation.

The IR bands of the oximato groups of dimethylglyoximato and α-benzildioximato complexes are almost identical with those of nickel and palladium dimethylglyoxime complexes[5] indicating close structural similarities. The hydrogen bonding involved in these complexes, therefore, is not symmetrical and the observed two bands at *ca.* 2380 and 2900 cm^{-1} are probably due to a split in the ν(O—H) frequency. This suggests that the oximato part of the complex should be planar which is supported by the appearance of bands *ca.* 1020 cm^{-1} and 850 cm^{-1}

which are associated with ring deformations in complexes having this geometry of the groups.[6] In complexes of dimethylglyoxime, α-benzildioxime and 8-hydroxyquinoline, the antimony atom probably acquires a seven-coordinated polyhedral structure.

The 8-hydroxyquinolinato complexes show no IR bands in the region 4000–3000 cm^{-1} indicating the absence of OH group meaning thereby its participation in coordination after deprotonation. The bands occurring in the range 450–380 cm^{-1} in the IR spetra of the complexes may be assigned to ν(Sb—O) (Sb-amide oxygen and Sb-quinoloxy oxygen). The band at *ca.* 550 cm^{-1} may be assigned to ν(Sb—N) which provides evidence for the coordination of 8-hydroxyquinolinato-nitrogen atom to antimony. The ν(C==N) in the free ligand appears at 1500 cm^{-1}, but in the complexes it is assigned at *ca.* 1380 cm^{-1} which is considerably lower pointing nitrogen coordination to antimony.[7,8]

The IR spectra of salicylaldoximato complexes showed no bands *ca.* 3500 cm^{-1} due to ν(O—H) indicating the absence of a free OH group and its participation in bonding after deprotonation. Bands in the range 470–440 cm^{-1} may be assigned to ν(Sb—O). The band at *ca.* 950 cm^{-1} may be due to ν(N—O) which is lower than that in the free ligand. A band at *ca.* 1490 cm^{-1} may be assigned to ν(C==N) which is also lower than that in the free ligand. The band at *ca.* 540 cm^{-1} may be assigned to ν(Sb—N). All these observations suggest the coordination of the oximato group through nitrogen.[9]

The UV spectra of dimethyl glyoxime show only one band at 228 nm, while α- and γ-benzildioximes show 2–3 bands between 220–260 nm. In the UV spectra of the complexes the bands split and occur in the broad range 220–260 nm, 300 nm and 350 nm. The bands between 200–300 nm are good evidence for chelation. The bands in the 300–350 nm region have intensities comparable to that of the ligand band, indicating L→M charge transfer transitions.[1]

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