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CHARACTERIZATION AND STRUCTURE OF COMPLEXES OF ACETATE AND PYRAZOLINATES WITH ANTIMONY (III)

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ABSTRACT

Antimony (III) complexes with Nitrogen/Oxygen donor ligand have been synthesized in dry benzene in 1:2 molar ratios at the elevated temperature. These newly synthesized derivatives have been characterized by elemental analysis, molecular weight measurements as well as spectral IR, ^{1}H NMR, ^{13}CNMR, studies. Pyrazolinates is bi-coordinated, and acetate mono-coodinated, to antimony leading to distorted trigonal bipyramidal tructure respectively.

I. INTRODUCTION

The coordination chemistry of antimony is of great practical and theoretical interests regarding synthesis and structural aspects. The medicinal and cosmetic use of antimony complexes goes back at least to the Egyptian **(1-3).** Potassium antimony tartrate or tartar emetic was widely used for the treatment of cancer and parasitic diseases until the early 1900s, despite the somewhat toxic nature of the material. More recently, the use of antimony complexes in cancer chemotherapy has become topic of interest. Antimony (III) complexes have been intensively studied owing to their versatile bonding modes and biological perspectives. These complexes show wide structural diversity from discrete monomeric molecular species to associated structures and supramolecular assemblies **(4-8).**Antimony derivatives also exhibit significant functions as biocides, fungicides, catalyst components and antioxidants. Therefore, synthesis of new antimony compounds and study of their structure and properties are of interesting modern coordination chemistry. In addition, the carboxylate ion can coordinate to metals in many ways including as unidentate ligand, as chelating ligand and as bridging bidentate ligand. The role of antimony compounds as chemotherapeutic agents dates back to sixteen century. However, their uses have never been particularly widespread and it is only in recent years with the identification of various antimonials of gluconic acid being the most effective treatment of patients with leishmania infection that a resurgence of interest has occurred **(9-18).**

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II. EXPERIMENTAL

All organic solvents were purchased from E. Merck and Aldrich, and were distilled, dried and saturated with nitrogen before use according to the reported methods **[19-23].**

2.1 *Physical Measurements*

Infrared spectra were recorded on Perkin Elmer Model 557 FT-IR spectrophotometer using CsI cell in the range 4000-200 cm^{-1}. NMR spectra were recorded at room temperature on a Bruker DRX-300 spectrometer operated at 300.1 and 75.45 MHz for ^{1}H, 13C, using TMS (tetramethylsilane) as internal standard respectively. The splitting of proton resonances in the reported 1HNMR spectra are defined as s = singlet, d = doublet and m = complex pattern.

	Product in gm	Molar ratio	Yield	M.p.	m.wf ound (calcd)	analysis (calculated) found %				
1	$(C_{17}H_{18}N_2O_5X)Sb$	1:2	75	201	(522.75) 520	(43.61) 43.84	(3.63) 3.65	(5.35) 5.38	(23.29) 23.41	-
2	$(C_{17}H_{18}N_2O_5X)Sb$	1:2	73	214	(536.75) 532	(44.71) 45.11	(3.91) 3.94	(5.21) 5.26	(22..62) 22.88	-
3	$(C_{17}H_{18}N_2O_5X)Sb$	1:2	73	217	(552.75) 550	(43.41) 43.63	(3.79) 3.81	(5.06) 5.09	(21.97) 22.13	-
4	$(C_{17}H_{18}N_2O_5X)Sb$	1:2	88	198	(558.203) 556	(40.84) 41.07	(3.22) 3.23	(5.01) 5.03	(22.81) 21.87	(6.35) 6.37

III. SYNTHESIS OF COMPLEXES

The acetone solution dichloroantimony (III) pyrazolinate (0.655 g; 1.524 mmol) was then dropwise added benzene solution of sodium acetate (0.25g, 3.048mmole with consant stirring.. The reaction mixture was further stirred at room temperature for 4-5 hours, till the colour of the reaction mixture underwent a change. Reaction mixture was filtered to remove precipitated NaCl. The solvent was removed under reduced pressure from the filtrate. The yellow coloured solid thus obtained was recrystallized in chloroform-methanol and dried in vacuum. The analytical details are summarized in table.

Table 1: Synthetic, Physical and analytical data for $(C_{17}H_{18}N_2O_5X)Sb$

IV.CHARACTERIZATION OF COMPLEXES

IR Spectral studies:

The infrared spectral data for these compounds are summarized in Table 1. All compounds exhibit bands of medium intensity in the region3324-3314cm^{-1} and 1601-1628cm^{-1} due to ν(N-H)and ν(C=N) stretching vibrations. The band presents in the region 1015 cm^{-1} in compound **3** may be assigned to ν(C-O) stretching indicating the presence of $–OCH_3$ group. The band presents in the region 460-474cm-and 1,440-435cm^{-1} assigned to (Sb-O) and (Sb-N) stretching vibration Presence of new band (medium intensity and broad) in comparison to dichloroantiomony (III)pyrazolinates in the region ν_s(1344-1338cm^{-1}) and ν_{as}(1645-1635) have been assigned to carboxylic (COO)stretching vibration.

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Tab 2: IR spectral data (cm^{-1}) for mixed ligand complex of $(C_{17}H_{18}N_2O_5X)Sb$

S. No.	Compound	ν(N-H)	ν(C=N)	ν(C-O)	ν_s(COO)	ν_{as}(COO)	ν(Sb-O)	ν(Sb-N)
1.	$(C_{17}H_{18}N_2O_5X)Sb$	3322	1639	-	1332	1648	469	438
2.	$(C_{17}H_{18}N_2O_5X)Sb$	3322	1643	-	1333	1655	470	442
3.	$(C_{17}H_{18}N_2O_5X)Sb$	3321	1642	1024	1337	1650	465	440
4.	$(C_{17}H_{18}N_2O_5X)Sb$	3312	1644	-	1328	1647	464	439

Where X = H in 1, CH_3 in 2; OCH_3 in 3 and Cl in4 compounds respectively,

Multinuclear ^{1}H NMR and ^{13}C NMR Spectral Studies

In ^{1}H NMR spectra the aromatic protons of mixed ligand complexes $(C_{17}H_{18}N_2O_5X)Sb$ observed as a multiplet in the region δ 8.6-7.1 ppm. The integration ratio is in accordance with the presence of 12 protons in compounds 2-4. The peak due to hydroxyl proton (originally present at δ~11.00 ppm in free pyrazolines) is completely missing from the spectra of compounds suggesting the bonding through hydroxyl oxygen atom. The appearance of a peak at δ 5.7-5.5 ppm as a broad singlet could be assigned to N-H group (originally present at δ 5.5-5.0 ppm in free pyrazolines) suggesting the non-involvement of N-H group in bond formation. The skeletal protons of five membered ring are observed at δ 3.8-3.5 ppm as a triplet and at δ 2.9-2.5 ppm as a doublet could be assigned to CH and CH_2 group respectively.

Table 3: ^{1}HNMR IR spectral data (cm^{-1}) $(C_{17}H_{18}N_2O_5X)Sb$

Comp. No.	Chemical shift (inδ ppm)
1	7.7-7.0 (9 H, mAr-H), 5.4 (3H, s, NH),3.3 (3H, t, CH), 2.2 (2H, d, CH_2), 3.8(6H.m CH_3COO)
2	7.8-6.9 (8H, m, Ar-H),5.1 (1H, s, NH), 3.6 (1H, t, CH), 2.5 (2H, d, CH_2), 0.9 (3H, s, CH_3) 3.8(6Hm, CH3COO)
3	7.8-6.9 (24H, m, Ar-H), 5.5 (1H, s, NH), 3.7 (1H, t, CH), 2.0 (2H, d, CH_2), 3.8 (3H, b, OCH_3) 4.2(6H s CH_3COO)
4	7.8-6.9 (8H, m, Ar-H), 5.4 (1H, s, NH), 3.4 (1H, t, CH), 2.2 (2H, d, CH_2), 3.7(6H.m CH_3COO)

The proton decoupled ^{13}NMR spectra of mixed ligand complexes of $(C_{22}H_{17}N_2O_4X)Sb$ show presence of all important signals with reference to antimony (III) pyrazolinates. The signal observed in the region δ 137.5-121.8 ppm as multiplet could be assigned to aromatic carbon [13]. The signal observed at δ 165.2-162.9 ppm is

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due to imino carbon of C=N group In all compounds the signal due to carbon of C=N group is shifted to down field in comparison to the spectra of free pyrazolines (at δ 143.5-142.8 ppm) suggesting the involvement of imino nitrogen in coordination. The signal observed in the region δ174.5-173.5ppm is due to carboxylic carbon (COO). All other signal was found at their respective positions as in dichloroantimony (III) pyazolinates.

Table 4:[13] CNMR (in δ ppm $(C_{17}H_{18}N_2O_5X)Sb$

Comp. No.	Chemical shift (inδ ppm)
1.	133.8-126.6 (Ar-C),167.6 (C=N), 43.5 (CH), 26.7 (CH_2), 21.6(3H, CH_3COO), 172.5(COO)
2.	132.5-129.4 (Ar-C), 167.5(C=N),43.1(CH), 26.5(CH_2), 13.6 (CH_3), 21.5(3H, CH_3COO), 171.3(COO)
3.	132.9-126.9 (Ar-C), 166.9 (C=N), 43.3 (CH), 26.8 (CH_2), 51.5 (OCH_3), 21.4(3H, CH_3COO), 171.5(COO)
4.	133.7-128.7 (Ar-C), 167.8 (C=N), 43.3 (CH), 26.2 (CH_2), 21.3(3H, CH_3COO), 170.4(COO)

V. STRUCTURE ELUCIDATION

Although it is difficult to comment on the molecular structure of these compounds in solid state without actual X-ray crystal structure analysis of at least one of the products. However the bidentatebehaviour of the ligands in $C_{17}H_{15}N_2O_3X)SbCl$has been confirmed by IR, ^1H NMR and ^{13}C NMR data.In these complexes the centralantimoy (III) atom appears to acquire the coordination four and most plausible geometry around the antimony atom is distorted trigonalbipyramidal.

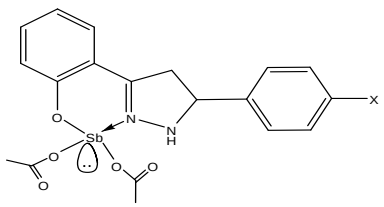

Fig 1: Proposed Structure $(C_{17}H_{15}N_2O_3X)SbCl$

VI.CONCLUSIONS

Although it is quiet difficult to comment on the molecular structure of these compounds in solid state without actual X-ray crystal structure analysis of at least one of the products. However the bidentatebehaviour of the ligands in $C_{17}H_{15}N_2O_3X)SbCl$has been confirmed by IR, ^1H NMR and ^{13}C NMR data. In these complexes the centralantimony(III)atom appears to acquire the coordination four and most plausible geometry around the antimony atom is distorted trigonalbipyramidal.

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REFERENCE

[1] P.G.Avaji, G.B. Bagihalli. S.A. patil and P.S. Badami, Journal of Coordination Chemistry 62, no. 3 481-492 **(2009).**

[2] K. Sharma, R.V. Singh and N.Fermi,SpectrochimicaActa part A , 78, 1 80-87,**(2001).**

[3] T.S. Basu,Applied organomatallic Chemistry 22, 195-204, **(2008)**

[4]. M-X Li, J. Zhou, H Zhao, C-L Chen, and J.P. Wang, Journal of Coordination Chemistry 62, no.9 , 1423-1429. **(2009)**

[5]. D. Shanker, R.K. Sharma, J. Sharma, A.K.Rai, and Y.P. Singh Hetero Atom Chemistry 18, 1, 70- 75, **(2007).**

[6] K. Singh, P.P. Singh M. Singh, Barwa, P.Tyagiand,Y. Mirza, Journal of Enzyme Inhibition and Medicinal chemistry, 21,no.6,749-755 **(20006).**

[7] S. Yadav and R.V. Singh,SpectrochimicaActa part A, 1, 298-306 **(2001).**

[8] H. Sun, H.Li, I. Harvey and P. Sadler, Journal of Biological Chemistry, 274, 41. 29094-29101 **(1999).**

[9] J.R. Shah and N.R. ShahIndian J. Chem**.** A, 21, 312,**(1982)**

[10] J.R. Shah, S.K Das and R.P. Patel, J. Indian Chem. Soc.,50, 228**(1973).**

[11] N.R Shah and J.R. Shah, J. Inorg.NuclChem 43, 1593, **(1981).**

[12] U.N. Tripathi, K.V. Sharma, A Chaturvedi and T.C. Sharma, Polish J.Chem. 77 109-115 **(2003).**

[13] U.N. Tripathi, M. Safi Ahmad, G. Venubabu and RamkrishanaJ. Coord Chem.60, 16, 1777-1788, **(2007).**

[14] U.N. Tripathi, M. Safi. Ahmad, G. Venubabu andRamkrishana, J.Coord.Chem.60, 16, 1709-1720, (2007).

[15] E. Robert, T. Charle and G .Ram, J. Agric.Food Chem., 31**,** 85-88, **(1983).**

[16] J.S. Solanki,U.N. Tripathi,A. Bhardwaj, V. Jena. Phosphorus, Sulfur, and silicon Silicon, 184, 2169–2178, **(2009)**.

[17] J. S. Solanki, U. N. Tripathi, A.Bhardwajand T. R. Thapak, J. Coord.Chem. 61, 24, 4025 - 4032**, (2009).**

[18] J. S. Solanki, Tripathi, U.N. Tripathi, and A. Bhardwaj, J. Coord.Chem, 62, 4, 636- 644 **(2009).**

[19] U.N. Tripathi,G. Venubabu. M Safi Ahmad, S.S. RaoKolisetty. A.K. Srivastav Appl.Organomet.Chem**.** 20, (10)669, **(2006)**.

[20] T.C. Sharma, V. Saxena, and N., J. Readdy, ActaChim.93, 415-421 **(1977).**

[21] A.I. Vogel, A Text Book of quantitative Inorganic Analysis, ELBS and Longman London (1978).

[22] A.I. Vogel. A Text Book of quantitative Inorganic Analysis, LBS and Longman London (1985).

[23] J.H. Benson, Microbiological Application Microbiology 5th Edn, p.459, Wm.C. Brown Publication, Oxford **(1990).**

IJARSE
ISSN (O) 2319 - 8354
ISSN (P) 2319 - 8346

[24] S. Sharma, R. K. Sharma, and A. K. Rai, Heteroatom Chem.15 , 1 **(2004).**

[25] K.Nakmoto, " Infrared and Raman Spectra of Inorganic and Co-ordination Compounds '' New York.**(1997).**

[26] R.M Silverstin, F.X. Webster, Spectrometric identification of Organic Compounds 6th Ed. Pp.228-232 John Wiley& Sons Inc.New York **(1998).**

[27] G. Fegrguson, B. Kaither, C. Glidewell and S. Smith J. Organomet.Chem 419,**283**-291 **(1991).**