Synthesis and Spectroscopic Studies of Mixed Catechol-Salicylaldiminate Derivatives of Antimony (III) and Tin (IV)

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Abstract

Mixed catechol– salicyladiminenate derivatives of antimony (III) and tin (IV) of the general formula M(cate)L^n]X, [where:M= Sb, X= 0; M=Sn, X= Cl; cate=catechol; n=1, L=aniline, n=2, L=m-bromo-aniline, n=3, L=p-bromoaniline] were prepared by the reaction of equimolar amount of [(cate)MCln], [where n=1 or 2] with N-arylsalicylaldimines $HOC_6H_4CH=NC_6H_5$ (HL^1), $HOC_6H_4CH= NC_6H_4$ (HL^1) and p-$HOC_6H_4CH = NC_6H_4Br$ (HL^3) in methanol as a solvent. These new derivatives were characterised by elemental analysis and spectroscopic methods [(I.R), (U.V-Vis) and (^1H, ^{13}C NMR for HL^2)] along with conductivity and melting point measurements. These studies revealed that the geometry about Sb (III) and Sn (IV) is tetrahedral.

Introduction

Antimony and tin complexes have widely studied and showed great utilization as antifungal, antibacterial and anticancer (Renal carcinoma and melanoma) agent, the complexes showed more activity than the metals salts or free ligands (1). In spite of that there is some untouched area, such as tin (IV) and antimony (III) complexes with mixed glycols or catechols and chelating ligands to be explored (2). Synthesis and spectroscopic properties of mixed glycolate–salicyldiminate derivatives of arsenic (III) have been reported (3). Therefore this study included the synthesis and spectroscopic characterisation of mixed catechol–salicylaldiminate derivatives of antimony (III) and tin (IV).

Experimental

Reagents were purchased from Fluka and Rediel- Dehenge Chemical Co. I.R spectra were recorded as (KBr) discs using a Shimadzu 8400 S FTIR spectrophotometer in the range (4000-400) cm^{-1}. Electronic spectra of the prepared compounds was measured in the region (200-900) nm for 10^{-3} M solution in (DMF) at 25 ^{0}C by using a Shimadzu160 spectrophotometer with 1.000+0.001 cm matched quartz cell. Nuclear Magnetic Resonance Spectrum ^{1}H, ^{13}C NMR for (HL^2) ligand was recorded in DMSO-d^6 by using a Jeol EX 270 MHz instrument with a tetramethylsilane (TMS) as an internal standard. Elemental microanalyses were performed on a (C.H.N.) analyser from Heraeus (Vario EL) at the University of Free Berlin/Germany. While metal contents of the complexes was determined by atomic absorption (A.A) technique by using a Shimadzu A.A 680G atomic absorption spectrophotometer. The chloride contents for complexes were determined using potentiometric titration method on 686-Titro Processor Dosimat-Metrahm-Swiss. Electrical conductivity measurements of the complexes were recorded at 25 ^{0}C for 10^{-3} M solutions of the samples in (DMF) by using a PW 9526 digital conductivity meter.

Synthesis

Synthesis of the ligands

Synthesis of [HL^1]

Salicylaldehyde (0.23g, 2.1mmole) was added to a solution of aniline (0.26g, 2.1mmole) in methanol (10ml). The resulting mixture was stirred at room temperature for 1 hour to give the ligand as a yellow solid. Yield 0.21g, (74%), m.p.(249-250°C).

Synthesis of [HL^2]

A similar procedure to that described for [HL^1], was employed but with m-bromoaniline (0.2g, 0.58mmole) in place of aniline. The quantities of the other regents were adjusted accordingly and an identical work-up procedure gave a green precipitate, yield 0.28g (65%), m.p(218 -220 ^{0}C).

Synthesis of [HL^3]

The method used to prepare [HL^3] was analogous to the procedure given for [HL^1] but with p-bromoaniline (035g, 1.26mmole) in place of aniline. The quantities of the other regents were adjusted

accordingly and an identical work-up procedure gave a green precipitate 0.54g (68%) of the title compound, m.p (236 -238^{0}C).

Synthesis of catechol derivatives

Synthesis of [Sb(cate)Cl]

To a benzene solution (25ml) consisting of $SbCl_3$ (1.5g, 6.5mmole) and triethylamine (1ml) was added (0.75g, 6.5mmole) of catechol. The resulting exothermic reactants mixture was stirred at room temperature for (7-8) hrs, and then followed by refluxing for 4 hrs to give the new derivative as a white solid. Yield 0.106g, (61%) of the title compound, m.p (280-282)°C.

Synthesis of [Sn(cate)Cl_2]

The method used to prepare [Sn(cate)Cl_2] was analogous to the procedure given for the derivative [Sb(cate)Cl] but with $SnCl_4.6H_2O$ (2.38g, 6.8mmole) instead of $SbCl_3$. The quantities of the other regents were adjusted accordingly and an identical work-up procedure gave 0.85g, 65 % of the derivative.

Synthesis of the complexes

Synthesis of [Sb(cate)L^1] complex (1)

Methanolic solution of [HL^1] (0.38g, 1.93mmole) in (30ml) MeOH was added slowly to Sb(cate)Cl (0.502g, 1.93mmole). The mixture was stirred at room temperature for (2hrs) to give white solid, yield (0.57) (60%), m.p (198-200°C) dec.

Synthesis of [Sn(cate)L^1]Cl complex (2)

A similar procedure to that described for [Sb(cate)L^1] was employed but with Sn(cate)Cl_2 (0093g, 0.36mmole) in place of Sb(cate)Cl. The quantities of the other regents were adjusted accordingly and an identical work-up procedure gave a green precipitate, which was washed with (10mL) diethyl ether to yield 0.16g (75%), m.p(300 -301°C) dec.

Synthesis of [Sb(cate)L^2] complex (3)

A similar procedure to that described [Sb(cate)L^1] was used but with HL^2 (0.15g, 0.54mmole) in place of HL^1. The quantities of the other regents were adjusted accordingly and an identical work-up procedure gave a red precipitate 0.15g (62%) of the title compound, m.p (220 -222 °C).

Synthesis of [Sn(cate)L^2]Cl complex (4)

The method used to prepare [Sn(cate)L^2]Cl was analogous to the procedure given for the complex [Sb(cate)L^1] but with HL^2 (0.13g, 0.5 mmole) in place of HL^1. The quantities of the other regents were

adjusted accordingly and an identical work-up procedure gave a deep green precipitate 0.126g (66%), m.p(178-179 ^{0}C).

Synthesis of [Sb(cate)L^3] complex (5)

A similar procedure to that described for [Sb(cate)L^1] was used but with HL^3 (0.15g, 0.54 mmole) in place of HL^1. The quantities of the other regents were adjusted accordingly and an identical work-up procedure gave a pale brown precipitate, yield 0.165g (65%), m.p (238-240 °C).

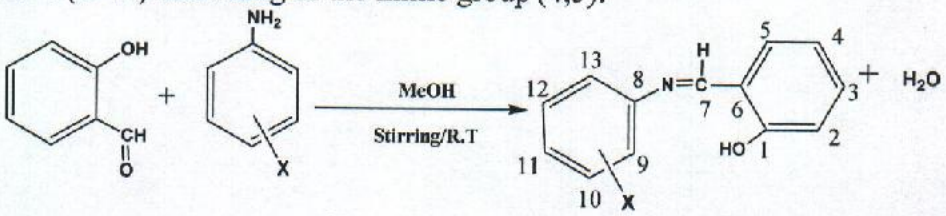
Synthesis of [Sn(cate)L^3]Cl complex (6)

The method used to prepare [Sn(cate)L^3]Cl was analogous to the procedure given for the complex [Sb(cate)L^1] but with HL^3 (0.13g, 0.46mmole) in place of HL^1. The quantities of the other regents were adjusted accordingly and an identical work-up procedure gave a deep green precipitate 0.16g (66%), m.p(193-195 ^{0}C).

Results and Discussion

Synthesis of the ligands

The ligands were prepared according to the general method shown in Scheme (1). The (I.R) spectra for the ligands [HL^1], [HL^2] and [HL^3], displayed bands in the range (1598.9, 1618 cm^{-1}) attributed to the υ(C=N) stretching of the imine group (4,5).



X= H = HL^1: X =*m*-Br =HL^2: X = *p*-Br = HL^3

Scheme (1) The synthesis route of the ligands

The broad band in the range (3415.7-3421.5 cm^{-1}) was assigned to a hydroxyl group of the salicyaldehyde, while the phenolic υ(C-O) stretching band appeared in the range (1282.5-1290.3cm^{-1}). The bands in the ranges (2364-2594cm^{-1}) could be assigned to the iminic proton. The appearance of the new imine band and the disappearance of carbonyl band indicate the formation of the ligands. Table (2)

summarises the characteristic IR bands of the ligands. The (U.V-Vis) spectra of the ligands, shows absorption peaks in the ranges (239-241nm), (280-287nm) and (342- 496 nm) assigned to ($\pi \rightarrow \pi^*$), ($n \rightarrow \pi^*$) and charge transfer (C.T) transitions respectively(6). The results are summarised in Table (3). Fig (1) displays the ^1H NMR spectrum of the ligand [HL^1]. The broad chemical shift at 12.68 ppm is equivalent to one proton, attributed to the phenolic proton (OH). This chemical shift disappeared on the addition of D_2O, Fig (2). While the chemical shift at 8.97 ppm which is equivalent to one proton can be attributed to the iminic proton (H-C=N). The chemical shifts at 7.96 (2H, S), 7.425(5H, m, ,J=32.2Hz) and 7.67(2H, m,J=29.3Hz) ppm are assigned for aromatic protons. The ^{13}C NMR spectrum of the ligand [HL^2], Fig (3) displays chemical shifts at (164, 160 and 150) ppm can be assigned to (C=N), (C-O) and (C-N) carbon atoms respectively(7). The chemical shifts in the range (116-123) ppm could be attributed to the aromatic carbon atoms. The chemical shifts are summarised in Table (4).

Synthesis of the complexes

The reaction of the ligands with catechol derivatives was carried out in methanol under reflux; these complexes were stable in solution. The analytical and physical data Table (1) and spectral data Table (2), and (3) are compatible with the suggested structures Fig (4).

The (I.R) spectral data of the complexes were presented in Table (2). The strong υ(C=N) band of imine group in the free ligands (1598, 1618 and 1612) cm^{-1} was shifted to alower frequency in the complexes (1, 2, 3, 4 and 5) and appeared at the range (1591-1618) cm^{-1}, indicated the coordination of the ligands through the iminic nitrogen. While for complex (6) the band was shifted to ahigher wave number which indicated a weak linkage between the nitrogen of the iminic group and Sn(IV) ion(8). The phenolic υ(C-O) bands in the range (1282.57-1290.29) cm^{-1} were shifted to lower wave numbers and appeared at the range (1242.07-1249.8) cm^{-1}, indicating the involving of the phenolic oxygen atoms in the coordination. The appearance of a new strong absorption band in the region (573-513) cm^{-1} was assigned to υ(M-O)(9). While the bands at (475-403) cm^{-1} were assigned to υ(M-N) stretching, indicating also that the imine nitrogen and the oxygen of hydroxyl group were involved in coordination with metal ion(10,11).

The molar conductance of the compounds in (DMF) lies in two ranges (8.45-20.40 $S.cm^2.mol^{-1}$) and (87.65-102.00 $S.cm^2.mol^{-1}$), for the complexes (1, 3 and 5) and (2, 4 and 6) respectively. Table (3), indicates their non electrolytic and (1: 1) molar ratio nature respectively (12).

The electronic spectral data of the complexes are summarised in Table (3). The bands at the range (239-241) and (280-287) nm in the free ligands were shifted to alower frequency and appeared at the range (226-239) and (275-279) nm for the complexes (1, 2, 3, 4, 5 and 6) respectively. While the bands at (351 and 304) nm for the complexes (2 and 6) respectively, may be due to the charge transfer transition.

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Table (1) Analytical and physical data of the ligands and their complexes

Complexes formula	Colour	m.p°C	Yield %	M.wt of compounds	Found (calc)			
					C	H	N	Metal
$C_{13}H_{11}NO$	Yellow	249-250	74	197	78.50 (78.55)	5.36 (5.40)	6.80 (6.89)	-
m-$C_{13}H_{10}NOBr$	Yellow	218-220	65	277	55.78 (55.84)	3.39 (3.45)	4.87 (4.90)	-
p-$C_{13}H_{10}NOBr$	Green	236-238	68	277	55.80 (55.84)	3.41 (3.45)	4.90 (4.90)	-
$C_{19}H_{14}O_3NSb$	Pale Brown	198-200	68	425	53.54 (53.60)	3.10 (3.17)	3.11 (3.15)	28.14 (28.20)
m-$C_{19}H_{13}O_3NBrSb$	Red-Brown	220-222	62	504	45.23 (45.03)	2.47 (2.50)	2.55 (2.57)	23.91 23.94
p-$C_{19}H_{13}O_3NBrSb$	Pale-Brown	238-240	66	504	45.00 (45.03)	2.45 (2.50)	2.30 (2.32)	23.91 23.94
$C_{19}H_{14}O_3NSnCl$	Green	300-302	75	457.5	49,49 (49.53)	2.89 (3.00)	3.00 (3.01)	25.55 25.59
m-$C_{19}H_{13}O_3NBrSnCl$	Deep-Green	178-180	66	537.5	42.11 (42.21)	2.16 (2.20)	2.27 (2.30)	21.80 21.85
p-$C_{19}H_{13}O_3NBrSnCl$	Deep-Green	193-195	60	537.5	42.16 (42.21)	2.18 (2.20)	2.49 (2.50)	21.79 21.85

Table (2) I. R. spectral data of the ligand and its complexes

Compound	υ(C-O) cat υ(C-O) phen	υ(C=N)	υ(C-H) Iminic	υ(M-O)	υ(M-N)
HL^1	(1290.29)	1598.90	2559.36	-	-
[Sb(cate)L^1]	1037.60 (1249.8)	1591.00	2526.57	550.00	403.00
[Sn(cate)L^1]Cl	1035.70 (1242.07)	1593.09	2526.57	525.00	460.00
HL^2	(1282.57)	1618.17	2594.08	-	-
[Sb(cate)L^2]	1068.50 (1247.80)	1593.09	2503.43	577.00	455.00
[Sn(cate)L^2]Cl	1033.80(1247.90)	1591.20	2374.20	549.70	470.10
HL^3	(1282.60)	1612.38	2516.93	-	-
[Sb(cate)L^3]	1035.70 (1247.80)	1591.00	2364.50	513.00	475.00
[Sn(cate)L^3]Cl	1029.90 (1247.90)	1618.20	2518.90	520.70	468.70

Table (3) Electronic spectral data and conductance measurements of ligands and their complexes

Compound	λ (nm)	εmax (molar^{-1}cm^{-1})	Λm (S.cm^2.mol^{-1})	Medium	Ratio
HL^1	241 287	1531 192	-		
[Sb(cate)L^1]	232 277	200 1625	20.4	DMF	Neutral
[Sn(cate)L^1]Cl	237 277 351	145 1722 702	87.65	DMF	1:1
HL^2	239 282	1401 784	-		
[Sb(cate)L^2]	226 279	265 2100	8.45	DMF	Neutral
[S(cate)L^2]Cl	238 276	105 1611	102.00	DMF	1:1
HL^3	240 280 342	1495 948 1691	-		
[Sb(cate)L^3]	238 277	200 1763	10.25	DMF	Neutral
[Sn(cate)L^3]Cl	238 275 304	43 1444 1451	93.77	DMF	1:1

Table (4) ^{1}H, ^{13}C NMR data for the ligand measured in DMSO–d_6 and chemical shift in ppm (δ)

	Funct .group	δ (p.p.m)
[HL^1]	O-H	12.68(H,s)
	H-C=N	8.97 (H,s)
	Aromatic H	6.96-7.68

	Funct .group	δ (p.p.m)
[HL^1]	C=N	164
	C-N	150
	C-O	160
	Aromatic C	116-123

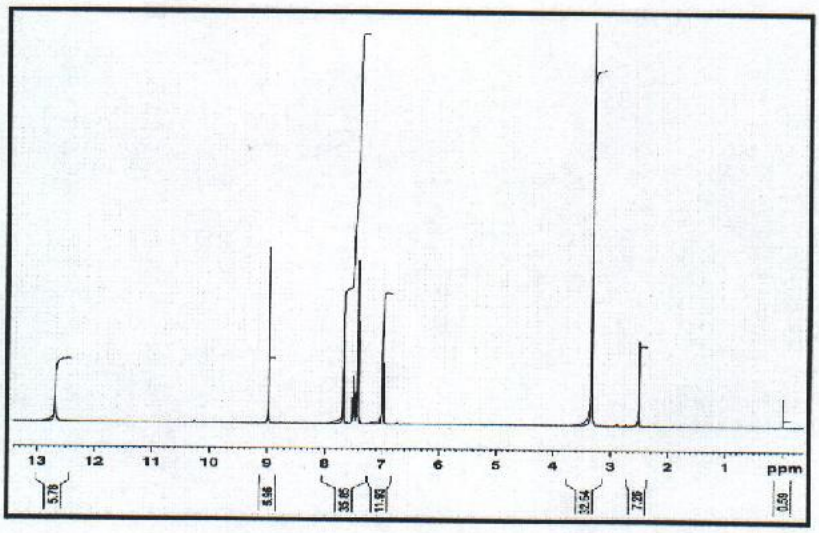


Fig. (1) The ^{1}H NMR spectrum of the ligand [HL^{1}] in DMSO-d^{6}

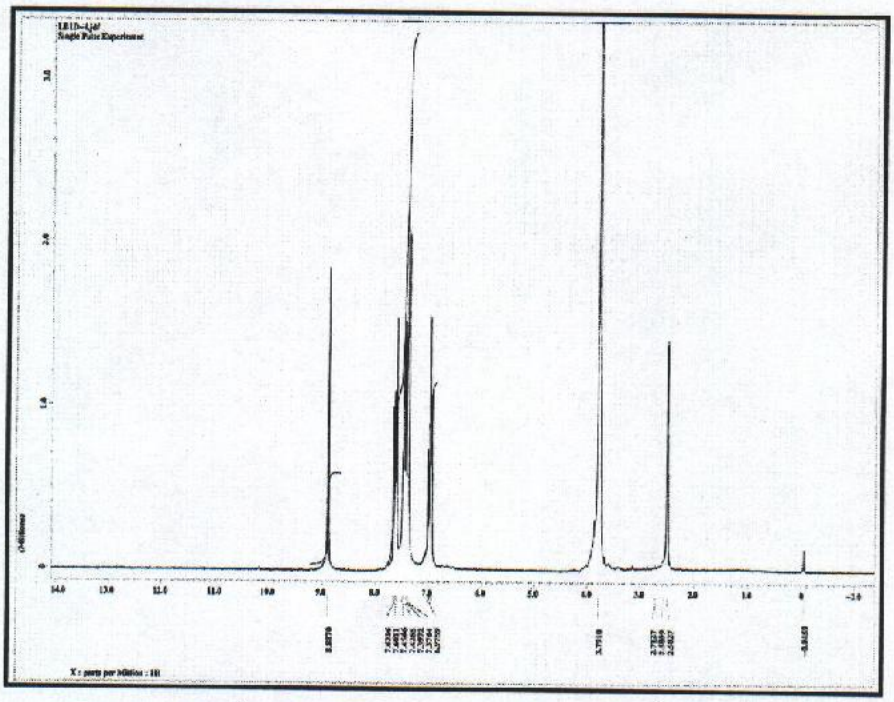


Fig. (2) The ^{1}H NMR spectrum of the ligand [HL^{1}] in D_2O

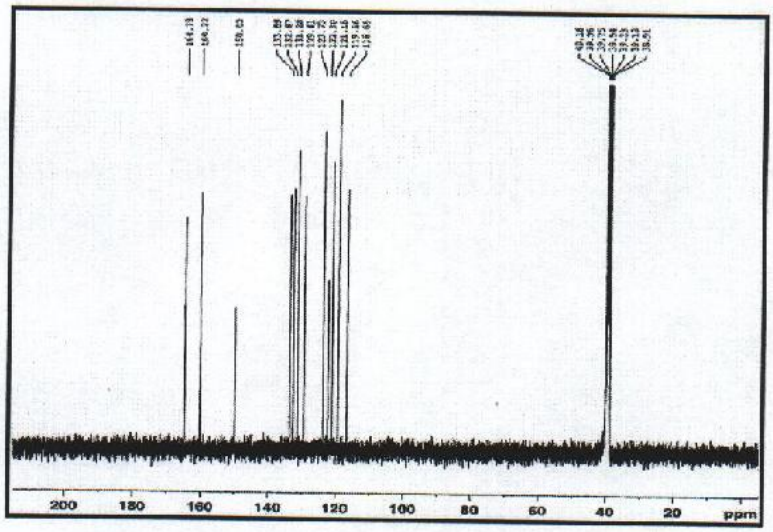
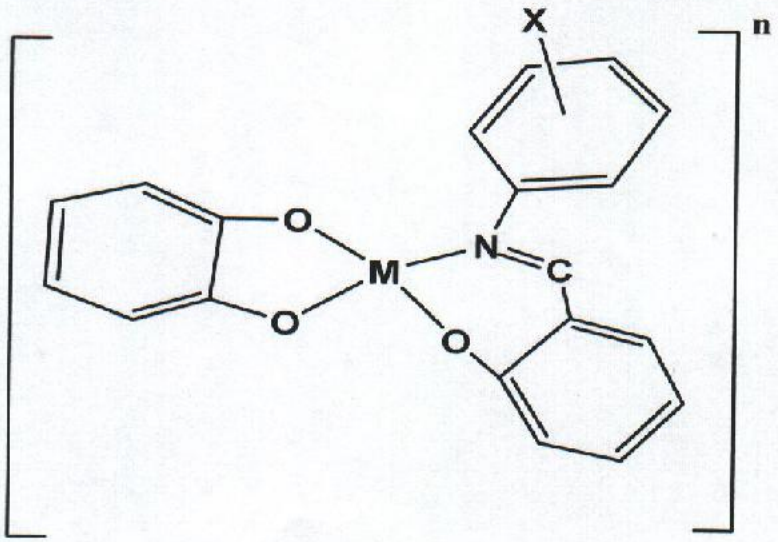


Fig. (3) The ^{13}C NMR spectrum of the ligand [HL^1] in DMSO-d^6



M = Sb^{III}, n = 0: M = Sn^{IV}, n = +1
X = H = L^1; X = *m*-Br = L^2; X = *p*-Br = L^3
Fig. (4) The suggested structure of the compounds

تحضير ودراسة طيفية لمشتقات مختلطة من الكاتيكول والساليسايل ديمنيت للانتمون (III) والقصدير (IV)

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الخلاصة

تضمن البحث تحضير ثلاثة ليكاندات جديدة HL^3 و HL^2 و HL^1 وذلك من مفاعلة الانلين او الانلين المعوض بالبروم في الموقع m او p مع السلسديهايد (تفاعل شف) ثم مفاعلة الليكندات الثلاثة مع مشتقات الكاتيكول ل Sb(III) و Sn(IV) وباستعمال الميثانول مذيبا، اذ تكونت معقدات جديدة ، شخصت المركبات المحضرة بالطرائق الطيفية [الاشعة تحت الحمراء، فوق البنفسجة و الرنين النووي المغناطيسي] التحليل الدقيق للعناصر والتوصيلية الكهربائية. ومن النتائج اعلاه فان الشكل الفراغي المقترح للمعقدات هورباعي السطوح وكما في الشكل (4).