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Synthesis & Characterization of OxoZirconium(IV) Complexes of 4- [N-Substituted Amino]Antipyrine Morpholino Methyl Thiourea

Dr. Ravindra Singh Yadav& Dr. Seema Kohli
Associate Professor
Department Of Chemistry M.M.H. College Ghaziabad (U.P.) India.
Email : ravindra11yadav67@gmail.com & seemakohli20@yahoo.co.in

Abstract:
New oxozirconium complexes were synthesized. Schiff's base of 4-amino antipyrine with different aromatic aldehydes were prepared which were then condensed with morpholino methyl thiourea to give ligands($L_1 - L_4$).The ligands were reacted with oxozirconium(IV) chloride to form complexes. The complexes were characterized and their structures established by various physio chemical techniques viz elemental analysis, molecular weight, molar conductance, IR . On the basis of above observation the complexes may be formulated as $[ZrO(L)_2O]Cl_2$

Keywords: Oxozirconium, complexes, Schiff's base, Ligands, Molar conductance

1. Introduction:

The Synthesis of transition metal complexes with thiosemicarbazone ligands have been receiving considerable attention due to the pharmacological properties[1-7] of both ligands and complexes, variable bonding models[8-10], promising biological implications[11], structural diversity and ion sensing ability. In the present work we synthesized oxozirconium complexes with 4-[N-Substituted amino] antipyrine morpholino methyl thiourea which have been characterized through elemental analysis, molecular weight, molar conductance and IR.

2. Experimental:

2.1. Materials Used :

All the chemical used were of Analytical R grade and procured from Aldrich,spectrochem and Flucka oxozirconium(IV) chloride was purchased from Reidal. All solvents obtained commercially were distilled before use.

2.2. Synthesis of Ligands :

L_1 – N-[(P-Chloro benzalidene)amino] antipyrine morpholino methylthiourea($C_{24}H_{27}ON_6SCl$)
An ethanolic to a solution of 4-amino antipyrine(10mmol,2.03gm) was added to a solution of P-chlorobenzaldehyde(10mmol,1.40gm) in ethanol(10ml).The mixture was refluxed for one hour. The coloured precipitation was obtained by slow evaporation of the solution to give N-[(P-Chlorobenzalidene) amino]antipyrine. This was then condensed with morpholino methyl urea to give N-[(P-Chlorobenzaldene) amino] antipyrine morpholino methylthiourea($C_{24}H_{27}ON_6SCl$). Similarly other ligands were synthesized.
L_2- 4-[N(4-diethyl aminobenzalidene)amino] antipyrine morpholino methylthiourea($C_{28}H_{37}ON_7S$).
L_3- 4-[N-(4-ethoxybenzalidene)amino]antipyrine morpholino methyl thiourea ($C_{26}H_{32}O_2N_6S$)
L_4- 4-[N-(4-hydroxy-3-ethoxybenzalidene)amino]antipyrine morpholino methyl thiourea ($C_{26}H_{32}O_3N_6S$)

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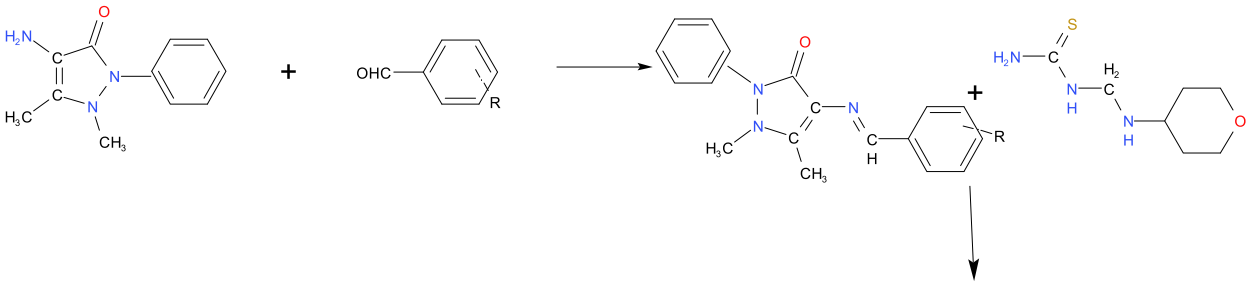


Synthesis of Ligands
(L_1-L_4)

2.3. Synthesis of complexes:

To a solution of ligands (L_1-L_4) 0.002M dissolved in ethanol (25 ml), solution of oxozirconium(IV) chloride in ethanol was added dropwise with constant stirring. The mixture was refluxed on a water bath for 5-6 hours. The precipitated complexes were filtered , washed with water and dried over fused calcium chloride.

2.4. Physical Measurements:

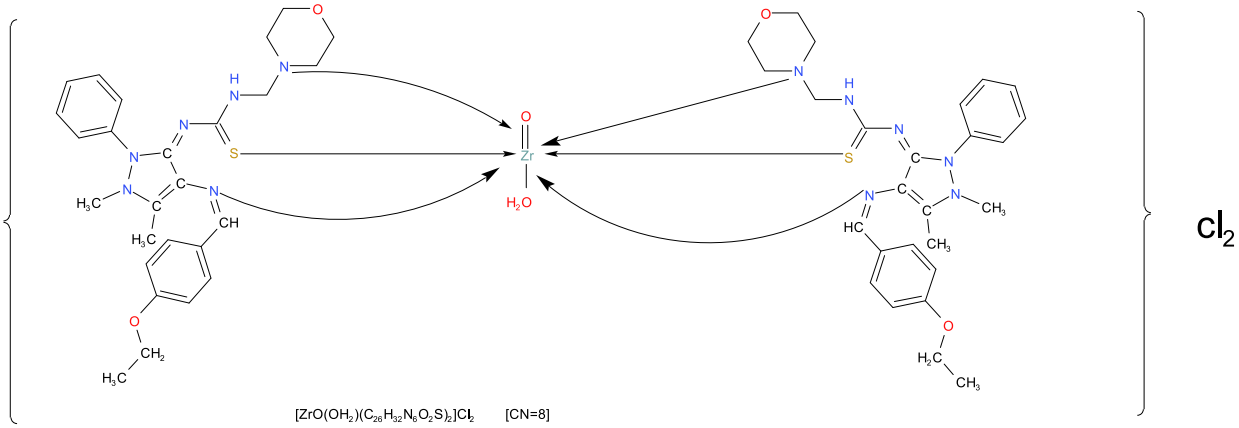
C,H,N were analyzed using Perkin-Elmer 240 elemental analyzer. Molar conductance was measured on the systronics, conductivity bridge. Infrared spectra of ligand and there complexes have been recorded in KBr pellets on a Perkin-Elmer infracord spectrophotometer. The molar conductance data of the complexes suggest that all the complexes are conic in nature and both the chloro ions are present outside the coordination sphere. The complexes were 1:2 electrolytes in nature and may be formulated as [ZrO(L_2)H2O]Cl_2

2.5. Magnetic moment:

Since oxozirconium ion does not have unpaired electrons in the ground state the complexes are diamagnetic in nature.

3. Results and Discussion:

The reaction of ethanolic solution of ligands ($L_1 - L_4$) with metal salts gave the complexes [ZrO$(L)_2H_2$O]Cl_2 as established on the basis of microanalysis and conductance value. The proposed structure of the complex.



Probable Structures Of OxoZirconim(IV) Complex

3.1. Nature of Coordination:

Infrared spectrum of free ligands($L_1 - L_4$) and their respective metal complexes reveal that these ligands behave as neutral tridentate and the coordination sites are azomethine nitrogen atom, morpholine nitrogen and thioketosulphur (N,N,S donors) and the coordination number of zirconium is found to be eight.IR data of ligands & complexes are given in tabular form

TABLE 1: Analytical & Physical data of Schiff bases & thiosemicarbazones and the complexes

S.No.	Schiff Bases	Yield (%) Colour	% Chemical Analysis Found Calculated			M.Pt. (C)
			C	H	N	
1	N-[P-Chloro(benzalidene) amino] (CBAAP) ($C_{18}H_{16}N_3OCl$)	80 Yellow	(66.35) 66.22	(4.91) 4.80	(12.90) 12.78	164
2	4[N-Chloro(benzalidene) amino]antipyrine (DEABAAP) ($C_{22}H_{26}N_4O$)	75 Yellow	(72.92) 72.75	(7.18) 7.10	(15.46) 15.36	200
3	4[N-(4-ethoxybenzalidene) amino]antipyrine (EBAAP) ($C_{20}H_{21}N_3O_2$)	80 Yellow	(71.64) 71.54	(6.26) 6.16	(12.53) 12.40	155
4	4[N-(4-hydroxy-3-ethoxybenzalidene)amino]antipyrine (HEBAAP) ($C_{20}H_{21}N_3O_3$)	75 Yellow	(68.57) 68.45	(5.98) 5.82	(11.96) 11.86	185
5	[N-(P-Chloro benzalidene)amino] antipyrine morpholino methyl thiourea($C_{24}H_{27}ON_6SCl$)	75 Yellow	(59.68) 5.50	(5.59) 5.50	(17.40) 17.30	165
6	4[N-(4-diethylaminobenzalidene) amino]antipyrine morpholino thiourea ($C_{26}H_{32}O_2N_6$S)	70 Yellow	(68.71) 68.60	(7.56) 7.46	(20.04) 19.90	210
7	4[N-(4-ethoxybenzalidene)amino] antipyrine morpholino methyl thiourea ($C_{26}H_{32}O_2N_6$S)	75 Yellow	(63.41) 63.30	(6.50) 6.38	(17.07) 16.90	175
8	4[N-(4-hydroxy-3-ethoxybenzalidene)amino] antipyrine morpholino methyl thiourea ($C_{26}H_{32}O_3N_6$S)	80 Yellow	(61.41) 61.30	(6.29) 6.15	(16.53) 16.40	190

TABLE 2: Analytical, Conductivity and Molecular weight data of ZrO^{2+} complexes of morpholine methyl thiourea Schiff bases.

S.No.	Complex	Yield (%)	Chemical analysis Found (Calcd.) %					Mol. Wt Found (Calcd.)	ΩM
			Zr	C	H	N	S		
1	$ZrOCl_2.2(C_{24}H_{27}ON_6SCl)H_2O$	70	7.71 (7.85)	49.40 (49.60)	4.68 (4.82)	14.32 (14.46)	5.40 (5.57)	377 (1161.22)	55.12
2	$ZrOCl_2.2(C_{28}H_{37}ON_7S)H_2O$	70	7.60 (7.76)	57.09 (57.22)	6.30 (6.47)	16.50 (16.69)	5.30 (5.45)	381 (1174.22)	54.86
3	$ZrOCl_2.2(C_{26}H_{32}O_3N_6S)H_2O$	65	7.48 (7.53)	52.10 (52.25)	5.35 (5.52)	13.86 (14.06)	5.30 (5.35)	388 (1194.22)	55.15
4	$ZrOCl_2.2(C_{26}H_{32}O_2N_6S)H_2O$	70	7.58 (7.72)	52.70 (52.87)	5.43 (5.59)	14.05 (14.23)	5.28 (5.42)	379 (1180.22)	55.85

TABLE 3: Infrared absorption frequencies of oxozirconium(IV) complex of [N-(P-Chloro benzalidene)amino] antipyrine morpholino methyl thiourea($C_{24}H_{27}ON_6SCl$);4[N-(4-diethylaminobenzalidene) amino]antipyrine morpholino thiourea ($C_{26}H_{32}O_2N_6$S);4[N-(4-ethoxybenzalidene)amino] antipyrine morpholino methyl thiourea ($C_{26}H_{32}O_2N_6$S);4[N-(4-hydroxy-3-ethoxybenzalidene)amino] antipyrine morpholino methyl thiourea ($C_{26}H_{32}O_3N_6$S)

Assignments	$C_{24}H_{27}ON_6SCl$	$ZrO_2Cl_2.2(C_{24}H_{27}ON_6SCl)$	$C_{28}H_{37}ON_7S$	$ZrO_2Cl_2.2(C_{28}H_{37}ON_7S)H_2O$	$C_{26}H_{32}O_2N_6S$	$ZrO_2Cl_2.2(C_{26}H_{32}O_2N_6S)$	$C_{26}H_{32}O_3N_6S$	$ZrO_2Cl_2.2(C_{26}H_{32}O_2N_6S)H_2O$
1	2	3	4	5	6	7	8	9
V(NH)	3440s 3270s	3430m 3265m	3360s 3330s	3345m 3315m	3420s 3310s	3400m 3275m	3440s 3280s	3335m 3290m
V(C=N)	1600vs	1570m	1600vs	1565m	1600vs	1570m	1600vs	1560m
V(C=S)+V(C=N) + V(C-N)	1330s 1300s	1380s 1330m	1310m 1290m	1370m 1330m	1320s 1190m	1326m 1210m	1315s 1180m	1370m 1190m
$\delta(NCS)$+CS	1120s 1095s	1160m 1130m	1115m 1095w	1170m 1330m	1120m 1095m	1170m 1130m	1120m 1095m	1160m 1130m
v(N-N)	1050s	1065m	1050m	1060m	1060m	1070m	1040m	1055m
v(C=S)	820s 760vs	790s 780m	830s 730m	840m 820s	840m 820s	770m 760m 715m	840s 820m 780s	810s 790m 730s
v(Zr-N)/v(Zr-S)	-	380m 340w	-	-	-	375m 340w	-	380m 350w

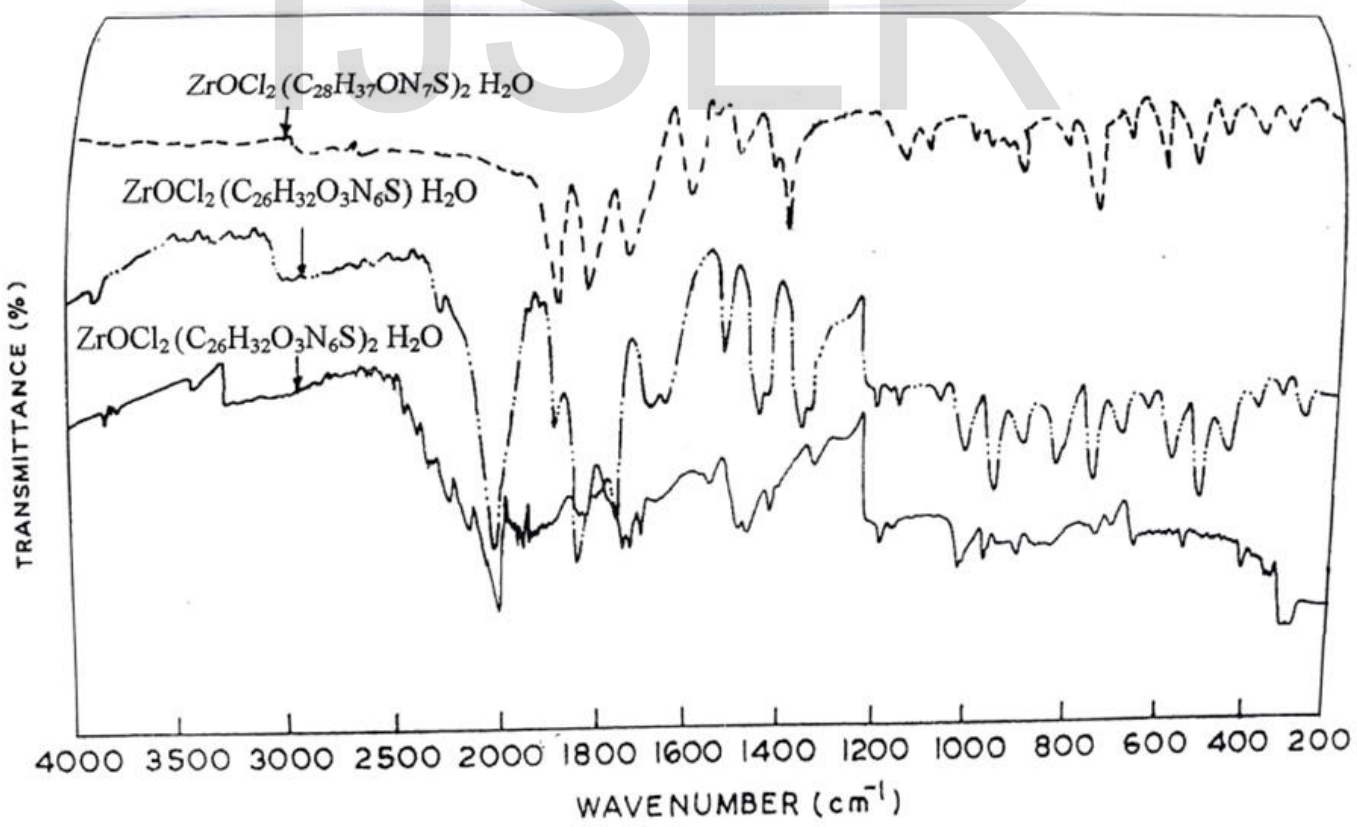


Figure-1 – IR SPECTRA OF COMPLEXES
1, $ZrOCl_2(C_{28}H_{37}ON_7S)_2\ H_2O$ 2, $ZrOCl_2(C_{26}H_{32}O_3N_6S)\ H_2O$ 3, $ZrOCl_2(C_{26}H_{32}O_3N_6S)_2\ H_2O$

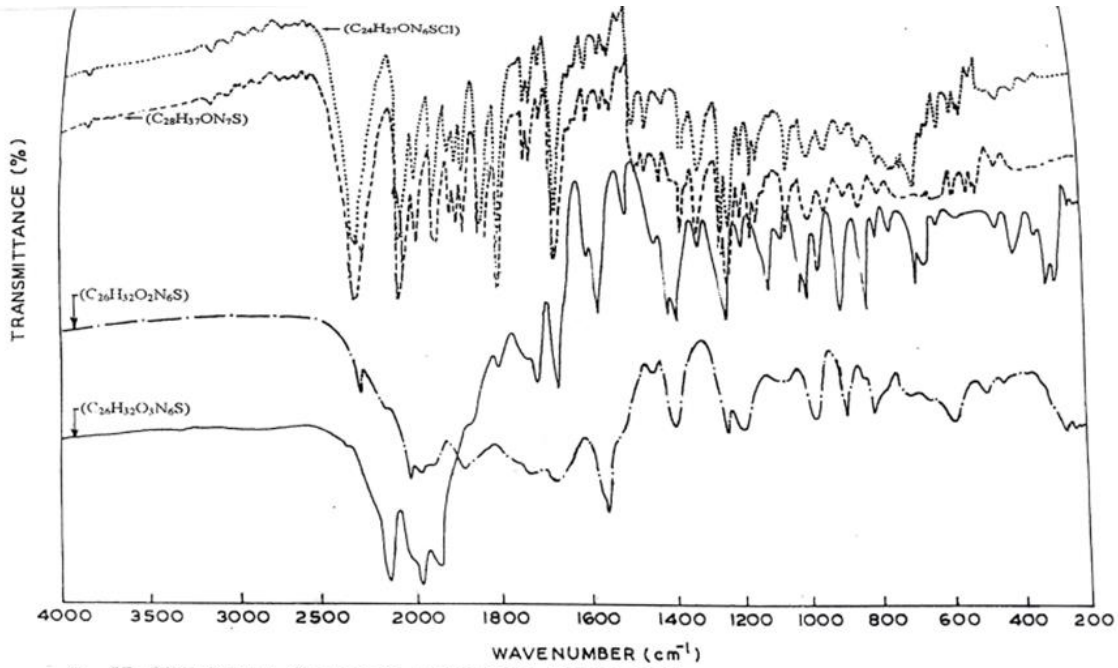


Figure-2– IR SPECTRA OF ORGANIC COMPOUNDS

1, ($C_{24}H_{27}ON_6SCl$) [N(P-Chloro benzalidene)-amino]antipyrine Morpholino Methyl Thio Urea
2, ($C_{28}H_{37}ON_7S$)-4[N-(4-Diethyl amino benzalidene)amino]antipyrine Morpholino Methyl Thio Urea
3, ($C_{26}H_{32}O_2N_6S$)-4[N-(4-ethoxy benzalidene)amino] antipyrine Morpholino Methyl Thio Urea
4, ($C_{26}H_{32}O_3N_6S$)-4[N-(4-Hydroxy-3-ethoxy benzalidene)amino]antipyrine Morpholino Methyl Thio Urea

4. Acknowledgements:

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