



STUDIES OF SOME NEW COORDINATION COMPOUNDS OF Al(III) WITH SEMICARBAZONES AND THIOSEMICARBAZONES.

Shilpa Sharma, Monica Bedi, Monika Gupta, S. Varshney and
A. K. Varshney*

Department of Chemistry, University of Rajasthan, Jaipur-302004, India.

*E-mail- anilakv123@rediffmail.com

ABSTRACT

Reactions of Aluminium isopropoxide with the ligands having donor groups $\text{N} \begin{array}{c} \text{SH} \\ \text{OH} \end{array}$ and $\text{N} \begin{array}{c} \text{SH} \\ \text{OH} \end{array}$ have resulted in complexes of the type $[\text{Al}_2(\text{N} \begin{array}{c} \text{XH} \\ \text{XH} \end{array})_2(\text{OPr}^i)_2]$, $[\text{Al}_2(\text{N} \begin{array}{c} \text{XH} \\ \text{XH} \end{array})_3]$ (where X = O or S). The reaction products from equimolar (M:L) ratios are dimeric, whereas 2:3 (M:L) ratios yield monomeric reaction products in boiling benzene. The resulting derivatives have been characterised on the basis of elemental analysis, molecular weight determination and conductivity measurement, IR, ^1H NMR and electronic spectral studies. The antibacterial and antifungal activities of the ligands and their Al(III) coordination compounds have been screened in vitro against the organism *Escherichia coli*, *Staphylococcus aureus*, *Proteus mirabilis*, *Bacillus thurengilensis*, *P. capsacicola* (bacteria) and *F. oxysporum*, *A. flavus*, *R. phaseoli* (Fungi).

Keywords : Aluminium isopropoxide; Semicarbazone; Thiosemicarbazone; Spectral studies; Antimicrobial activities.

INTRODUCTION

Amongst the nitrogen, oxygen and sulphur donor ligands, semicarbazones and thiosemicarbazones are considered to be very important molecules because of their potentially beneficial biological activities such as antitumor, antibacterial antiviral and antimalarial activities. Their activity increases on complexation with metal ion¹⁻⁷. A considerable interest in their coordination is also arised due to their interesting stereochemistry as only the β - nitrogen coordinate to the metal atom⁸.

However, little is known about the complexing behaviours of non-transition elements with these ligands. Amongst the non-transition elements aluminium occupies an important position as a number of modern physico-chemical techniques can be applied for the detailed structural study of its compounds. It was therefore, considered worthwhile to synthesize and characterize aluminium(III) complexes of semicarbazone and thiosemicarbazone. The ligands used in the present investigation are shown as below in Fig. 1. Semicarbazones and thiosemicarbazones of 2-hydroxypropiophenone (a), 1-acetyl-2-nephthol (b) and 2-acetyl-1-Nephthol (c).

EXPERIMENTAL

Analytical methods and physical measurements

All the chemicals used in this work of AR grade and solvents were dried by standard method. All reactions were carried out under strictly anhydrous conditions.

Nitrogen was determined by Kjeldahl's method and sulphur by Messenger's method⁵. The IR spectra were recorded on a Perkin-Elmer 577 IR spectrometer in the region 4000-200 cm^{-1} using KBr optics. The electronic spectra (in mentioned) were taken with a Toshniwal spectrophotometer. A Jeol 300 MHz spectrometer was used to obtain the ^1H NMR spectra using DMSO- d_6 as solvent.

Molar conductance measurements were made in anhydrous dimethyl formamide at $36 \pm 1^\circ\text{C}$ using a model 305 systronics conductivity bridge. Molecular weight determinations were carried out by the Rast Camphor Method.

Antibacterial and Antifungal Test

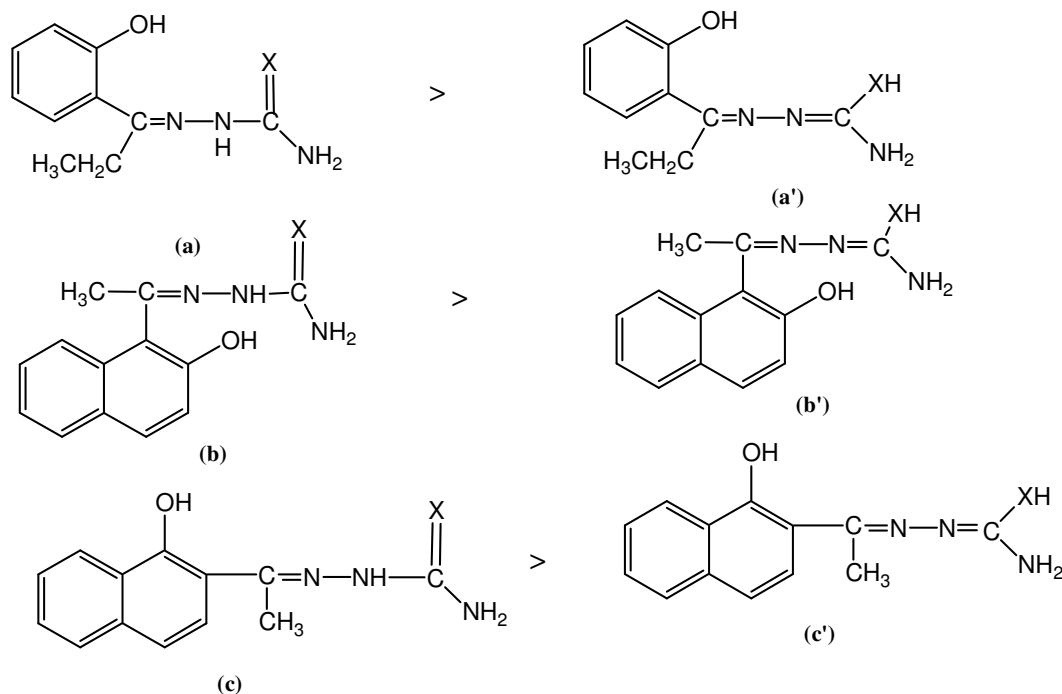
In vitro antibacterial and antifungal activities of the ligands and the complexes were tested using the paper disc diffusion method⁴ at a concentration of 100 ppm. Streptomycin was used as reference compound for antibacterial activities *Escherichia coli*, *Staphylococcus aureus*, *P. capacicola* (Bacteria) *F. oxysporum*, *A. flavus*, *R. phaseoli* (Fungi).

Synthesis of ligands

The Schiff bases were synthesized by the condensation of 2-hydroxypropiophenone, 1-acetyl-2-naphthol, 2-acetyl-1-naphthol with semicarbazide hydrochloride and thiosemicarbazide in 1:1 molar ratio using ethanol as reaction medium. The solution was refluxed on a water bath for 2h and then allowed to cool at room temperature. The crystalline solids were separated out and purified by recrystallization from the same solvent. The list of ligands is given in the Table-1.

Synthesis of Aluminium(III) Compounds

A weighed amount of Aluminium(III) isopropoxide was added to the calculated amount of Schiff bases in a molar ratio 1:1 and 2:3 molar ratio in dry benzene and refluxed under a fractionating column. The isopropanol liberated during the reaction by deprotonation of the ligand was removed azeotropically with benzene. After the complexation of the reaction the products were dried under reduced pressure and analysed. The purity of the compounds was checked by TLC using silica gel-G as an adsorbent. The physical properties and analytical data are recorded in Table-2.



(Where X = O or S)

(O = Semicarbazone)

(S = Thiosemicarbazones)

Fig.-1: Semicarbazone and thiosemicarbazone used as ligands in this work

RESULTS AND DISCUSSION

All the newly synthesized aluminum complexes are coloured solids, stable to ~200°C, undergoing decomposition above this temperature and soluble in most common organic solvents. The 1:1 products are hygroscopic and dimeric in boiling benzene, the dimerization possibly taking place through the

bridging isopropoxy groups^{6,7} (Fig. 2). In these compound $[(Pr^iO)Al(O \overset{\curvearrowright}{N} X)]_2$ obtained by treating $Al(OPr^i)_3$ with equimolar bibasic tridentate Schiff bases, in two aluminum atoms appear to exist in the pentacoordinated environment.

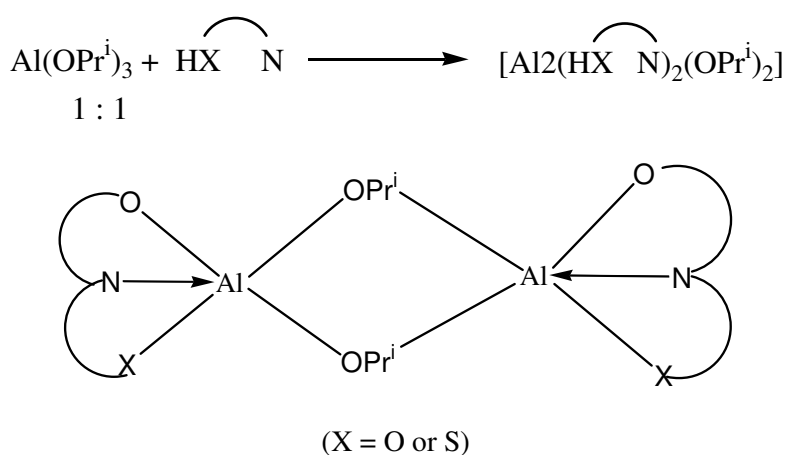


Fig.-2 : Proposed structure of monoisopropoxy aluminium Schiff bases complex

Although such a state is uncommon in case of aluminium, it has been claimed to exist⁸⁻¹⁰. The reaction of $Al(OPr^i)_3$ with bibasic tridentate (Fig. 1a, b & c) Schiff bases in a 2:3 (M:L) ratio lead to the isolation of tris Schiff base derivatives (Fig. 3). These are quite stable in the open atmosphere. On account of their apparent monomeric nature in boiling benzene, the aluminium atoms acquire a four coordination member in the products of bibasic tridentate Schiff base complexes.

Molecular weight measurements in boiling benzene show the complexes to be dimeric. Results of elemental analysis and physical characteristics of the resulting products are given in Table-1.

A comparative study of 1:1 and 2:3 aluminium complexes shows that as expected the 1:1 complexes are more reactive and less stable than the 2:3 complexes. This is probably due to the presence of the isopropoxy group in the former case and on account of which the product dimerizes.

In 2:3 complexes, however there is no isopropoxy group present either to undergo dimerization or replacement reaction with a suitable ligand moiety. Moreover, these are planar ligand molecules with highly conjugated chelate rings and these further enhance the stability of the molecules.

Electronic Spectra

Two intense maxima were observed in the ligands at 250 nm and 315 nm. These bands are fully consistent with the typical spectrum of semicarbazones and thiosemicarbazones (cyclic form) and may be attributed to the $\Phi - \Phi^*$ and $\pi - \pi^*$ benzenoid transitions. In the corresponding 2:3 aluminium complexes (Fig. 3) an additional band around 400 nm is observed. This new band may be assigned to either the $n - \pi^*$ transitions or the $\pi - \pi^*$ transitions of the double bond of the azomethine group.

IR Spectra

In the IR spectra of the ligands, a very strong and sharp band in the region $3260-3390\text{ cm}^{-1}$ is observed and this may be attributed to the $\nu(\text{NH})$ stretching vibration of semicarbazones and thiosemicarbazones (Fig.

1). A broadening in this band in the ligand indicates a probable association of $\nu\text{N-H}$ with phenolic OH vibration. This band does not exist in the aluminium complexes suggesting chelation through nitrogen of the azomethine group¹¹. The appearance of a sharp band around 1610 cm^{-1} in the aluminium complexes may be attributed to a coordinated $>\text{C}=\text{N}$ group. Several new bands in the region $700\text{-}300\text{ cm}^{-1}$ are observed in the aluminium complexes¹²⁻¹⁶ and these may be attributed to the different vibrational modes of Al-O ($760\text{-}610\text{ cm}^{-1}$) Al-N ($570\text{-}420\text{ cm}^{-1}$) and Al-S ($410\text{-}300\text{ cm}^{-1}$) bonds. These frequency are listed in Table-3.

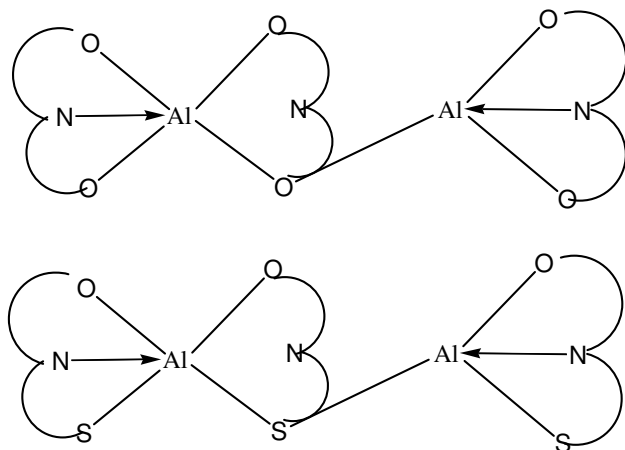


Fig.-3 : Possible structure of bisaluminium tris Schiff base complexes

¹H NMR Spectra

The ligands showed a signal at $\delta \sim 8.55\text{ ppm}$ assignable to azomethine proton [$\text{CH}=\text{N}$]. The downfield in the spectra of aluminium complexes indicated coordination through the azomethine nitrogen to the aluminium atom resulting in the formation of a coordinate $\text{Al} \leftarrow \text{N}$ linkage.

Further, the azomethine proton ($\begin{array}{c} \text{---C}=\text{N---} \\ | \\ \text{H} \end{array}$) signal at $\delta 8\text{ ppm}$ in the ligand, shifts downfield in the aluminium complexes. This indicates metal azine interaction in chelate ring^{17,18}.

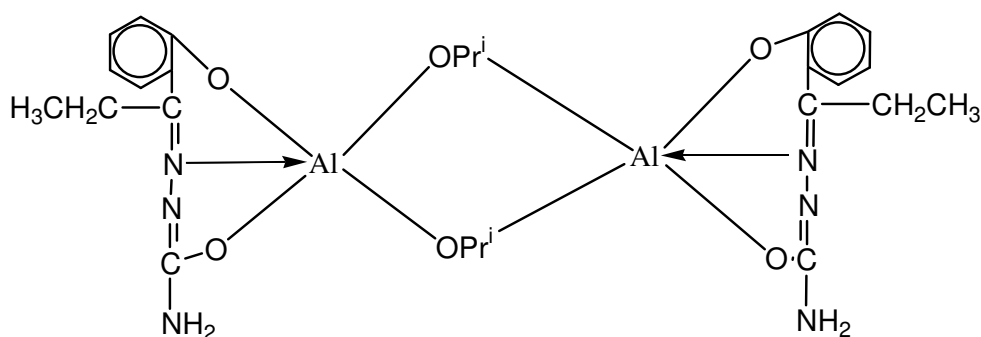


Fig.-4 : Complexes of Aluminium with 2-hydroxy propiophenone semicarbazone

Antibacterial Results

All the Aluminium(III) coordination compounds were tested against gram positive and gram negative bacteria. The result shows that all the complexes were active against gram positive bacteria while less active against *E. coli*, which is gram negative.

The result further show that complexes were more active than the ligands¹⁹⁻²¹ which indicates that metallation increases the activity.

CONCLUSION

A comparative study of 1:1 and 2:3 aluminium complexes shows that as expected the 1:1 complexes are more reactive and less stable than the 2:3 complexes. This is probably due to the presence of the isopropoxy group in the former case and on account of which the product dimerizes.

In 2:3 complexes, however there is no isopropoxy group present either to undergo dimerization or replacement reaction with a suitable ligand moiety. Moreover, these are planner ligand molecules with highly conjugated chelate rings and these further enhance the stability of the molecules. The result further show that complexes were more active than the ligands which indicates that metallation increases the activity.

ACKNOWLEDGEMENTS

The authors are thankful to the Head, Department of Chemistry, University of Rajasthan, Jaipur for providing laboratory facilities and constant encouragement. Shilpa Sharma and Monica Bedi are thankful to CSIR New Delhi for providing financial assistance. AKV and SV are thankful to UGC, Bhopal for providing financial assistance.

REFERENCES

1. A.E.Liberta ,and D.X.West, *BioMetals*,**5**,121 (1992).
2. D.X.West, S.B.Padhye, and P.B.Sonawane ,*Struct. Bonding*, **76**,1 (1991).
3. M.J.M.Campbell,*Coord. Chem..Rev.* ,**15** ,279 (1975).
4. M.C.Lin, T.S.Lin, and A.C.Sartorelli,*J.Med.Chem.*, **35**,3672 (1992).
5. D.X.West,A.E.Liberta,K.G.Rajendran, and I.H.Hall ,*Anti-cancer Drugs*,**4** ,241 (1993).
6. I.H.Hall,M.C.Miller III, and D.X.West ,*Metal-basesd Drugs*,**4**,89 (1997).
7. A.G.Quirga, and C.N.Ranninger ,*Coord. Chem.Revs.* ,**248**,119 (2004).
8. D.Lui ,and Kwasniewska, *Bull. Environm. Toxicol.*, **27**,289 (1981).
9. H.H. Waung, and K.M. Huri, *J. Organometal. Chem.*, **6**,504 (1966).
10. R.N. Prasad ,and J.P. Tandon, *J. Inorg. Nucl. Chem.*, **36**,1473 (1974).
11. R.N. Prasad,and J.P. Tandon,*Z. Naturforsch*, **28B**,63 (1973).
12. V.J. Shiner Jr., and D. Wittaker, *J. Am. Chem. Soc.*, **87**,843 (1965).
13. J.K. Ruff ,and M.F. Hawthorne, *J. Am. Chem. Soc.*, **82**,2141 (1960).
14. N.R. Fetter, B. Bartocha, F.E. Brinckman Jr., and D.W. Moore, *Canad. J. Chem.*, **41**,1359 (1963).
15. M. Nath, and S. Goyal, *Bull. Chem. Soc. Japan*, **69**,605 (1996).
16. M.D. Hobday, and T.D. Smith, *J. Chem. Soc.*, **31A**,1549 (1971).
17. A.K. Varshney, and J.P. Tandon, *Polyhedron*, **5**,1853 (1986).
18. A.K. Varshney, J.P. Tandon, and A.J. Crowe ,*Polyhedron*, **5**,739 (1986).
19. P.F.R. Ewings, P.G. Harison, and A. Mamgia, *J. Organomet. Chem.*,**114**,35 (1976).
20. A.K. Varshney, S. Varshney, and H.L. Singh, *Bull. Pol. Acad. Chem. Science*, **45**,373 (1997).
21. M.P. Koef , and Prog. Clin., *Bio. Chem. Med.*,**10**,151 (1989).
22. M. Vazquez, M.R. Bermjo, M. Fond, A. Deibe Garcia, A.M. Gondez, and R. Pedrido, *Appl. Organomet Chem.*, **16**,465 (2002).
23. C. Pettinari, F. Marchetti, A. Cingolani ,and S. Bartolani, *Polyhedron*, **15**,1263 (1996).
24. J. G. Horsfall, "Fungicides and their action" in: *Chronica Botanica*, Waltham, Massachusetts, (1945)
25. H. L. Singh, B. Khungar, U.D. Tripaathi, and A.K. Varshney, *Main Group Met. Chem.*, **24**,5 (2001).
26. R. Maheshwari, S. Sharma, M. Bedi, S. Varshney, and A.K. Varshney, *Polish J. Chem.*, **82**,1361-1365 (2008).
27. A.Sexena ,and J.P.Tandon,*Polyhedron*,**3**,681 (1984).
28. M.R.Maurya, A. Kumar, A.R. Bhat, A. Azam, C. Bader, D. Rehder, *Inorg Chem.*,**45**, 1260(2006).

29. L.Pellerito, and L. Nagy, *Coord. Chem. Rev.*, 224(2002).
30. M.R.Maurya, A. Kumar, A.R. Bhat, A. Azam, C. Bader, and D. Rehder, *Inorg Chem.*, **45**,1260(2002).
31. L.^a Papanthanas, M.A.^a Demertzis, P.N.^a Yadav, D.K.^a Demertzi, C.^a Prentjas, A.^b Castmeiaras, S.^a Skoulika and D.X.West, *Inorganica Chimica Acta*, **357**, 4113(2004).
32. T. Sedaghat and F. Jalilian *J.Iran. Chem.Soc.*, **6**,271(2009).

(Received: 2 August 2010

Accepted: 18 August 2010

RJC-611)

Table-1 : Analytical and Physical Properties of Ligands

Ligands	Colour & State	M.P.	Analysis (%)				M. Wt. Found (Calcd.)
			C Found (Calcd.)	H Found (Calcd.)	N Found (Calcd.)	S Found (Calcd.)	
2-hydroxypropionophenone semicarbazones (L ¹ H) (C ₁₀ H ₁₅ N ₃ O ₂)	Light yellow solid	160°C	57.0 (57.39)	7.0 (7.2)	18.0 (20.0)	-	209.50 (209.24)
2-hydroxypropionophenone (L ² H) thiosemicarbazones (C ₁₀ H ₁₅ N ₃ OS)	Dark yellow crystal	178°C	52.5 (53.32)	6.5 (6.7)	18.2 (18.6)	14.0 (14.2)	230.00 (225.21)
1-acetyl-2-naphthol semicarbazone (L ³ H) (C ₁₃ H ₁₇ N ₃ O ₂)	Brown solid	156°C	62.5 (63.13)	5.9 (6.9)	16.5 (16.99)		247.55 (247.28)
1-acetyl-2-naphthol thiosemicarbazone (L ⁴ H) (C ₁₃ H ₁₇ N ₃ O ₂)	Light brown solid	152°C	58.5 (59.28)	6.0 (6.5)	15.0 (15.95)	12.0 (12.15)	265 (263.34)
2-acetyl-1-naphthol semicarbazone (L ⁵ H) (C ₁₃ H ₁₇ N ₃ O ₂)	Yellow solid	149°C	62.0 (63.13)	5.8 (6.9)	16.0 (16.99)	-	250.00 (247.28)
2-acetyl-1-naphthol thiosemicarbazone (L ⁶ H) (C ₁₃ H ₁₇ N ₃ O ₂)	Pale yellow solid	164°C	59.0 (59.28)	6.0 (6.5)	14.0 (15.95)	11.5 (12.15)	265.00 (263.34)

Table-2: Synthesis new coordination compounds of Aluminum(III) isopropoxide with Semicarbazones and thiosemicarbazones.

Reactant metal	Ligand	Molar ratio	Product	Colour and State	M.P. C°	Mol. wt. found (Calcd.)	% Analysis found (Calcd.)		
							NFound (Calcd.)	SFound (Calcd.)	AlFound (Calcd.)
Al(OPr ⁱ) ₃	C ₁₀ H ₁₅ N ₃ O ₂ (L ¹ H)	1:1	[(Pr ⁱ O)Al(C ₁₀ H ₁₄ N ₃ O ₂) ₂]	Yellow solid	192	585.0 (588.42)	14.0 (14.28)	-	9.0 (9.1)
Al(OPr ⁱ) ₃	C ₁₀ H ₁₅ N ₃ O ₂ (L ¹ H)	2:3	(C ₁₀ H ₁₄ N ₃ O ₂) ₃ Al ₂	Orange solid	-	675.0 (680.65)	18.5 (18.51)	-	7.9 (7.92)
Al(OPr ⁱ) ₃	C ₁₀ H ₁₅ N ₃ OS (L ² H)	1:1	[(Pr ⁱ O)Al(C ₁₀ H ₁₄ N ₃ OS) ₂]	Yellow solid	-	620.5 (620.42)	13.5 (13.54)	10.30 (10.31)	8.6 (8.69)
Al(OPr ⁱ) ₃	C ₁₀ H ₁₅ N ₃ OS (L ² H)	2:3	(C ₁₀ H ₁₄ N ₃ OS) ₃ Al ₂	Orange solid	180	710.0 (726.65)	17.32 (17.34)	13.20 (13.21)	7.4 (7.42)
Al(OPr ⁱ) ₃	C ₁₃ H ₁₇ N ₃ O ₂ (L ³ H)	1:1	[(Pr ⁱ O)Al(C ₁₃ H ₁₆ N ₃ O ₂) ₂]	Brown solid	-	630.5 (638.44)	13.00 (13.16)	-	8.4 (8.45)
Al(OPr ⁱ) ₃	C ₁₃ H ₁₇ N ₃ O ₂ (L ³ H)	2:3	(C ₁₃ H ₁₆ N ₃ O ₂) ₃ Al ₂	Brown semi solid	-	810.0 (819.78)	15.0 (15.37)	-	6.5 (6.58)
Al(OPr ⁱ) ₃	C ₁₃ H ₁₇ N ₃ O ₂ (L ⁴ H)	1:1	[(Pr ⁱ O)Al(C ₁₃ H ₁₆ N ₃ OS) ₂]	Brown solid	-	665.0 (670.44)	12.5 (12.53)	9.5 (9.5)	8.0 (8.04)
Al(OPr ⁱ) ₃	C ₁₃ H ₁₇ N ₃ OS (L ⁴ H)	2:3	(C ₁₃ H ₁₆ N ₃ OS) ₃ Al ₂	Brown semi	-	865.0 (867.78)	14.5 (14.52)	11.00 (11.06)	6.2 (6.21)

				solid					
Al(OPr ⁱ) ₃	C ₁₃ H ₁₇ N ₃ O ₂ (L ⁵ H)	1:1	[(Pr ⁱ O)Al(C ₁₃ H ₁₆ N ₃ O ₂) ₂]	Yellow solid	179	630.0 (638.44)	13.10 (13.16)	-	8.4 (8.45)
Al(OPr ⁱ) ₃	C ₁₃ H ₁₇ N ₃ O ₂ (L ⁵ H)	2:3	(C ₁₃ H ₁₆ N ₃ O ₂) ₃ Al ₂	Orange solid	-	810.0 (819.78)	15.3 (15.37)	-	6.50 (6.58)
Al(OPr ⁱ) ₃	C ₁₃ H ₁₇ N ₃ OS (L ⁶ H)	1:1	[(Pr ⁱ O)Al(C ₁₃ H ₁₆ N ₃ OS) ₂]	Yellow solid	-	665.0 (670.44)	12.5 (12.53)	9.50 (9.54)	8.00 (8.04)
Al(OPr ⁱ) ₃	C ₁₃ H ₁₇ N ₃ OS (L ⁶ H)	2:3	(C ₁₃ H ₁₆ N ₃ OS) ₃ Al ₂	Dark solid	-	862.0 (867.78)	14.5 (14.52)	10.9 (11.0)	6.2 (6.21)

C and H analysis are found satisfactory

Table-3: IR spectral data (cm⁻¹) of Schiff bases and their complexes of Aluminium (III)

Compound	$\nu(\text{N-H})$ or $\nu(\text{OH})$	$\nu(\text{C=N})$	$\nu\text{Al-O}$	$\nu\text{Al-N}$	$\nu(\text{Al-S})$
L ¹ H	3240	-	-	-	-
[(Pr ⁱ O)Al(C ₁₀ H ₁₄ N ₃ O ₂) ₂] (C ₁₀ H ₁₄ N ₃ O ₂) ₃ Al ₂	-	1610	680, 620	540, 460	420, 360
	-	1618	720, 680	560, 435	320, 300
L ² H	3260	-	-	-	-
[(Pr ⁱ O)Al(C ₁₀ H ₁₄ N ₃ OS) ₂] (C ₁₀ H ₁₄ N ₃ OS) ₃ Al ₂	-	1620	740, 650	570, 460	410, 370
	-	1610	710-650	560, 460	415, 320
L ³ H	3280	-	-	-	-
[(Pr ⁱ O)Al(C ₁₃ H ₁₆ N ₃ O ₂) ₂] (C ₁₃ H ₁₆ N ₃ O ₂) ₃ Al ₂	-	1618	690, 620	570, 450	409, 380
	-	1610	730, 680	560, 440	410, 350
L ⁴ H	3340	-	-	-	-
[(Pr ⁱ O)Al(C ₁₃ H ₁₆ N ₃ OS) ₂] (C ₁₃ H ₁₆ N ₃ OS) ₃ Al ₂	-	1620	720, 620	540, 460	400, 350
	-	1620	680, 610	530, 435	420, 360
L ⁵ H	3280	-	-	-	-
[(Pr ⁱ O)Al(C ₁₃ H ₁₆ N ₃ O ₂) ₂] (C ₁₃ H ₁₆ N ₃ O ₂) ₃ Al ₂	-	1618	690, 620	570, 450	409, 380
	-	1618	730, 680	560, 440	410, 350
L ⁶ H	3340	-	-	-	-
[(Pr ⁱ O)Al(C ₁₃ H ₁₆ N ₃ OS) ₂] (C ₁₃ H ₁₆ N ₃ OS) ₃ Al ₂	-	1620	720, 620	540, 460	400, 350
	-	1620	680, 610	530, 435	420, 360

Table-4: Nuclear magnetic resonance data for the Schiff bases and the corresponding Aluminium complexes in δ ppm.

Compound	-OH	H-C=N	-C(CH) ₃ =N	NH ₂	Aromatic protons
L ¹ H	12.36	8.25	-	3.80	7.90-6.80
[(Pr ⁱ O)Al(C ₁₀ H ₁₄ N ₃ O ₂) ₂] (C ₁₀ H ₁₄ N ₃ O ₂) ₃ Al ₂	-	9.26	-	3.92	7.95-6.79
	-	9.80	-	3.86	6.80-6.00
L ² H	13.20	8.30	1.80	3.90	7.72-7.15
[(Pr ⁱ O)Al(C ₁₀ H ₁₄ N ₃ OS) ₂] (C ₁₀ H ₁₄ N ₃ OS) ₃ Al ₂	-	9.60	1.95	3.99	7.75-7.10
	-	9.45	-	3.95	7.72-7.15
L ³ H	12.50	8.95	1.99	3.80	7.80-7.20
[(Pr ⁱ O)Al(C ₁₃ H ₁₆ N ₃ O ₂) ₂] (C ₁₃ H ₁₆ N ₃ O ₂) ₃ Al ₂	-	9.08	-	3.92	7.90-7.15
	-	9.25	-	3.95	7.15-6.90
L ⁴ H	12.80	8.86	1.80	3.75	7.80-7.25