



Aluminium(III) derivatives of N and O chelating ligands: Preparation, spectral [IR (^1H , ^{13}C and ^{27}Al) NMR] and mass studies

Meenakshi^a, Ajeet Kumar Kushwaha^a, Avadhesh Pratap Singh^{*a,b} and Raj Kumar Dubey^{†a}

^aSynthetic Inorganic and Metallo-organic Research Laboratory, Department of Chemistry, University of Allahabad, Allahabad-211 002, Uttar Pradesh, India

^bDepartment of Chemistry, Kamala Nehru Institute of Physical and Social Sciences, Sultanpur-228 118, Uttar Pradesh, India

E-mail: avadheshchem@ymail.com

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Reaction of $\text{Al}(\text{OPr}^i)_3$ with 2-(*o*-hydroxy phenyl)-benzimidazole (pbmzH) and 2-(*o*-hydroxy phenyl)-benzothiazole (pbtzH) in different molar ratio in benzene solution afforded complex of the types $[(\mu\text{-OPr}^i)\text{Al}_2(\text{pbmz})_2(\text{OPr}^i)_2]$ **1**, $[\text{Al}(\text{OPr}^i)(\text{pbmz})_2]$ **2**, $[\text{Al}(\text{pbmz})_3]$ **3**, $[(\mu\text{-OPr}^i)\text{Al}_2(\text{pbtz})_2(\text{OPr}^i)_2]$ **4**, $[\text{Al}(\text{OPr}^i)(\text{pbtz})_2]$ **5** and $[\text{Al}(\text{pbtz})_3]$ **6**. All these white to creamy white solid complexes are soluble in common organic solvents (such as C_6H_6 , CCl_4 , *n*-hexane, DMSO, DMF etc.) and were characterized by elemental (C, H, N and Al) analysis as well as spectral [IR (^1H , ^{13}C and ^{27}Al) NMR] and mass studies. On the basis of these spectroscopic data a plausible structure tentatively has been proposed for these complexes.

Keywords: Aluminium isopropoxide, 2-(*o*-hydroxy phenyl)-benzimidazole, 2-(*o*-hydroxy phenyl)-benzothiazole, ^{27}Al NMR.

Introduction

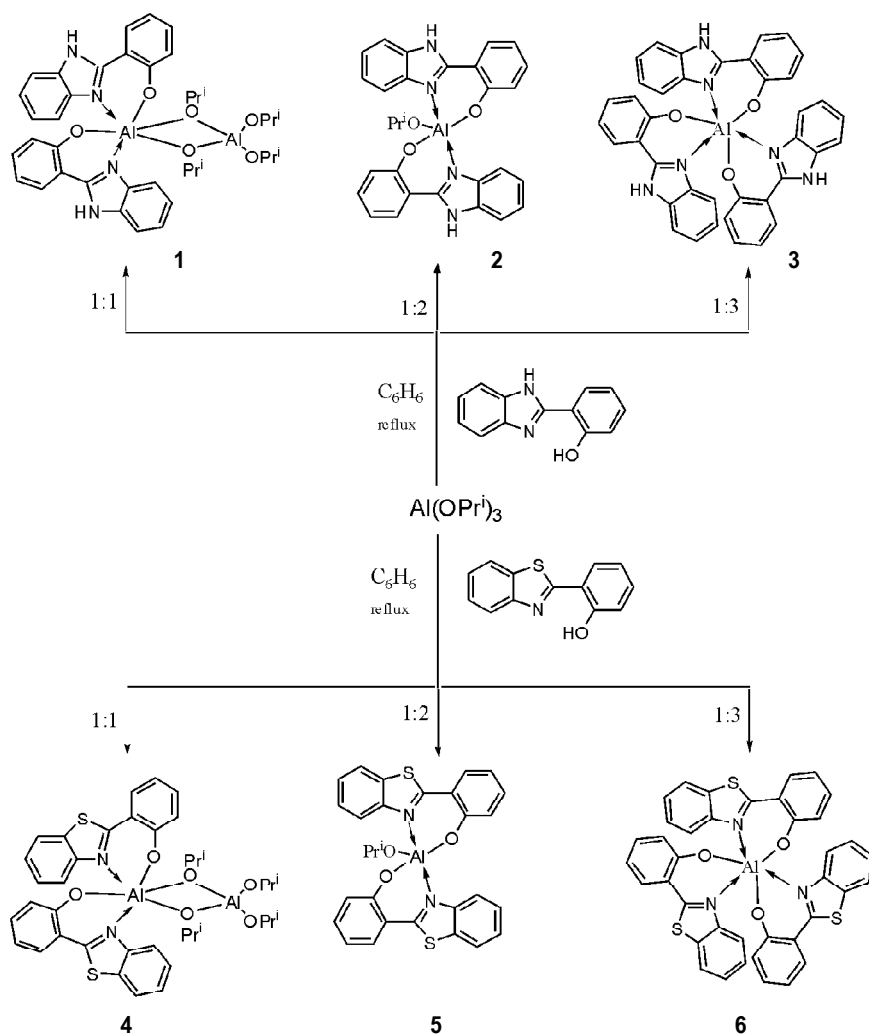
Coordination environment around the aluminium centre in $\text{Al}(\text{OPr}^i)_3$ can be modified by the reaction of $\text{Al}(\text{OPr}^i)_3$ with the organic compounds containing reactive hydroxyl group which provide useful steric and electronic properties essential for the reactivity and fine tuning of structure. During the recent past considerable attention have been paid in the coordination chemistry of group 13 elements because of their involvement in the application of electroluminescence¹⁻⁷. Furthermore, aluminium(III) complexes with N, O donor ligands have shown to be very important in electroluminescence devices^{1,2}. For example aluminium(III) complexes of 8-hydroxy quinoline (Alq_3) has been used as a green emitter and one of the electron transport material with high emission efficiency. Molecules containing benzimidazole and benzothiazole moieties are of great interest for synthesis⁸ due to their important biological and electroluminescence applications⁹. These heterocycles have shown variety of pharmacological properties⁸⁻¹¹ such as antifungal, antibiotic,

antiviral, antioxidant, anticancer, antiparkinson, antihistaminic, antihelminthic, antiamebic, antihypertensive and also have been used for asymmetric transformations¹², toxic reagents, catalysts or solvents effective against human cytomegalovirus. Taking above facts in view we report in this paper synthesis of aluminium(III) complexes containing O and N donor atoms and their characterization by elemental (C, H, N and Al) analysis, spectral [IR, (^1H , ^{13}C and ^{27}Al) NMR] and mass studies.

Results and discussion

Aluminium(III) complexes (**1-6**) have been synthesized by the interaction of aluminium isopropoxide with 2-(*o*-hydroxy phenyl)-benzimidazole and 2-(*o*-hydroxy phenyl)-benzothiazole in different molar ratios (1:1, 1:2, 1:3) in benzene as shown in Scheme 1. All these colorless to creamy white solid complexes are soluble in common organic solvents (such as C_6H_6 , CCl_4 , *n*-hexane, DMSO, DMF etc.). Some physical properties of these complexes are listed in Table 1.

[†]Deceased since November 2018.



Scheme 1. Synthetic route for preparation of aluminium(III) complexes.

Infrared spectral studies:

The characteristic infrared frequency of aluminium(III) complexes are given in Table 2. The strong and broad absorption band of 2-(*o*-hydroxy phenyl)-benzimidazole and 2-(*o*-hydroxy phenyl)-benzothiazole in the region 3420–3063 cm^{-1} due to hydrogen bonded OH stretching vibration¹³, this band was absent in the aluminium(III) complexes indicating the involvement of phenolic oxygen in the formation of metal-oxygen bond¹⁴ due to metallation of OH group. The strong intensity band observed in the region 1270–1267 cm^{-1} in the parent Schiff bases attribute to the phenolic C-O stretching vibration were shifted to higher frequency supporting the bonding through phenolic oxygen of the ligand¹⁵ to aluminium(III) atom and appearance of new band¹⁶ assign-

able to $\nu_{\text{Al-O}}$ in the region 696–655 cm^{-1} . The coordination through nitrogen of C=N bond was supported appearance of a band in the region 1625–1608 cm^{-1} , which was further supported by appearance of band in the region 592–513 cm^{-1} due to $\nu_{\text{Al-N}}$ stretching vibration. $\nu_{\text{N-H}}$ of 2-(*o*-hydroxy phenyl)-benzimidazole show a sharp band¹⁷ at 3479 cm^{-1} . In the complex $\nu_{\text{N-H}}$ band observed at 3400–3399 cm^{-1} . Thiocarbonyl group (C=S) of 2-(*o*-hydroxy phenyl)-benzothiazole ligand show absorption¹⁸ at 1250 cm^{-1} and in complex at 1230–1226 cm^{-1} . Stretching vibration of $\nu_{\text{C-O}}$ alcoholic 1039–980 cm^{-1} of isopropoxide group in the complexes **1**, **2**, **4**, **5** and complex **1**, **4** additional medium bands was also observed 751–741 cm^{-1} assigned¹⁶ as $\nu_{\text{Al-O-Al}}$.

Table 1. Synthetic and analytical details of Al(III) complexes 1-6

Sr. No.	Reactant (g, mmol)	Product (g, %) yield	M.p. (°C)	Ref. time (Δh)	Amount of PrOH in azeotrop Found (Calcd.) g	Elemental analysis (%):					
						C	H	N	S	Al	
1.	Al(OPr) ₃ (0.80, 3.91)	+ pbzH (0.82, 3.90)	308	7	0.23 (0.23)	64.29	6.43	7.82	–	7.53	
						(64.40)	(6.54)	(7.90)	–	(7.61)	
2.	Al(OPr) ₃ (0.33, 1.61)	+ 2pbzH (0.68, 3.23)	320	9	0.17 (0.19)	68.96	4.87	10.98	–	5.22	
						(69.04)	(4.99)	(11.11)	–	(5.35)	
3.	Al(OPr) ₃ (0.27, 1.32)	+ 3pbzH (0.81, 3.96)	325	10	0.22 (0.23)	71.46	4.08	12.78	–	4.02	
						(71.55)	(4.16)	(12.84)	–	(4.12)	
4.	Al(OPr) ₃ (0.68, 3.32)	+ pbtzH (0.75, 3.29)	350	7	0.18 (0.19)	61.36	5.86	3.71	8.59	7.12	
						(61.44)	(5.97)	(3.77)	(8.63)	(7.26)	
5.	Al(OPr) ₃ (0.43, 2.10)	+ 2pbtzH (0.95, 4.09)	365	9	0.28 (0.28)	64.62	4.21	5.12	11.86	4.98	
						(64.67)	(4.30)	(5.20)	(11.91)	(5.01)	
6.	Al(OPr) ₃ (0.23, 1.12)	+ 3pbtzH (0.76, 3.34)	378	10	0.20 (0.20)	66.28	3.39	5.89	13.57	3.78	
						(66.37)	(3.43)	(5.95)	(13.63)	(3.82)	

Table 2. Characteristic IR frequencies (cm^{-1}) of Schiff base and their aluminium(III) complexes

Sr. No.	Complex	$\nu(\text{OH})$	$\nu(\text{C}=\text{S})$	$\nu(\text{C}=\text{N})$	$\nu(\text{C}=\text{O})$ Phenolic	$\nu(\text{C}=\text{O})$ Alcoholic	$\nu(\text{Al}-\text{O}-\text{Al})$	$\nu(\text{Al}-\text{O})$	$\nu(\text{Al}-\text{N})$	$\nu(\text{N}-\text{H})$
1.	pbzH	3420	–	1655	1250	–	–	–	–	3479
2.	$[(\mu\text{-OPr}^i)_2\text{Al}_2(\text{pbz})_2(\text{OPr}^i)_2]$ 1	–	–	1608	1270	1039, 991	741	669	592, 569, 541, 515	3399
3.	$[(\text{pbz})_2\text{Al}(\text{OPr}^i)]$ 2	–	–	1625	1267	1038, 992	–	702	591, 568, 513	3397
4.	$[\text{Al}(\text{pbz})_3]$ 3	–	–	1623	1270	–	–	655, 684	591, 568, 513	3400
5.	pbtzH	3063	1250	1658	1269	–	–	–	–	–
6.	$[(\mu\text{-OPr}^i)_2\text{Al}_2(\text{pbtz})_2(\text{OPr}^i)_2]$ 4	–	1230	1604	1284	1029, 1015	751	660, 696	575, 541, 519	–
7.	$[(\text{pbtz})_2\text{Al}(\text{OPr}^i)]$ 5	–	1226	1603	1280	1027	–	659, 682	574, 538	–
8.	$[\text{Al}(\text{pbtz})_3]$ 6	–	1228	1603	1270	–	–	744, 723	576, 539	–

¹H NMR spectral studies:

¹H NMR spectra of the complexes (**1-6**) have been recorded in DMSO-*d*₆. The ¹H NMR spectra of the complexes display the expecting multiplicity of signal and integrated proton ratios correspond to the stoichiometric formula of the complexes. Comparison of the chemical shifts shows that signal due to phenolic proton (OH) in the parent Schiff bases at 11.28–10.88 ppm region is absent in the complexes suggesting coordination¹⁴ of phenolic oxygen to the metal after deprotonation. Aromatic proton signal appears in 7.78–6.26 ppm region and methyl and methine protons of isopropoxy group were observed in the region 1.78–1.13 and 3.86–3.41 ppm in complexes **1, 2, 4, 5**, whereas in complexes **1** and **4** additional signal observed in the region 1.22–1.16 and 4.39–4.05 due to bridging¹⁹ isopropoxy group.

¹³C NMR spectral studies:

¹³C NMR spectra of three typical aluminium(III) complexes **1, 3** and **5** were recorded in DMSO-*d*₆. ¹³C spectra of the parent ligand and their corresponding aluminium(III) complexes are also supportive of complex formation, showing bonding through phenolic oxygen and nitrogen of ligand. The ligands signals due to carbon of CH=N are observed at 150.35–156.51 ppm region, whereas, the corresponding signals in the complexes are observed at 165.15–163.52 ppm region. Such a downfield shift is characteristic of coordination²⁰ of nitrogen to aluminium(III) atom. The signal appearing in the 151.14–149.72 ppm region in the spectra of free ligand due to phenolic carbon shifted to 168.39–161.06 ppm region in the corresponding aluminium(III) complexes. Such downfield shifts are consistent with the formation²⁰ of alu-

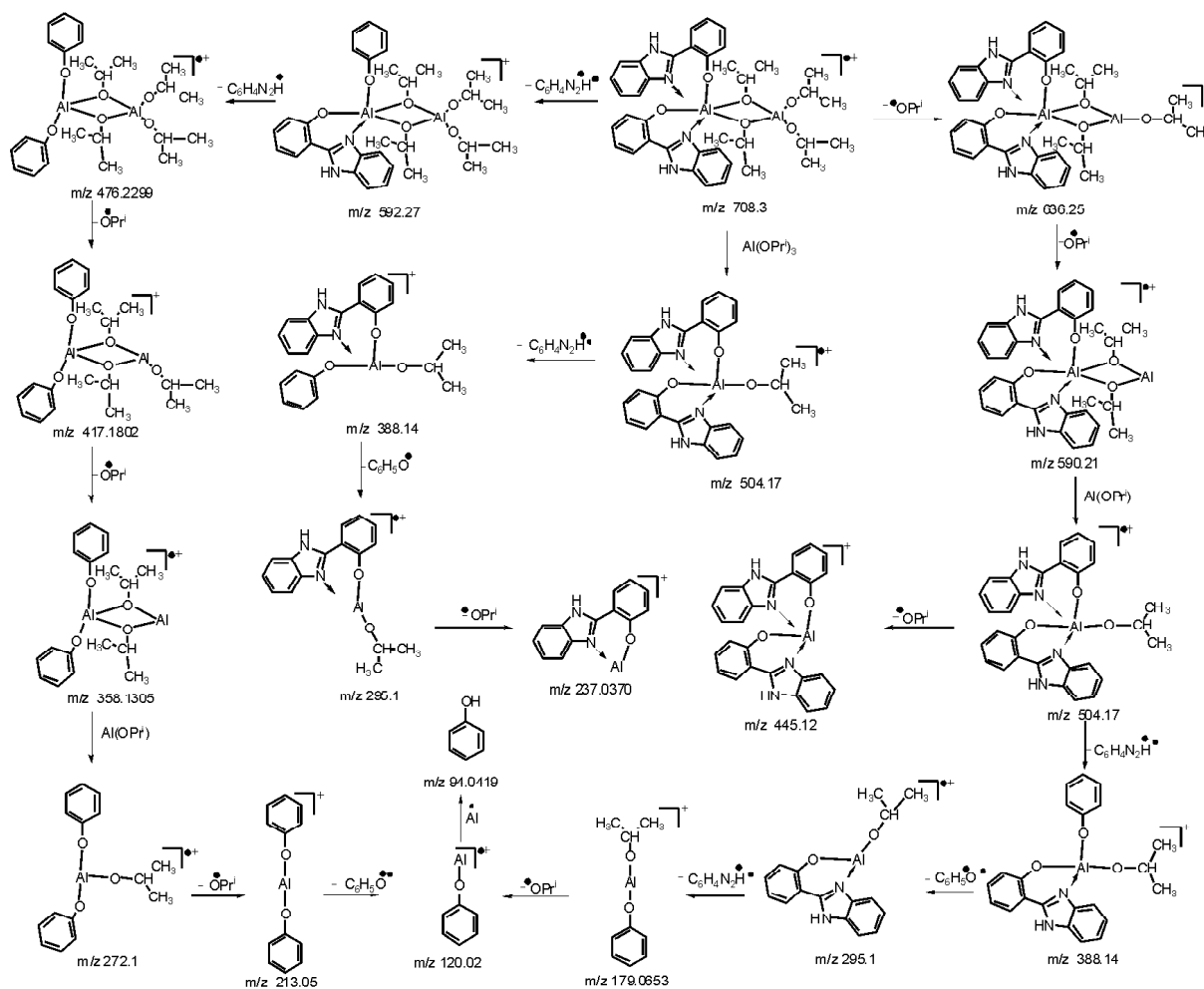
minium-oxygen bond resulting from metallation of phenolic OH group. In the complexes **1** and **5** signals due to methyl and methine carbon observed in the region 40.14–25.26 and 78.97–68.62 ppm, which is consistent with the presence of Al-OPrⁱ group.

²⁷Al NMR spectral studies:

In the ²⁷Al NMR spectra complexes **3** and **5** exhibit a broad signal at 13.76 and 7.20 ppm respectively, which is consistent with the penta²⁰ and hexa²¹ coordinated geometry around aluminium(III) atom. Whereas, interestingly complex **4** exhibits two signals at 74.90 and 7.49 ppm respectively, which are indicative of the presence of both six and four coordinated²² aluminium(III) in the complex.

Mass spectral studies:

The QTOF LC-MS spectra of the complexes (**1, 2** and **6**) were recorded and fragmentation pattern (Scheme 2) with *m/z* has been suggested²³ for complex **1**. In the spectra of complexes **1** (Fig. 1), **2** and **6** molecular ion peaks observed at *m/z* 725.12 [C₃₉H₅₀Al₂N₄O₆; calculated mass = 724.34], 505.15 [C₂₉H₂₅AlN₄O₃; calculated mass = 504.17] and 706.34 [C₃₉H₂₄AlN₃O₃S₃; calculated mass = 705.08], respectively, correspond to the complex **1** which shows dimeric molecular composition, whereas, complex **2** and **6** are monomeric in nature. Furthermore in the spectrum of complex **1**, the base peak was observed due to formation of [C₆H₅O]⁺ at about *m/z* 93.04. Other important peaks also observed at *m/z* 708.3, 636.25, 592.27, 590.21, 504.17, 476.22, 445.12, 417.18, 388.14, 358.13, 295.1, 272.1, 236.05, 213.05, 166.06, 120.02 due to formation of various radicals in the spectrum of the complex **1**.



Scheme 2. Fragmentation pattern of complex $[(\mu\text{-OPr})_2\text{Al}_2(\text{pbz})_2(\text{OPr})_2]$ **1**.

Conclusion

Reactions of $\text{Al}(\text{OPr})_3$ with 2-(*o*-hydroxy phenyl)-benzimidazole (pbmzH) and 2-(*o*-hydroxy phenyl)-benzothiazole

(pbtzH) in 1:2 and 1:3 molar ratios in benzene solution afforded penta- and hexa- coordinated aluminium(III) complexes, whereas complex obtained in equimolar reaction with

Table 3. ^1H NMR data (ppm) for new complexes of aluminium(IV) **1-6**

Sr. No.	Complex	NH	Ar-H	Isopropoxy moiety	
				OCH	CH ₃
1.	$[(\mu\text{-OPr})_2\text{Al}_2(\text{pbz})_2(\text{OPr})_2]$ 1	11.58	7.41–6.34 (16H, m)	4.05 (2H, br) _{br} , 3.41 (2H, br) _t	1.16 (12H, d) _{br} , 1.13 (12H, d) _t
2.	$[(\text{pbz})_2\text{Al}(\text{OPr})]$ 2	11.77	7.44–6.33 (16H, m)	3.80 (2H, br) _t	1.78 (6H, d) _t
3.	$[\text{Al}(\text{pbz})_3]$ 3	12.39	7.78–6.26 (24H, m)	–	–
4.	$[(\mu\text{-OPr})_2\text{Al}_2(\text{pbtz})_2(\text{OPr})_2]$ 4	–	7.55–6.98 (16H, m)	4.39 (2H, br) _{br} , 3.86 (2H, br) _t	1.22 (12H, d) _{br} , 1.72 (12H, d) _t
5.	$[(\text{pbtz})_2\text{Al}(\text{OPr})]$ 5	–	7.57–7.00 (16H, m)	3.83 (2H, br) _t	1.78 (6H, d) _t
6.	$[\text{Al}(\text{pbtz})_3]$ 6	–	7.47–7.26 (24H, m)	–	–

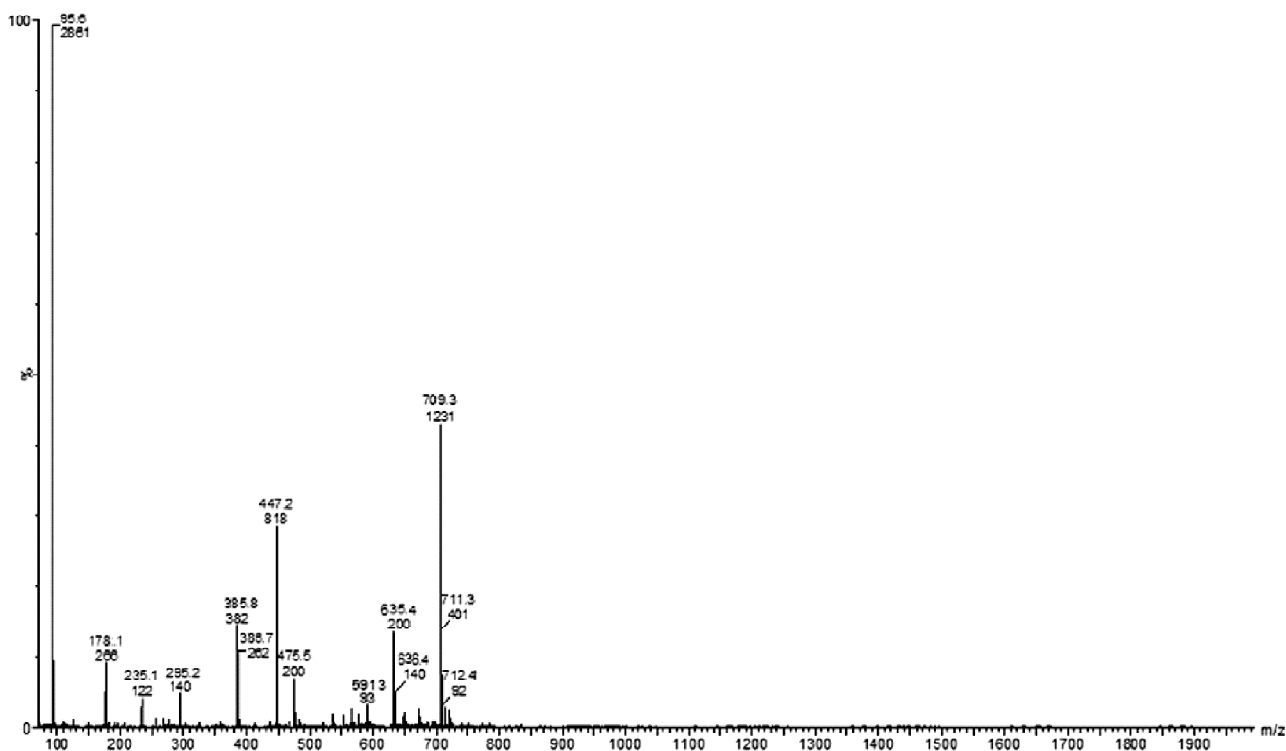


Fig. 1. Q-TOF (LC-MS) spectrum of complex $[(\mu\text{-OPr}^i)_2\text{Al}_2(\text{pbz})_2(\text{OPr}^i)_2]$ **1**.

both of the mentioned ligands give complex, which shows both six and four coordination around the two aluminium atoms.

Experimental

Materials and physical measurement:

All the chemicals and reagent were of analytical grade. Salicylaldehyde (CDH), sodium meta bisulphite (Sigma Aldrich), EtOH, 1,2-phenyl diamine (Loba), 2-aminophenol (Loba) were commercially available and used as without further purification. Benzene (AR Merck) and n-hexane (AR Merck) were dried by refluxing over sodium benzophenone followed by distillation under anhydrous conditions²⁴ and

other solvents were purified by standard procedure. 2-(*o*-Hydroxy phenyl)-benzimidazole and 2-(*o*-hydroxy phenyl)-benzothiazole, were synthesized as reported earlier²⁵.

Elemental analyses for C, H, N, were performed on a Haraeus carlo Erba 1108 elemental analyser. Aluminium was estimated gravimetrically as the oxinate method²⁶. Infrared spectra were recorded on a Perkin-Elmer 100 FT-IR spectrophotometer in the range 4000–400 cm^{-1} . ^1H , ^{13}C and ^{27}Al NMR spectra were recorded on Bruker Avance II 400 NMR spectrometer. Chemical shifts were given in ppm relative to TMS for carbon, hydrogen and $\text{Al}(\text{NO}_3)_3$ for aluminium in $\text{DMSO-}d_6$ solvent. ESI-MS spectra were recorded on agilent 6520 Q-TOF LC-MS, MS/MS spectrometers.

Table 4. ^{13}C NMR data (ppm) for aluminium(III) complexes **1**, **3** and **5**

Sr. No.	Complex	C-O phenolic	C=N	Ar-C	Isopropoxy moiety	
					OCH	CH_3
1.	$[(\mu\text{-OPr}^i)_2\text{Al}_2(\text{pbz})_2(\text{OPr}^i)_2]$ 1	162.58	163.52	122.04–110.08	78.97, 78.31	40.13, 25.26
2.	$[\text{Al}(\text{pbz})_3]$ 3	161.06	164.93	122.65–110.66	–	–
3.	$[(\text{pbtz})_2\text{Al}(\text{OPr}^i)]$ 5	168.39	165.15	122.08–116.94	78.31, 68.62	40.09, 38.84

Synthesis of complexes:

A benzene solution (~70 cm³) containing Al(OPrⁱ)₃ (0.80 g, 3.91 mmol) and 2-(*o*-hydroxy phenyl)-benzimidazole (pbmzH) (0.82 g, 3.90 mmol) was heated under reflux for ~5 h. The liberated PrⁱOH was fractionated azeotropically and estimated (0.23 g,) periodically to check completion of the reaction. Removal of volatile components from the reaction mixture under reduced pressure yielded a white solid. Yield: 1.31 g (95%). Compound was dissolved in minimum amount of chloroform and then started to add n-hexane when turbidity start, 1–2 drop chloroform was added and clear solution was obtained, and kept for ~12 h compound was precipitated and remaining solvent decant off and solid obtained washed 2–3 times with n-hexane to obtain in the pure form.

Similar procedure was adopted to prepare complexes **2** and **3** by carrying out the reactions of Al(OPrⁱ)₃ and pbtzH in 1:2 and 1:3 molar ratios, respectively. Similarly complexes of aluminium(III) (**4-6**) have been synthesized with 2-(*o*-hydroxy phenyl)-benzothiazole (pbtzH) in 1:1, 1:2 and 1:3 molar ratios.

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