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Reactions of (*N*-phenylsalicylideneiminato)aluminium(III)di(μ -isopropoxo)di(isopropoxo)aluminium(III) with simple and internally functionalized oximes. Molecular structure of the penta-coordinated complex (2-acetylthiophenyloximato)bis(*N*-phenylsalicylideneiminato)aluminium(III)

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Abstract

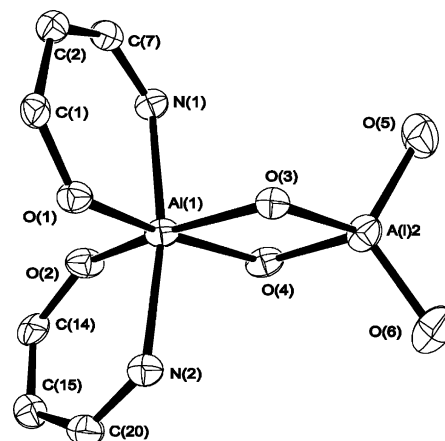
Reactions of bis(*N*-phenylsalicylideneiminato)aluminium(III)di(μ -isopropoxo)di(isopropoxo) aluminium(III), $[\text{C}_6\text{H}_4\text{O}\{\text{CH}=\text{N}(\text{C}_6\text{H}_5)\}]_2\text{Al}(\mu\text{-OPr}^i)_2\text{Al}(\text{OPr}^i)_2$ (**1**) with simple and internally functionalized oximes in 1:1 and 1:2 molar ratios in refluxing anhydrous benzene yield binuclear complexes of the type, $[\text{C}_6\text{H}_4\text{O}\{\text{CH}=\text{N}(\text{C}_6\text{H}_5)\}]_2\text{Al}(\mu\text{-OPr}^i)_2\text{Al}(\text{ON}=\text{CRR}')(\text{OPr}^i)$ and $[\text{C}_6\text{H}_4\text{O}\{\text{CH}=\text{N}(\text{C}_6\text{H}_5)\}]_2\text{Al}(\mu\text{-OPr}^i)_2\text{Al}(\text{ON}=\text{CRR}')_2$ [where $\text{R}=\text{R}'=\text{CH}_3$; $\text{R}=\text{CH}_3$, $\text{R}'=\text{C}_4\text{H}_3\text{S}-2$, $\text{C}_4\text{H}_3\text{O}-2$ and $\text{C}_5\text{H}_4\text{N}-2$], respectively containing aluminium(III) atoms in six- and four-coordination sites. All these binuclear complexes are characterised by elemental analysis, molecular weight measurements and spectroscopy [IR and NMR (^1H , ^{13}C and ^{27}Al)]. Reaction of bis(*N*-phenylsalicylideneiminato)(isopropoxo)aluminium(III) with 2-acetylthiophenyloxime in 1:1 molar ratio in refluxing anhydrous benzene, yields a novel heteroleptic compound, $[\text{C}_6\text{H}_4\text{O}\{\text{CH}=\text{N}(\text{C}_6\text{H}_5)\}]_2\text{Al}\{\text{ON}=\text{C}(\text{CH}_3)\text{C}_4\text{H}_3\text{S}-2\}$ (**10**). The crystal structure of $[\text{C}_6\text{H}_4\text{O}\{\text{CH}=\text{N}(\text{C}_6\text{H}_5)\}]_2\text{Al}\{\text{ON}=\text{C}(\text{CH}_3)\text{C}_4\text{H}_3\text{S}-2\} \cdot \text{CH}_2\text{Cl}_2$ shows five-coordination around the aluminium(III) atom.

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Keywords: *N*-phenylsalicylideneiminato; Isopropoxo; Aluminium(III) atoms; Molecular structures

1. Introduction

We have recently reported that the dinuclear complex $[\text{C}_6\text{H}_4\text{O}\{\text{CH}=\text{N}(\text{C}_6\text{H}_5)\}]_2\text{Al}(\mu\text{-OPr}^i)_2\text{Al}(\text{OPr}^i)_2$ (**1**) displays unsymmetrical geometry containing six- and four-coordinated aluminium(III) atoms [1,2] rather than the symmetrical five-coordinated structure found in, $[\text{C}_6\text{H}_4\text{O}\{\text{CH}=\text{N}(\text{C}_6\text{H}_5)\}] (\text{OPr}^i)\text{Al}(\mu\text{-OPr}^i)_2\text{Al}(\text{OPr}^i)$ [$\text{C}_6\text{H}_4\text{O}\{\text{CH}=\text{N}(\text{C}_6\text{H}_5)\}$].



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Table 1

Synthetic and analytical data of $[C_6H_4O\{CH=N(C_6H_5)\}]_2Al(\mu-OPr^i)_2(ON=CRR')(OPr^i)$ and $[C_6H_4O\{CH=N(C_6H_5)\}]_2Al(\mu-OPr^i)_2Al(ON=CRR')_2$

S. No.	Reactants (g) *	Molar ratio	Pr ⁱ OH (g) Found (Calc.)	%Yield	%OPr ⁱ	% Al	%N	MW Found (Calc.)	M.p. (°C)
1	(a) 2.33 (g) (b) {2-SC ₄ H ₃ C(CH ₃)=NOH} 0.48 (g)	1:1	0.20 (0.20)	97.3	23.0 (23.2)	7.04 (7.07)	5.10 (5.49)	701 (764)	80
2	(a) 2.90 (g) (b) {2-SC ₄ H ₃ C(CH ₃)=NOH} 1.20 (g)	1:2	0.50 (0.51)	98.7	13.0 (13.9)	6.23 (6.38)	6.06 (6.62)	780 (845)	78
3	(a) 2.03 (g) (b) {2-OC ₄ H ₃ C(CH ₃)=NOH} 0.37 (g)	1:1	0.15 (0.17)	98.6	23.5 (23.7)	7.13 (7.22)	5.19 (5.61)	659 (748)	74
4	(a) 2.81 (g) (b) {2-OC ₄ H ₃ C(CH ₃)=NOH} 1.03 (g)	1:2	0.47 (0.49)	96.0	13.9 (14.5)	6.36 (6.64)	6.68 (6.88)	745 (813)	68
5	(a) 2.40 (g) (b) {2-NC ₅ H ₄ C(CH ₃)=NOH} 0.48 (g)	1:1	0.20 (0.21)	98.8	22.9 (23.3)	7.06 (7.11)	7.09 (7.37)	715 (759)	120
6	(a) 2.14 (g) (b) {2-NC ₅ H ₄ C(CH ₃)=NOH} 0.85 (g)	1:2	0.34 (0.37)	96.8	13.9 (14.1)	6.26 (6.46)	9.87 (10.0)	795 (835)	125
7	(a) 2.34 (g) (b) (CH ₃) ₂ C=NOH 0.25 (g)	1:1	0.20 (0.21)	99.0	24.6 (25.4)	7.61 (7.76)	5.97 (6.03)	603 (696)	60
8	(a) 2.04 (g) (b) (CH ₃) ₂ C=NOH 0.43 (g)	1:2	0.33 (0.35)	99.5	16.2 (16.6)	7.17 (7.62)	7.04 (7.90)	675 (708)	135

* (a) $[C_6H_4O\{CH=N(C_6H_5)\}]_2Al(\mu-OPr^i)_2Al(OPr^i)_2$, (b) $RR'C=NOH$.

In order to examine whether the stable basic unit (**I**) can survive further nucleophilic attack, we carried out reactions with simple and internally functionalized oximes [3–5]. The nucleophilic substitution reactions are quantitative and the binuclear products are stable exhibiting different coordination sites for the two aluminium(III) atoms. We report herein the reactions of $[C_6H_4O\{CH=N(C_6H_5)\}]_2Al(\mu-OPr^i)_2Al(OPr^i)_2$ with simple and internally functionalized oximes and the molecular structure of a new penta-coordinated (2-acetyl thiophenyl oximate) bis(*N*-phenylsalicylideneimino)aluminium(III) complex.

2. Experimental

All manipulations were carried out under strictly anhydrous conditions. Solvents were purified and dried according to standard procedures [6]. Aluminium isopropoxide was prepared as described in the literature [7]. Aluminium was estimated gravimetrically as the oxinate [6]. Nitrogen and isopropanol were estimated as reported earlier [6]. The starting material $[C_6H_4O\{CH=N(C_6H_5)\}]_2Al(\mu-OPr^i)_2Al(OPr^i)_2$ was prepared by the reaction of aluminium isopropoxide with *N*-phenyl salicylidene imine in 1:1 molar ratio in refluxing

anhydrous benzene [1]. Infrared spectra were recorded as Nujol mulls on a Nicolet Magna 550 spectrophotometer in the range 4000–400 cm^{-1} . ¹H and ¹³C NMR spectra were recorded on a JEOL FX90Q spectrometer using TMS as an internal reference in CDCl₃ and CHCl₃, respectively. ²⁷Al NMR spectra were carried out in toluene using aluminium nitrate as an external reference in aqueous solution. Molecular weight measurements were carried out by elevation in boiling point using a Beckmann's Thermometer (Einstellthermometer n-Beckmann, Labortherm-N, Skalenwert, 0.01 K, made in GDR) fitted in glass assembly (supplied by JSGW, India) in anhydrous benzene.

2.1. Synthesis of $[C_6H_4O\{CH=N(C_6H_5)\}]_2Al(\mu-OPr^i)_2Al\{ON=C(CH_3)C_4H_3S-2\}_2$

Typically, the reaction mixture containing $[C_6H_4O\{CH=N(C_6H_5)\}]_2Al(\mu-OPr^i)_2Al(OPr^i)_2$ (2.90 g) and (2-SC₄H₃C(CH₃)=NOH) (1.20 g) in anhydrous benzene (~60 ml) was refluxed for 4 h under a fractionating column. The isopropanol formed in the reaction was fractionated out azeotropically with benzene. The progress as well as the completion of the reaction was checked by the estimation of the liberated isopropanol in the azeotrope by the oxidimetric method.

A yellow, clear solution was obtained. After stripping off the excess solvent under reduced pressure, a shiny-yellow foamy solid was obtained in quantitative yield, which was recrystallized from benzene/hexane. The complexes **1–8** were prepared by a similar route and the details are summarized in Table 1.

2.2. Synthesis of $[C_6H_4O\{CH=N(C_6H_5)\}]_2Al(OPr^i)$

To a benzene solution (~35 ml) of aluminium isopropoxide (3.72 g) was added $\{C_6H_4(OH)CH=N(C_6H_5)\}$ (7.20 g) in benzene (30 ml). The contents were refluxed for 4 h and the progress of the reaction was monitored by the determination of isopropanol liberated azeotropically with benzene. A yellow, clear solution was obtained. After stripping off the solvent under reduced pressure, a yellow solid was obtained in quantitative yield; *Anal.* Found: Al, 5.33; N, 2.43%; Calc. Al, 5.64; N, 2.92%.

2.3. Synthesis of $[C_6H_4O\{CH=N(C_6H_5)\}]_2Al\{ON=C(CH_3)C_4H_3S-2\}$

Typically, 2-acetylthiophenoxime (0.36 g) was added to a benzene solution (~40 ml) of $[C_6H_4O\{CH=N(C_6H_5)\}]_2Al(OPr^i)$ (1.20 g) and the reaction mixture was refluxed on a fractionating column for 4 h. The isopropanol in the reaction was collected azeotropically with benzene. The progress as well as the completion of the reaction was checked by the estimation of the liberated isopropanol in the azeotrope by the oxidimetric method. A yellow, clear solution was obtained. After stripping off the excess solvent under reduced pressure, a shiny-yellow foamy solid was obtained in quantitative yield which was recrystallized from a (7:1) mixture of dichloromethane and *n*-hexane: *Anal.* Found: Al, 4.79; N, 7.01%; Calc. Al, 4.82; N, 7.5%. Analytical data of **9–12** are summarized in Table 5.

2.4. X-ray diffraction analysis

A colourless, plate crystal of $[C_6H_4OCH=N(C_6H_5)]_2Al\{ON=C(CH_3)C_4H_3S-2\} \cdot CH_2Cl_2$ (**10**) was mounted on a glass fibre. Cell dimensions and intensity data were recorded on an Enraf Nonius KCCD diffractometer, with ϕ and ω scans chosen to give a complete asymmetric unit. The data collection and cell refinement [8] gave cell constants corresponding to a monoclinic cell whose dimensions are given in Table 10 along with other experimental parameters. An absorption correction was applied [9] which resulted in transmission factors ranging from 0.9931 to 0.9341. The structure was solved by direct methods [10], and the structure was refined using the WINGX [11] version of SHELX-97 [12]. All of the non-hydrogen atoms were treated anisotropically. Hydrogen atoms were included

Table 2

Compound	N-Phenylsalicylidene imine-		Oximate moiety		Isopropoxy moiety	
	to moiety		v(N–O)		v(C–O)	
	v(C=C)	v(C=N)	v(C–O)	v(Al–N)	v(Al–O)	v(Al–O–Al)
(1) $[C_6H_4O\{CH=N(C_6H_5)\}]_2Al(\mu-OPr^i)_2Al\{ON=C(CH_3)C_4H_3S-2\}(OPr^i)$	1460m	1610s	1240m	1360m	1000m	760w
(2) $[C_6H_4O\{CH=N(C_6H_5)\}]_2Al(\mu-OPr^i)_2Al\{ON=C(CH_3)C_4H_3S-2\}_2$	1475m	1615s	1275m	1360m	1005m	750w
(3) $[C_6H_4O\{CH=N(C_6H_5)\}]_2Al(\mu-OPr^i)_2Al\{ON=C(CH_3)C_4H_3O-2\}(OPr^i)$	1475m	1620s	1250m	1375m	1000m	745w
(4) $[C_6H_4O\{CH=N(C_6H_5)\}]_2Al(\mu-OPr^i)_2Al\{ON=C(CH_3)C_4H_3O-2\}_2$	1475m	1620s	1260m	1355m	998m	745w
(5) $[C_6H_4O\{CH=N(C_6H_5)\}]_2Al(\mu-OPr^i)_2Al\{ON=C(CH_3)C_5H_4N-2\}(OPr^i)$	1475m	1610s	1260m	1375m	1005m	750w
(6) $[C_6H_4O\{CH=N(C_6H_5)\}]_2Al(\mu-OPr^i)_2Al\{ON=C(CH_3)C_5H_4N-2\}_2$	1470m	1610s	1260m	1360m	1000m	750w
(7) $[C_6H_4O\{CH=N(C_6H_5)\}]_2Al(\mu-OPr^i)_2Al\{ON=C(CH_3)C_5H_4N-2\}(OPr^i)$	1470m	1620s	1255m	1350m	1005m	740w
(8) $[C_6H_4O\{CH=N(C_6H_5)\}]_2Al(\mu-OPr^i)_2Al\{ON=C(CH_3)C_5H_4N-2\}_2$	1475m	1620s	1275m	1375m	1010m	750w

Table 3

¹H NMR spectra for [C₆H₄O{CH=N(C₆H₅)}]₂Al(μ-OPrⁱ)₂Al(ON=CRR')(OPrⁱ) and [C₆H₄O{CH=N(C₆H₅)}]₂Al(μ-OPrⁱ)₂Al(ON=CRR')₂

S. No.	Compound	<i>N</i> -Phenylsalicylidene imineto moiety		Isopropoxy moiety		Oximate moiety
		CH=N	Aromatic proton	CH ₃	OCH	
1	[{C ₆ H ₄ O{CH=N(C ₆ H ₅)}] ₂ Al(μ-OPr ⁱ) ₂ Al{ON=C(CH ₃)C ₄ H ₃ S-2}(OPr ⁱ)	8.78,s 8.68,s (2H)	7.16–7.79,m (18H)	1.26,d (12H) 1.83,d (6H)	3.93,m (2H) 4.24,m (1H)	2.29,s(3H,CH ₃); 6.97,d(1H,H-4); 7.03,d(1H,H-3); 7.10(1H,H-5)
2	[{C ₆ H ₄ O{CH=N(C ₆ H ₅)}] ₂ Al(μ-OPr ⁱ) ₂ Al{ON=C(CH ₃)C ₄ H ₃ S-2} ₂	8.78,s 8.68,s (2H)	7.22–7.98,m (18H)	1.33,d (12H)	4.10,m (2H)	2.21,s(3H,CH ₃); 6.84,d(1H,H-4); 6.97,d(1H,H-3); 7.03(1H,H-5)
3	[{C ₆ H ₄ O{CH=N(C ₆ H ₅)}] ₂ Al(μ-OPr ⁱ) ₂ Al{ON=C(CH ₃)C ₄ H ₃ O-2}(OPr ⁱ)	8.78,s 8.68,s (2H)	7.22–7.60,m (18H)	1.26,d (12H) 1.96,d (6H)	3.86,m (2H) 4.24,m (1H)	2.09,s(3H,CH ₃); 6.40,d(1H,H-4); 6.72,d(1H,H-3); 7.16(1H,H-5)
4	[{C ₆ H ₄ O{CH=N(C ₆ H ₅)}] ₂ Al(μ-OPr ⁱ) ₂ Al{ON=C(CH ₃)C ₄ H ₃ O-2} ₂	8.78,s 8.68,s (2H)	7.00–7.54,m (18H)	1.20,d (12H)	3.77,m (2H)	2.18,s(3H,CH ₃); 6.68,d(1H,H-4); 6.78,d(1H,H-3); 6.87(1H,H-5)
5	[{C ₆ H ₄ O{CH=N(C ₆ H ₅)}] ₂ Al(μ-OPr ⁱ) ₂ Al{ON=C(CH ₃)C ₃ H ₄ N-2}(OPr ⁱ)	8.52,s 8.46,s (2H)	6.53–7.38,m (18H)	1.23,d (12H) 1.48,d (6H)	3.86,m (2H) 4.15,m (1H)	2.21,s(3H,CH ₃); 7.44,t(1H,H-4); 7.51,t(1H,H-3); 7.70,t (1H,H-5); 8.05,d(1H,H-6)
6	[{C ₆ H ₄ O{CH=N(C ₆ H ₅)}] ₂ Al(μ-OPr ⁱ) ₂ Al{ON=C(CH ₃)C ₃ H ₄ N-2} ₂	8.87,s 8.81,s (2H)	6.65–7.32,m (18H)	1.20,d (12H)	4.05,m (2H)	2.15,s(3H,CH ₃); 7.44,t(1H,H-4); 7.57,t(1H,H-3); 7.73,t (1H,H-5); 7.79,d(1H,H-6)
7	[{C ₆ H ₄ O{CH=N(C ₆ H ₅)}] ₂ Al(μ-OPr ⁱ) ₂ Al{ON=C(CH ₃) ₂ (OPr ⁱ)	8.90,s 8.84,s (2H)	6.78–7.48,m (18H)	1.33,d (12H) 1.94,d (6H)	3.86,m (2H) 4.37,m (1H)	1.96,s(6H,CH ₃)
8	[{C ₆ H ₄ O{CH=N(C ₆ H ₅)}] ₂ Al(μ-OPr ⁱ) ₂ Al{ON=C(CH ₃) ₂ ₂	8.71,s 8.65,s (2H)	6.62-7.48,m (18H)	1.17,d (12H)	4.02,m (2H)	1.83,s(6H,CH ₃)

in idealized positions with isotropic thermal parameters set at 1.2 times that of the carbon atom to which they were attached. The final cycle of full-matrix least-squares refinement was based on 6945 observed reflections (3461 for $F^2 > 4\sigma(F^2)$) and 390 variable para-

meters and converged (largest parameter shift was 0.001 times its esd).

Selected distances and bond angles are given in Table 9 and the molecule is displayed in the ORTEP diagram in Fig. 4. Additional material available from the Cam-

Table 4

¹³C NMR spectra for [C₆H₄O{CH=N(C₆H₅)}]₂Al(μ-OPrⁱ)₂Al(ON=CRR')(OPrⁱ) and [C₆H₄O{CH=N(C₆H₅)}]₂Al(μ-OPrⁱ)₂Al(ON=CRR')₂

S. No.	Compound	<i>N</i> -Phenylsalicylidene imineto moiety		Isopropoxy moiety		Oximate moiety
		CH=N	Aromatic carbon	CH ₃	OCH	
1	[{C ₆ H ₄ O{CH=N(C ₆ H ₅)}] ₂ Al(μ-OPr ⁱ) ₂ Al{ON=C(CH ₃)C ₄ H ₃ S-2}(OPr ⁱ)	161.2; 162.6	117.2; 118.9; 119.2; 121.2; 123.4; 124.0; 125.6; 127.9; 133.1; 135.2	24.9; 25.3	62.1; 64.4	11.9(CH ₃); 126.6(C4); 126.8(C3); 127.0(C5); 140.4 (C2); 151.4(C=N)
2	[{C ₆ H ₄ O{CH=N(C ₆ H ₅)}] ₂ Al(μ-OPr ⁱ) ₂ Al{ON=C(CH ₃)C ₄ H ₃ S-2} ₂	162.6; 162.7	117.3; 119.0; 120.2; 121.2; 123.8; 124.0; 125.9; 128.3; 132.2; 133.8	25.4	62.2	12.1(CH ₃); 126.4 (C4); 126.8(C3); 127.4(C5); 140.2(C2); 151.6(C=N)
3	[{C ₆ H ₄ O{CH=N(C ₆ H ₅)}] ₂ Al(μ-OPr ⁱ) ₂ Al{ON=C(CH ₃)C ₄ H ₃ O-2}(OPr ⁱ)	161.2; 162.7	117.2; 118.7; 119.3; 121.9; 124.3; 125.6; 127.9; 128.3; 134.1; 135.0	23.5; 25.8	63.9; 64.1	11.2(CH ₃); 109.3(C4); 112.1(C3); 143.4(C5); 147.9 (C2); 151.4(C=N)
4	[{C ₆ H ₄ O{CH=N(C ₆ H ₅)}] ₂ Al(μ-OPr ⁱ) ₂ Al{ON=C(CH ₃)C ₄ H ₃ O-2} ₂	161.3; 162.1	117.5; 118.9; 121.9; 123.9; 124.0; 124.9; 125.9; 127.9; 132.9; 135.9	24.8	64.1	11.0(CH ₃); 109.9(C4); 111.9(C3); 143.3(C5); 146.9(C2); 150.9(C=N)
5	[{C ₆ H ₄ O{CH=N(C ₆ H ₅)}] ₂ Al(μ-OPr ⁱ) ₂ Al{ON=C(CH ₃)C ₃ H ₄ N-2}(OPr ⁱ)	162.6; 162.8	117.2; 119.0; 121.1; 124.9; 126.9; 128.1; 128.3; 129.4; 132.2; 133.1	23.9; 25.3	62.5; 64.1	10.2(CH ₃); 123.6(C5); 124.4 (C3); 137.5(C4); 148.8(C6); 153.1(C2); 156.9(C=N)
6	[{C ₆ H ₄ O{CH=N(C ₆ H ₅)}] ₂ Al(μ-OPr ⁱ) ₂ Al{ON=C(CH ₃)C ₃ H ₄ N-2} ₂	162.9; 163.3	117.9; 119.3; 121.4; 124.9; 126.7; 128.3; 128.9; 129.5; 132.4; 134.9	25.2	64.3	10.0(CH ₃); 123.5(C5); 126.1(C3); 135.2(C4); 149.2(C6); 153.2(C2); 157.3(C=N)
7	[{C ₆ H ₄ O{CH=N(C ₆ H ₅)}] ₂ Al(μ-OPr ⁱ) ₂ Al{ON=C(CH ₃) ₂ (OPr ⁱ)	161.5; 162.1	117.4; 119.3; 121.7; 123.0; 124.9; 126.5; 128.9; 132.7; 133.1; 135.4	23.7; 25.1	63.6; 64.6	11.7(CH ₃); 159.9(C=N)
8	[{C ₆ H ₄ O{CH=N(C ₆ H ₅)}] ₂ Al(μ-OPr ⁱ) ₂ Al{ON=C(CH ₃) ₂ ₂	161.2; 162.9	117.4; 119.3; 121.7; 123.0; 124.9; 126.5; 128.9; 132.7; 133.1; 135.4	24.9	64.1	11.4(CH ₃); 160.7(C=N)

Table 5

Synthetic and analytical data of $[\text{C}_6\text{H}_4\text{O}\{\text{CH}=\text{N}(\text{C}_6\text{H}_5)\}]_2\text{Al}(\text{OPr}^i)$ and $[\text{C}_6\text{H}_4\text{O}\{\text{CH}=\text{N}(\text{C}_6\text{H}_5)\}]_2\text{Al}(\text{ON}=\text{CRR}')$

S. No.	Reactants (g) ^{a,b}	Molar ratio	Pr ⁱ OH (g) Found (Calc.)	%Yield	%Al	%N	MW Found (Calc.)
9	(a) Al(OPr ⁱ) ₃ , 3.72 (g) (b) {C ₆ H ₄ (OH)CH=N(C ₆ H ₅)}, 7.20 (g)	1:2	2.01 (2.18)	100	5.33 (5.64)	2.43 (2.92)	440 (479)
10	(a) 1.20 (g) (b) {2-SC ₄ H ₃ C(CH ₃)=NOH}, 0.36 (g)	1:1	0.15 (0.15)	99	4.79 (4.82)	7.01 (7.50)	512 (560)
11	(a) 1.70 (g) (b) {2-NC ₅ H ₄ C(CH ₃)=NOH}, 0.48 (g)	1:1	0.21 (0.21)	99	4.83 (4.86)	7.42 (7.57)	523 (555)
12	(a) 1.51 (g) (b) {2-OC ₄ H ₃ C(CH ₃)=NOH}, 0.39 (g)	1:1	0.18 (0.19)	98	4.81 (4.96)	7.04 (7.72)	509 (544)

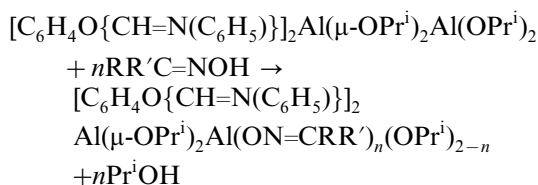
^a $[\text{C}_6\text{H}_4\text{O}\{\text{CH}=\text{N}(\text{C}_6\text{H}_5)\}]_2\text{Al}(\text{OPr}^i)$.^b RR'C=NOH.

bridge Crystallographic Data Centre comprises the final atomic coordinates for all atoms, thermal parameters and a complete listing of bond distances and angles.

3. Results and discussion

3.1. Preparation

The reactions of $[\text{C}_6\text{H}_4\text{O}\{\text{CH}=\text{N}(\text{C}_6\text{H}_5)\}]_2\text{Al}(\mu\text{-OPr}^i)_2\text{Al}(\text{OPr}^i)_2$ with simple as well as internally functionalized oximes in 1:1 and 1:2 molar ratios in refluxing anhydrous benzene solution yield the desired products:



[where R = R' = CH₃; R = CH₃, R' = C₄H₃S-2, C₄H₃O-2 and C₅H₄N-2 and n = 1 or 2]

All of these reactions are quantitative and the liberated isopropanol could be removed readily in 4 h. Their completion was checked by estimating the isopropanol liberated azeotropically. All of the products are yellow, foamy solids that are soluble in common organic solvents and show sharp melting points. Mole-

cular weight determinations indicate the binuclear nature of these complexes in refluxing anhydrous benzene (Table 1).

3.2. IR Spectra

Tentative assignments of significant bands are summarized in Table 2. The broad stretching bands at ~ 3300 cm⁻¹ due to the -OH groups of the free ligands do not appear in the IR spectra of the above derivatives indicating the deprotonation of the -OH groups and the formation of Al-O bonds. This is supported by the appearance of a new band in the region 655–680 cm⁻¹ assigned to ν(Al-O) [13]. Coordination of *N*-phenylsalicylideneimine to aluminium through the azomethine nitrogen atom is expected to reduce the electron density in the azomethine link and lower the ν(C=N) absorption frequency. In the spectra of all of the new complexes, the band due to ν(C=N) appears at lower wave-number, 1610–1620 cm⁻¹, indicative of coordination of the azomethine nitrogen to the aluminium atom [14,15]. This is supported by the appearance of a new band at 600–640 cm⁻¹ assigned to ν(Al-N) [13]. The medium intensity band observed in the region 998–1010 cm⁻¹ is assigned to ν(C-O) in the isopropoxy group. The Al-O-Al vibrations are observed in the region 740–760 cm⁻¹.

Table 6

IR spectra for $[\text{C}_6\text{H}_4\text{O}\{\text{CH}=\text{N}(\text{C}_6\text{H}_5)\}]_2\text{Al}(\text{OPr}^i)$ and $[\text{C}_6\text{H}_4\text{O}\{\text{CH}=\text{N}(\text{C}_6\text{H}_5)\}]_2\text{Al}(\text{ON}=\text{CRR}')_2$

S. No.	Compound	N-Phenylsalicylidene imineto moiety			Oximate moiety ν(N-O)	ν(Al-N)	ν(Al-O)
		ν(C=C)	ν(C=N)	ν(C-O)			
9	$[\text{C}_6\text{H}_4\text{O}\{\text{CH}=\text{N}(\text{C}_6\text{H}_5)\}]_2\text{Al}(\text{OPr}^i)$	1470m	1610s	1200m	1375m	610m	695m
10	$[\text{C}_6\text{H}_4\text{O}\{\text{CH}=\text{N}(\text{C}_6\text{H}_5)\}]_2\text{Al}\{\text{ON}=\text{C}(\text{CH}_3)\text{C}_4\text{H}_3\text{S}-2\}$	1470m	1615s	1230m	1325m	630m	695m
11	$[\text{C}_6\text{H}_4\text{O}\{\text{CH}=\text{N}(\text{C}_6\text{H}_5)\}]_2\text{Al}\{\text{ON}=\text{C}(\text{CH}_3)\text{C}_5\text{H}_4\text{N}-2\}$	1480m	1610s	1250m	1325m	605m	670m
12	$[\text{C}_6\text{H}_4\text{O}\{\text{CH}=\text{N}(\text{C}_6\text{H}_5)\}]_2\text{Al}\{\text{ON}=\text{C}(\text{CH}_3)\text{C}_4\text{H}_3-2\}$	1475m	1620s	1250m	1375m	610m	680m

Table 7

¹H NMR spectra for [C₆H₄O{CH=N(C₆H₅)}]₂Al(OPrⁱ) and [C₆H₄O{CH=N(C₆H₅)}]₂Al(ON=CRR')

S. No.	Compound	<i>N</i> -Phenylsalicylidene imineto moiety		Isopropoxy moiety		Oximate moiety	
		CH=N	Aromatic protons	CH ₃	OCH		
9	[{C ₆ H ₄ O{CH=N(C ₆ H ₅)}] ₂ Al(OPr ⁱ)	8.68, s (2H)	8.65, s (18H)	6.47–7.86, m (18H)	1.03, d (6H)	3.40, m (1H)	–
10	[{C ₆ H ₄ O{CH=N(C ₆ H ₅)}] ₂ Al{ON=C(CH ₃)C ₄ H ₃ S-2}	8.68, s (2H)	8.62, s (18H)	7.25–7.48, m (18H)	–	–	2.21, s(3H,CH ₃); 6.81, d(1H,H-4); 6.97, d(1H,H-3); 1.16(1H,H-5)
11	[{C ₆ H ₄ O{CH=N(C ₆ H ₅)}] ₂ Al{ON=C(CH ₃)C ₅ H ₄ N-2}	8.78, s (2H)	8.72, s (18H)	6.91–7.67, m (18H)	–	–	2.20, s(3H,CH ₃); 7.50, t(1H,H-4); 7.53, t(1H, H3); 7.72(1H,H5); 8.21, d(1H,H-6)
12	[{C ₆ H ₄ O{CH=N(C ₆ H ₅)}] ₂ Al{ON=C(CH ₃)C ₄ H ₃ O-2}	8.78, s (2H)	8.68, s (18H)	6.98–7.59, m (18H)	–	–	2.04, s(3H,CH ₃); 1.42, d(1H,H-4); 6.80, d(1H,H-3); 8.21(1H,H-5)

3.3. ¹H NMR spectra

The important signals in the ¹H NMR spectra of these derivatives are summarized in Table 3. Comparison of the spectra of the free oximes with the spectra of the corresponding derivatives shows the absence of signals attributable to –OH, indicating the deprotonation of the OH groups of the oxime ligands and the formation of Al–O bonds. This is supported by the significant shifting of the positions of the methyl signals of the ligand moiety. However, no appreciable shift was observed in the positions of the ring protons of the functionalized oximes ruling out the possibility of coordination through the hetero (N, O or S) atom [16]. The presence of two singlet for the azomethine proton signals of the *N*-phenylsalicylideneimine group in the spectra of all these complexes, indicates the nonequivalent nature of azomethine protons. These signals are downfield compared to the free Schiff's base, suggesting deshielding of the azomethine protons due to coordination to aluminium through the azomethine nitrogen [1]. Similarly, the presence of two doublets and two multiplets for the methyl and methine

protons, respectively, of the bridging and terminal isopropoxy groups (for compounds 1, 3, 5 and 7), indicate the nonequivalent nature of bridging and terminal isopropoxy groups. Aromatic protons of *N*-phenylsalicylidene imine are observed in the region δ 6.53–7.98 ppm as a multiplet [1].

3.4. ¹³C NMR spectra

The mode of bonding suggested above is confirmed by the ¹³C NMR spectra (Table 4). The C=N signal of the internally functionalized oximes in general is deshielded as compared to its position for the corresponding free oximes, indicating the formation the Al–O bond. The carbon signals due to the heterocyclic ring of the functionalized oximes do not show any shifting after complexation, indicating that the hetero (N, O or S) atom is not taking part in bonding with aluminium. The azomethine (>CH=N) carbon is deshielded and two signals appear at 161.2–162.9 and 162.1–163.32 ppm. This deshielding, as well as the presence of two carbon signals, provides further support of coordination through the azomethine nitrogen to the aluminium atom

Table 8

¹³C NMR spectra for [C₆H₄O{CH=N(C₆H₅)}]₂Al(OPrⁱ) and [C₆H₄O{CH=N(C₆H₅)}]₂Al(ON=CRR')

S. No.	Compound	<i>N</i> -Phenylsalicylidene imineto moiety		Isopropoxy moiety		Oximate moiety
		CH=N	Aromatic carbon	CH ₃	OCH	
9	[{C ₆ H ₄ O{CH=N(C ₆ H ₅)}] ₂ Al(OPr ⁱ)	165.2; 168.1	117.2; 118.9; 119.2; 121.2; 123.4; 124.0; 125.6; 127.9; 133.1; 135.2	24.8; 25.4	63.7; 65.2	–
10	[{C ₆ H ₄ O{CH=N(C ₆ H ₅)}] ₂ Al{ON=C(CH ₃)C ₄ H ₃ S-2}	162.8; 163.1	117.3; 119.0; 120.2; 121.2; 123.8; 124.0; 125.9; 128.3; 132.2; 133.8	–	–	12.4(CH ₃); 126.3(C4); 126.7(C3); 127.5(C5); 140.9(C2); 151.9(C=N)
11	[{C ₆ H ₄ O{CH=N(C ₆ H ₅)}] ₂ Al{ON=C(CH ₃)C ₅ H ₄ N-2}	162.7; 162.9	117.2; 118.7; 119.3; 121.9; 124.3; 125.6; 127.9; 128.3; 134.1; 135.0	–	–	10.9(CH ₃); 123.5(C5); 124.8(C3); 137.5(C4); 149.2(C6); 153.4(C2); 157.2(C=N)
12	[{C ₆ H ₄ O{CH=N(C ₆ H ₅)}] ₂ Al{ON=C(CH ₃)C ₄ H ₃ O-2}	161.8; 162.2	117.5; 118.9; 121.9; 123.9; 124.0; 124.9; 125.9; 127.9; 132.9; 135.9	–	–	11.2(CH ₃); 109.1(C4); 112.3(C3); 144.2(C5); 147.7(C2); 152.3(C=N)

Table 9
Selected bond lengths (Å) and angles (°) for $[\text{C}_6\text{H}_4\text{OCH}=\text{NC}_6\text{H}_5]_2\text{Al}\{\text{ON}=\text{C}(\text{CH}_3)\text{C}_4\text{H}_3\text{S}-2\} \cdot \text{CH}_2\text{Cl}_2$

Bond lengths			
Al(1)–O(1)	1.759(2)	Al(1)–N(1)	2.737(3)
Al(1)–O(2)	1.760(2)	Al(1)–O(3)	1.758(2)
Al(1)–N(2)	2.057(2)	Al(1)–N(3)	2.039(2)
Bond angles			
N(1)–Al(1)–N(3)	174.5(1)	O(1)–Al(1)–O(2)	119.9(1)
O(1)–Al(1)–O(3)	117.7(1)	O(2)–Al(1)–O(3)	122.3(1)
O(1)–Al(1)–N(2)	86.14(9)	O(1)–Al(1)–N(3)	98.6(1)
O(2)–Al(1)–N(2)	89.2(1)	O(2)–Al(1)–N(3)	85.9(1)
O(3)–Al(1)–N(2)	90.61(9)	O(3)–Al(1)–N(3)	89.8(1)
Al(1)–O(2)–C(7)	131.0(2)	Al(1)–O(3)–C(20)	129.0(2)
C(13)–N(2)–Al(1)	121.1(2)	C(26)–N(3)–Al(1)	123.6(2)
Al(1)–O(1)–N(1)	120.5(2)	O(1)–Al(1)–N(1)	25.9(1)

and the nonequivalent nature of azomethine carbon. The aromatic carbon signal of *N*-phenylsalicylideneimine appears in the range δ 117.2–135.9 ppm. Further, the presence of two carbon signals each for methyl and methine of the isopropoxy groups in compounds **1**, **3**, **5** and **7**, indicate that bridging and terminal isopropoxy groups are magnetically nonequivalent.

Table 10
Crystal data and structure refinement for $[\text{C}_6\text{H}_4\text{OCH}=\text{NC}_6\text{H}_5]_2\text{Al}\{\text{ON}=\text{C}(\text{CH}_3)\text{C}_4\text{H}_3\text{S}-2\} \cdot \text{CH}_2\text{Cl}_2$

Empirical formula	$\text{C}_{33}\text{H}_{28}\text{N}_3\text{O}_3\text{AlSCl}_2$
Formula weight	644.52
Temperature (°C)	–153(2)
Wavelength (Å)	0.71073
Crystal system	monoclinic
Space group	$P2_1/c$
<i>a</i> (Å)	14.7261(5)
<i>b</i> (Å)	9.3110(3)
<i>c</i> (Å)	22.6595(10)
β (°)	95.9330(10)
<i>V</i> (Å ³)	3090.3(2)
<i>Z</i>	4
<i>D</i> _{calc} (g cm ^{–3})	1.385
Absorption coefficient (mm ^{–1})	0.346
<i>F</i> (0 0 0)	1336
Crystal size (mm)	0.20 × 0.20 × 0.02
θ Range for data collection (°)	3.08–27.50
Index ranges	–19 <i>h</i> 17, –10 <i>k</i> 11, –29 <i>l</i> 24
Reflections collected	17 092
Independent reflections	6945 [<i>R</i> _{int} = 0.0819]
Max./min. transmission	0.9931 and 0.9341
Refinement method	Full-matrix least-squares on <i>F</i> ²
Data/restraints/parameters	6945/0/390
Goodness-of-fit on <i>F</i> ²	0.937
Final <i>R</i> indices [<i>F</i> ² > 4σ(<i>F</i> ²)]	<i>R</i> ₁ = 0.0568, <i>wR</i> ₂ = 0.1027
<i>R</i> indices (all data)	<i>R</i> ₁ = 0.1493, <i>wR</i> ₂ = 0.1291
Extinction coefficient	0.0004(4)
Largest difference peak and hole (e [–] Å ³)	0.734 and –0.321

3.5. ²⁷Al NMR spectra

²⁷Al NMR spectra of compounds, $[\text{C}_6\text{H}_4\text{O}\{\text{CH}=\text{N}(\text{C}_6\text{H}_5)\}]_2\text{Al}(\mu\text{-OPr}^i)_2\text{Al}\{\text{ON}=\text{C}(\text{CH}_3)\text{C}_4\text{H}_3\text{S}-2\}(\text{OPr}^i)$ [A], $[\text{C}_6\text{H}_4\text{O}\{\text{CH}=\text{N}(\text{C}_6\text{H}_5)\}]_2\text{Al}(\mu\text{-OPr}^i)_2\text{Al}\{\text{ON}=\text{C}(\text{CH}_3)\text{C}_4\text{H}_3\text{S}-2\}_2$ [B] and $[\text{C}_6\text{H}_4\text{O}\{\text{CH}=\text{N}(\text{C}_6\text{H}_5)\}]_2\text{Al}(\mu\text{-OPr}^i)_2\text{Al}\{\text{ON}=\text{C}(\text{CH}_3)\text{C}_5\text{H}_4\text{N}-2\}(\text{OPr}^i)$ [C] at room temperature exhibit two signals at δ 7.4 (linewidths 132.03 Hz), 7.6 (linewidths 100.35 Hz), 7.9 (linewidths 155.25 Hz) ppm and δ 54.1 (linewidths 176.04 Hz), 55.4 (linewidths 167.26 Hz), 53.1 (linewidths 186.31 Hz) ppm, respectively indicating the presence of both six- and four-coordination around the two aluminium atoms [2] (Fig. 1).

In view of the dinuclear nature of products **1–8** as well as the monodentate behaviour of the simple and internally functionalized oximes as indicated by the above studies, the following tentative structure may be proposed for these derivatives (Fig. 2).

From the above studies it appears that binuclear unsymmetrical structures containing aluminium(III) atoms in six- and four-coordination states, e.g. $[\text{C}_6\text{H}_4\text{O}\{\text{CH}=\text{N}(\text{C}_6\text{H}_5)\}]_2\text{Al}(\mu\text{-OPr}^i)_2\text{Al}(\text{OPr}^i)_2$, are relatively more stable compared to the symmetrical dimeric structure containing aluminium(III) atoms in five-coordination states, $[\text{C}_6\text{H}_4\text{O}\{\text{CH}=\text{N}(\text{C}_6\text{H}_5)\}](\text{OPr}^i)\text{Al}(\mu\text{-OPr}^i)_2\text{Al}[\text{C}_6\text{H}_4\text{O}\{\text{CH}=\text{N}(\text{C}_6\text{H}_5)\}](\text{OPr}^i)$.

It is rather difficult to explain why four- and six-coordinate geometries are favoured over symmetrical five-coordinate structures. A possible explanation could be that the β -diketone chelates exert a marked preference for spanning tetra- and hexa-coordinated aluminium sites and avoid participation in five-coordinate geometries. However, it is difficult to rule out the

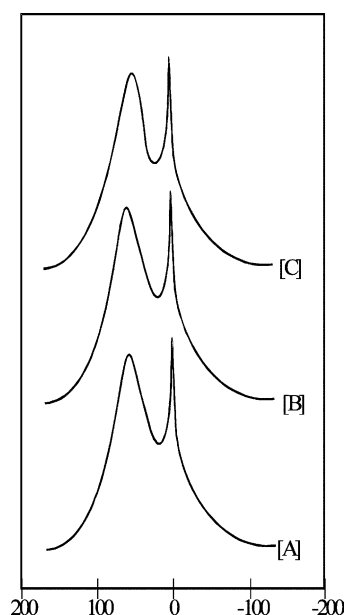


Fig. 1. ²⁷Al NMR spectra of [A], [B] and [C] at room temperature.

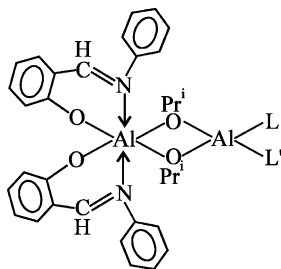
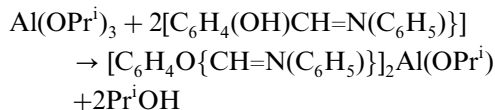


Fig. 2. Proposed structure of $[\text{C}_6\text{H}_4\text{O}\{\text{CH}=\text{N}(\text{C}_6\text{H}_5)\}_2\text{Al}(\mu\text{-OPr}^i)_2\text{Al}(\text{ON}=\text{CRR}')_n(\text{OPr}^i)_{2-n}]$ [where $\text{L} = \text{L}' = \text{RR}'\text{C}=\text{NOH}$; $\text{L} = \text{OPr}^i$ and $\text{L}' = \text{RR}'\text{C}=\text{NOH}$; $\text{R} = \text{R}' = \text{CH}_3$; $\text{R} = \text{CH}_3$, $\text{R}' = \text{C}_4\text{H}_3\text{S-2}$, $\text{C}_4\text{H}_3\text{O-2}$ and $\text{C}_5\text{H}_4\text{N-2}$ and $n = 1$ or 2].

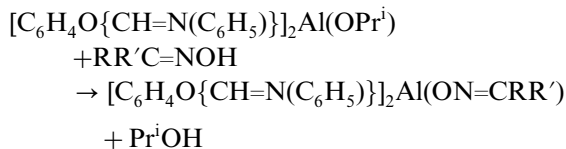
possibility that five-coordinate intermediates are formed in the synthesis of many of these compounds, and that these rapidly rearrange to the observed products containing four- and six-coordinated aluminium atom. In view of this, the preparation of monomeric heteroleptic Al(III) derivatives containing penta-coordinated Al(III) atoms were attempted using some sterically crowded ligands.

The reaction of $\text{Al}(\text{OPr}^i)_3$ with $[\text{C}_6\text{H}_4(\text{OH})\text{CH}=\text{N}(\text{C}_6\text{H}_5)]$ in 1:2 molar ratio in anhydrous benzene yields the aluminium(III) complex:



This reaction is quite facile and quantitative. The product was characterized by elemental analysis and IR and NMR spectroscopy.

Further reactions of $[\text{C}_6\text{H}_4\text{O}\{\text{CH}=\text{N}(\text{C}_6\text{H}_5)\}_2\text{Al}(\text{OPr}^i)]$ with internally functionalized oximes in 1:1 molar ratio in refluxing anhydrous benzene give products of the following type:



(where $\text{R} = \text{CH}_3$; $\text{R}' = \text{C}_4\text{H}_3\text{S-2}$, $\text{C}_4\text{H}_3\text{O-2}$, $\text{C}_5\text{H}_4\text{N-2}$)

These reactions are quite facile and quantitative. All these derivatives are yellow coloured solids, hygroscopic in nature and are soluble in common organic solvents. Molecular weight measurements indicate their monomeric nature in refluxing anhydrous benzene.

3.6. IR spectra

The broad stretching vibrations at $\sim 3300\text{ cm}^{-1}$ due to the $-\text{OH}$ groups of the free oximes are not present in the IR spectra of these derivatives suggesting the deprotonation of the $-\text{OH}$ group and the formation of Al–O bonds (Table 6). Bands in the region $670\text{--}690$

cm^{-1} can be assigned to $\nu(\text{Al}\text{--}\text{O})$ stretching vibrations and the lowering ($\sim 20\text{ cm}^{-1}$) of the $\nu(\text{N}\text{--}\text{O})$ stretching vibrations in all complexes further supports the formation of Al–O bonds. The bidentate nature of the *N*-phenylsalicylideneimine moiety in these compounds is supported by the presence of strong ($1610\text{--}1620\text{ cm}^{-1}$) and medium ($1470\text{--}1480\text{ cm}^{-1}$) bands due to $\nu(\text{C}=\text{N})$ and $\nu(\text{C}=\text{C})$, respectively.

3.7. ^1H NMR spectra

A comparison of the spectra of the free oximes with the spectra of the corresponding derivatives again shows the absence of $-\text{OH}$ signals indicating deprotonation of the OH groups of the free oxime ligands and the formation of Al–O bonds (Table 7). This is supported by the significant shifting of the positions of the methyl signals of the ligand moiety. However, no appreciable shift was observed in the positions of the ring protons of the functionalized oximes ruling out the possibility of coordination through the N, O or S atom.

The presence of two singlet for the azomethine proton signals of the *N*-phenylsalicylideneimine group in the spectra of all these complexes, indicates the nonequivalent nature of the azomethine protons. A multiplet in the region $\delta\ 6.47\text{--}7.86$ ppm is assigned to the aromatic protons of *N*-phenylsalicylideneimine moiety.

3.8. ^{13}C NMR spectra

In the ^{13}C NMR spectra of all these complexes, the $\text{C}=\text{N}$ signal in general is deshielded as compared to its position in the corresponding free oximes, indicating the formation of the Al–O bond (Table 8). The carbon signals due to the heterocyclic ring of the functionalized oximes are observed at their expected positions indicating that the heteroatom (O, N or S) does not take part in bonding with aluminium. The azomethine ($>\text{C}=\text{N}$) carbon is deshielded and two signals appear in the region $\delta\ 161.8\text{--}168.1$ ppm. This deshielding, as well as the presence of the two carbon signals, supports coordination through the azomethine to the aluminium atom and the nonequivalent nature of the azomethine carbon atom. The azomethine carbon signals of *N*-phenylsalicylideneimine appear in the range $\delta\ 115.2\text{--}151.4$ ppm.

3.9. ^{27}Al NMR spectra

The ^{27}Al NMR spectrum at room temperature of a representative derivative, $[\text{C}_6\text{H}_4\text{O}\{\text{CH}=\text{N}(\text{C}_6\text{H}_5)\}_2\text{Al}\{\text{ON}=\text{C}(\text{CH}_3)\text{C}_4\text{H}_3\text{S-2}\}]$, (**10**) exhibits a hump at $\delta\ 26.9$ ppm indicating the presence of penta-coordination around the aluminium atom.

In view of the mononuclear nature of the above products as well as the monodentate behaviour of the

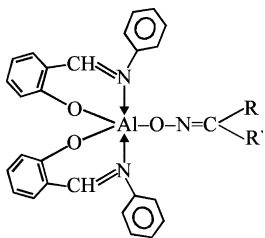


Fig. 3. Proposed structure of $[C_6H_4O\{CH=NC_6H_5\}_2]_2Al(ON=CRR')$ [where $R = CH_3$, $R' = C_4H_3S-2$, C_4H_3O-2 and C_5H_4N-2].

internally functionalized oximes as indicated by the above studies, the following tentative structure may be proposed for these derivatives (Fig. 3).

The single crystal X-ray diffraction of the complex $[C_6H_4O\{CH=N(C_6H_5)\}_2]_2Al\{ON=C(CH_3)C_4H_3S-2\}$, supports the inference drawn by the above studies that in these monomeric complexes the coordination number around the aluminium(III) atom is five.

3.10. Molecular structure of $[C_6H_4O\{CH=N(C_6H_5)\}_2]_2Al\{ON=C(CH_3)C_4H_3S-2\} \cdot CH_2Cl_2$

The structure of $[C_6H_4O\{CH=N(C_6H_5)\}_2]_2Al\{ON=C(CH_3)C_4H_3S-2\}$ (**10**) consists of a discrete monomeric unit with five coordination around the aluminium(III) atom as shown in Fig. 4. The geometry around the aluminium atom is a distorted trigonal bipyramid. The aluminium atom lies within the plane in which the equatorial positions are occupied by the oxygen atom of the oxime, O(1), and those of the two *N*-phenylsalicylideneiminato bidentate ligands, O(2) and O(3). The O–Al–O bond angles, which sum to 359.9° , are all close to 120° , Table 9. The axial positions are occupied by the

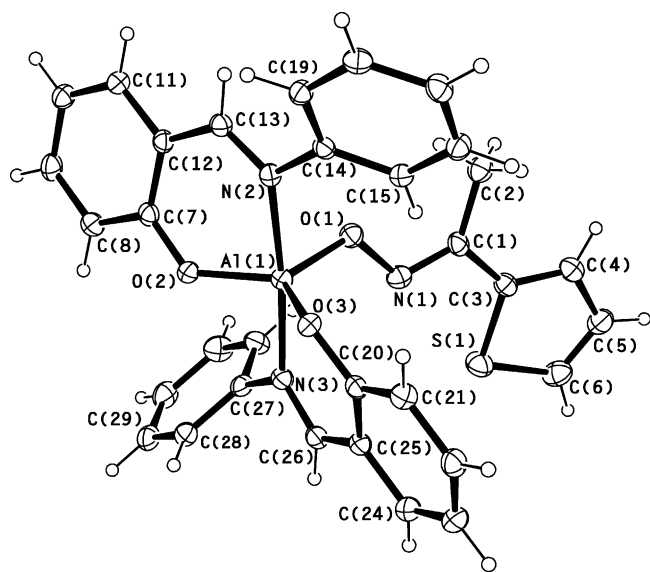


Fig. 4. ORTEP plot of the molecule $[C_6H_4OCH=NC_6H_5]_2Al\{ON=C(CH_3)C_4H_3S-2\} \cdot CH_2Cl_2$ **1**. The atoms are drawn with 30% probability ellipsoids and the atoms of CH_2Cl_2 are omitted for clarity.

nitrogen atoms of the *N*-phenylsalicylideneimine ligands resulting in O–Al–N bite-angles of $89.8(1)^\circ$ and $89.2(1)^\circ$ which are similar to those found for the same ligands, $89.5(1)^\circ$ and $88.7(1)^\circ$, in the six-coordinate aluminium environment found in $[C_6H_4O\{CH=N(C_6H_5)\}_2]_2Al(\mu-OPr^i)_2Al(OPr^i)_2$ [1]. The bite-angles accommodate the *cis*–*trans* arrangement in octahedral as readily as equatorial-axial in trigonal bipyramidal. The N(2)–Al(1)–N(3) angle of $174.5(1)^\circ$ for the axial positions in **10**, is closer to 180° than the N(1)–Al(1)–N(2) *trans* angle of $169.4(1)^\circ$ in $[C_6H_4O\{CH=N(C_6H_5)\}_2]_2Al(\mu-OPr^i)_2Al(OPr^i)_2$. Comparable bond lengths in the five-coordinate environment of aluminium in **10** are shorter than those in the six-coordinate environment in $[C_6H_4O\{CH=N(C_6H_5)\}_2]_2Al(\mu-OPr^i)_2Al(OPr^i)_2$, with Al–O and Al–N bond lengths averaging 1.759(1) and 2.048(13) Å respectively in **10** and 1.816(4) and 2.077(3) Å in $[C_6H_4O\{CH=N(C_6H_5)\}_2]_2Al(\mu-OPr^i)_2Al(OPr^i)_2$. The Al(1)–O(1) oxime bond of 1.759(2) Å in **10** is identical to those of the Al–O bonds to the bidentate *N*-phenylsalicylideneiminato ligands. However, the interatomic distance from aluminium to the nitrogen atom of the oxime moiety, Al(1)–N(1), is 2.737(3) Å; a distance that is sufficiently long to suggest there is no coordination. The bonds and angles within the ring systems are essentially as expected and are listed as supporting data. The molecular structure of $[C_6H_4O\{CH=N(C_6H_5)\}_2]_2Al\{ON=C(CH_3)C_4H_3S-2\}$ **10** probably represents the first known example of a five-coordinate heteroleptic aluminium(III) compound.

4. Supplementary material

The crystal code for $[C_6H_4O\{CH=N(C_6H_5)\}_2]_2Al\{ON=C(CH_3)C_4H_3S-2\} \cdot CH_2Cl_2$ is CCDC No. 192483. Supplementary data are available from the Director, 12 Union Road, Cambridge, CB2 1EZ, UK (fax: +44-1223-336033; e-mail: deposit@ccdc.cam.ac.uk or www: <http://www.ccdc.cam.ac.uk>) on request, quoting the deposition number 192483. Additional material available from the Cambridge Crystallographic Data Centre comprises the final atomic coordinates for all atoms, parameters, and a complete listing of bond distances and angles.

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