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Molecular structure of bis(*N*-phenylsalicylideneiminato)aluminium-di(μ-isopropoxy)di(isopropoxo)aluminium(III) and its reactions with alkoxyalkanols †

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A novel heterocyclic derivative of aluminium(III) $[C_6H_4O\{CH{=}N(C_6H_5)\}]_2Al(\mu\text{-}OPr^i)_2Al(OPr^i)_2$ **1** has been synthesized by the reaction of aluminium isopropoxide with *N*-phenylsalicylidene imine in 1 : 1 molar ratio in refluxing anhydrous benzene. Reactions of **1** with alkoxyalkanols in 1 : 1 and 1 : 2 molar ratios in refluxing anhydrous benzene yielded binuclear complexes of the types, $[C_6H_4O\{CH{=}N(C_6H_5)\}]_2Al(\mu\text{-}OPr^i)_2Al(OCH_2CH_2OR)(OPr^i)$ and $[C_6H_4O\{CH{=}N(C_6H_5)\}]_2Al(\mu\text{-}OPr^i)_2Al(OCH_2CH_2OR)_2$ (where R=CH_3, C_2H_5 and $C_4H_9^n$), respectively. All of these binuclear complexes have been characterized by elemental analysis, molecular weight measurements, and spectral studies. The FAB mass spectrum and ^{27}Al NMR spectrum of **1** indicate that it is a discrete unsymmetrical dimer containing four- and six-coordinated aluminium(III) atoms as confirmed by its single crystal X-ray structure.

Introduction

The role of metal alkoxides as precursors to metal oxide materials by sol–gel processing or metal organic chemical vapour deposition (MOCVD) has given new impetus to intensive investigations of the synthesis of heteroleptic derivatives in which the labile alkoxy ligands are replaced by chelating/sterically demanding ligands[1,2] such as β-diketones,[3,4] glycolate,[5,6] acetate,[7] or alkanolaminate.[8–10] These ligands have played a significant role in modifying the solubility and reactivity of the resulting alkoxide derivatives to make them suitable precursors for high-purity metal oxide-based ceramic materials.

The complex $[Al(OR)_2(acac)]_n$ is a monomer when R = $SiPh_3$ and a discrete unsymmetrical binuclear, $[(acac)_2Al(\mu\text{-}OPr^i)_2Al(OPr^i)_2]$, when R = Pr^i, due to the presence of comparatively stable four- and six-coordinated aluminium(III) atoms.[11] The replacement of the two terminal isopropoxy groups with ligands such as glycols,[12,13] thioglycols,[14] 8-hydroxyquinoline[15] or oximes[16] is quite facile, leading to products containing the same unsymmetrical structures. Recently we reported that steric and electronic factors play a very important role in aluminium (alkoxide) β-diketonate chemistry.[15–18] In continuation of our studies on the synthesis and structural elucidations of some novel heterocyclic compounds containing aluminium(III) atoms in different coordination environments, we report herein the chemistry of a new heteroleptic precursor, $[C_6H_4O\{CH{=}N(C_6H_5)\}]_2Al(\mu\text{-}OPr^i)_2Al(OPr^i)_2$.

† Synthesis and structural elucidations of some novel heterocyclic compounds containing aluminium(III) atoms at bridge-head positions. Part 2.[32]

Electronic supplementary information (ESI) available: mass spectrum assignments, IR, ^1H NMR and ^{13}C NMR spectral data. See http://www.rsc.org/suppdata/dt/b1/b109729f/

Results and discussion

A novel heteroleptic species, bis(*N*-phenylsalicylideneiminato)-aluminium-di-μ-isopropoxo-di-isopropoxoaluminium(III), has been prepared by the reaction of aluminium isopropoxide and *N*-phenylsalicylidene imine in 1 : 1 molar ratio in refluxing anhydrous benzene as shown in eqn. (1):

$$Al(OPr^i)_3 + C_6H_4(OH)CH{=}NC_6H_5 \longrightarrow 1/2[C_6H_4O\{CH{=}N(C_6H_5)\}]_2Al(\mu\text{-}OPr^i)_2Al(OPr^i)_2 \; \mathbf{1} + Pr^iOH \quad (1)$$

This reaction is quite facile and quantitative and its progress was followed by estimating the isopropanol liberated azeotropically. The complex **1** is a lemon coloured crystalline solid that is soluble in common organic solvents.

Reactions of **1** with alkoxyalkanols in 1 : 1 and 1 : 2 molar ratios in refluxing anhydrous benzene solution yield the desired products:

$$[C_6H_4O\{CH{=}N(C_6H_5)\}]_2Al(\mu\text{-}OPr^i)_2Al(OPr^i)_2 + n HOCH_2CH_2OR \longrightarrow [C_6H_4O\{CH{=}N(C_6H_5)\}]_2Al(\mu\text{-}OPr^i)_2 Al(OCH_2CH_2OR)_n(OPr^i)_{2-n} + n Pr^iOH \quad (2)$$

(where R = CH_3, C_2H_5, $C_4H_9^n$ and n = 1 or 2)

All of these reactions are quantitative and the liberated isopropanol could be removed readily in 4 hours. Their completion was checked by estimating the isopropanol liberated azeotropically. All the products are yellow coloured foamy solids and are soluble in common organic solvents. Molecular

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Table 1 Synthetic and analytical data for $[C_6H_4O\{CH{=}N(C_6H_5)\}]_2Al(\mu\text{-}OPr^i)_2Al(OCH_2CH_2OR)(OPr^i)$ and $[C_6H_4O\{CH{=}N(C_6H_5)\}]_2Al(\mu\text{-}OPr^i)_2\text{-}Al(OCH_2CH_2OR)_2$

Entry	$m_{[C_6H_4O\{CH=N(C_6H_5)\}Al(OPr^i)_2]_2}$ [a]/g	$m_{HOCH_2CH_2OR}$ [a]/g	Molar ratio	m_{PrOH} [b]/g found (calc.)	Yield (%)	Elemental analysis (%) Al	Elemental analysis (%) OPr^i	Melting Point/°C	Mol. Wt. Found (calc.)
1.	4.18 [$Al(OPr^i)_3$]	4.08 [$C_6H_4(OH)CH{=}NC_6H_5$]	1 : 1	1.21 (1.23)	98.7	7.4 (7.90)	34.01 (34.56)	142	674 (682.78)
2.	2.08	0.28 (R = CH_3)	1 : 1	0.18 (0.18)	98.9	7.24 (7.72)	25.2 (25.30)	158	701 (698.68)
3.	2.52	0.56 (R = CH_3)	1 : 2	0.42 (0.44)	97.5	7.33 (7.55)	16.41 (16.53)	180	760 (714.58)
4.	2.08	0.29 (R = C_2H_5)	1 : 1	0.16 (0.18)	98.9	7.44 (7.57)	24.57 (24.84)	Viscous	695 (712.78)
5.	2.14	0.58 (R = C_2H_5)	1 : 2	0.34 (0.38)	98.2	7.00 (7.21)	15.01 (15.89)	Viscous	730 (742.58)
6.	2.02	0.36 (R = C_4H_9)	1 : 1	0.16 (0.18)	99.2	7.16 (7.29)	23.39 (23.9)	98	728 (740.68)
7.	2.78	0.96 (R = C_4H_9)	1 : 2	0.45 (0.48)	96.0	6.36 (6.76)	14.32 (14.78)	Viscous	776 (798.58)

[a] Except where reagents are otherwise specified (entry 1). [b] Liberated during reaction.

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

FAB Mass spectra

The FAB mass spectral data also indicate the binuclear form of **1** (see ESI, Table S1 †).

IR Spectra

The IR spectra of the complexes were interpreted by comparing the spectra with that of the free ligands. A medium intensity band at 3300 cm^{-1} in the free ligands due to ν(OH) is absent in the IR spectra of the complexes, indicating deprotonation of the *N*-phenylsalicylideneimine as well as the alkoxyalkanol. This is further supported by the appearance of a new band in the region 685–630cm^{-1} assigned to ν(Al–O).[19] A strong band is observed in the free Schiff base, *N*-phenylsalicylideneimine, at 1625 cm^{-1}, characteristic of the azomethine (>C=N) group.[20] Coordination of *N*-phenylsalicylidene imine 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 the new complexes, the band due to ν(C=N) appears at lower wavenumber, 1625–1610 cm^{-1}, indicating coordination of the azomethine nitrogen to the aluminium atom.[21] This is further supported by the appearance of a new band at 610–550 cm^{-1} assigned to ν(Al–N).[19] The absorption frequency of phenolic C–O at 1310–1260 cm^{-1} in the aluminium complexes (1260 cm^{-1} in the free ligand), indicates that the other coordinating site of the Schiff base is through phenolic oxygen.[21,22] A medium intensity band observed at 1010–995 cm^{-1} may be assigned to ν(C–O) of the isopropoxy group. The Al–O–Al vibrations are observed in the region 760–745 cm^{-1} (see ESI, Table S2 †).

^{1}H NMR Spectra

The ^{1}H NMR spectra of **1** and its alkoxyalkanol derivatives exhibit characteristic peaks. The phenolic group resonance present in the free Schiff base (*N*-phenylsalicylideneimine) is absent in the ^{1}H NMR spectra of **1** as well as all the complexes, indicating deprotonation of the OH group and formation of the Al–O bond. The presence of a doublet at δ 8.16–8.62 ppm for the azomethine protons signal of the *N*-phenylsalicylideneimine group in the spectra of all of these complexes, indicates the nonequivalent nature of the azomethine protons. These signals are downfield compared to the free ligand, suggesting deshielding of the azomethine protons due to coordination to aluminium through the azomethine nitrogen. Similarly, the presence of two doublets (δ 1.03–1.17 and 1.18–1.28 ppm) and two multiplets (δ 3.41–3.68 and 3.99–4.08 ppm) for methyl and methine protons, respectively, of the bridging and terminal isopropoxy groups (for compounds **1**, **2**, **4** and **6**), indicate the inequivalent nature of the bridging and terminal isopropoxy groups, however, for compounds **3**, **5** and **7**, the presence of one doublet at δ 1.18 ppm and one multiplet at δ 3.90–4.02 ppm for methyl and methine protons, correspond to bridging isopropoxy groups only. A multiplet in the δ 6.27–7.92 ppm region can be assigned to the aromatic protons of *N*-phenylsalicylideneimine. No appreciable shift was observed in the position of alkoxyalkanol protons which were observed at their expected positions, ruling out the possibility of the coordination through the oxygen atom of the alkoxyalkanol moiety (see ESI, Table S3 †).

^{13}C NMR Spectra

The ^{13}C NMR chemical shifts provide further evidence of the presence of coordinated Schiff base in these aluminium(III) complexes. The azomethine carbon is deshielded and two signals appears at δ 161.1–167.5 and 162.1–170.2 ppm. This deshielding as well as the presence of two carbon signals again support coordination through the azomethine nitrogen to the aluminium atom and the nonequivalent nature of azomethine carbon, which is substantiated by the X-ray structure of complex **1**. The aromatic carbon signals of *N*-phenylsalicylideneimine appear in the range δ 115.2–151.0 ppm. Further, the presence of two carbon signals each for methyl (δ 23.9–25.1 ppm) and methine (δ 62.1–67.8 ppm) of the isopropoxy groups in compounds **1**, **2**, **4** and **6**, indicate the nonequivalent nature of bridging and terminal isopropoxy groups. Only one carbon signal each for methyl (δ 25.2–25.7) and methine (δ 63.9–64.3 ppm) appear for compounds **3**, **5** and **7** which correspond to bridging isopropoxy groups. The positions and number of alkoxyalkanol carbon signals are as expected. The fact that no significant shift was observed in the position of alkoxy carbon of these ligand moieties further suggest that the alkoxyalkanol moieties bind to aluminium atom in a monodentate fashion. (see ESI, Table S4 †).

^{27}Al NMR Spectra

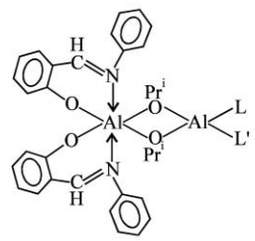
^{27}Al NMR spectrum of compound **1**, at room temperature, exhibits two signals (δ 7.8 and 40.1 ppm) indicating the presence of both 6- and 4-coordination around aluminium(III) atoms, respectively.[16]

^{27}Al NMR spectrum of a representative compound, $[C_6H_4O\{CH{=}N(C_6H_5)\}]_2Al(\mu\text{-}OPr^i)_2Al(OCH_2CH_2OC_2H_5)(OPr^i)$ at room temperature also exhibits two signals (δ 9.08 and 43.8 ppm) suggesting the presence of 6- and 4-coordinated aluminium(III) atoms.

In view of the binuclear nature of the above products **2**–**7** as well as the monodentate behaviour of the alkoxyalkanol ligand moieties as indicated by the above studies, the following tentative structure may be proposed for these derivatives (Fig. 1).

Crystal structure of $[C_6H_4O\{CH{=}N(C_6H_5)\}]_2Al(\mu\text{-}OPr^i)_2\text{-}Al(OPr^i)_2$ 1

A single-crystal X-ray diffraction study of $[C_6H_4O\{CH{=}N(C_6H_5)\}]_2Al(\mu\text{-}OPr^i)_2Al(OPr^i)_2$ **1** shows that the unsymmetrical binuclear structure contains tetra- and hexa-coordinated aluminium (Fig. 2). The hexa-coordinated aluminium is bound



Where L = L' = OCH_2CH_2OR; L = OPr^i and L' = OCH_2CH_2OR

Fig. 1 Proposed structure of $[C_6H_4O\{CH{=}NC_6H_5\}]_2Al(\mu\text{-}OPr^i)_2Al(OCH_2CH_2OR)_n(OPr^i)_{2-n}$ (R = CH_3, C_2H_5 and $C_4H_9^n$; n = 1 or 2).

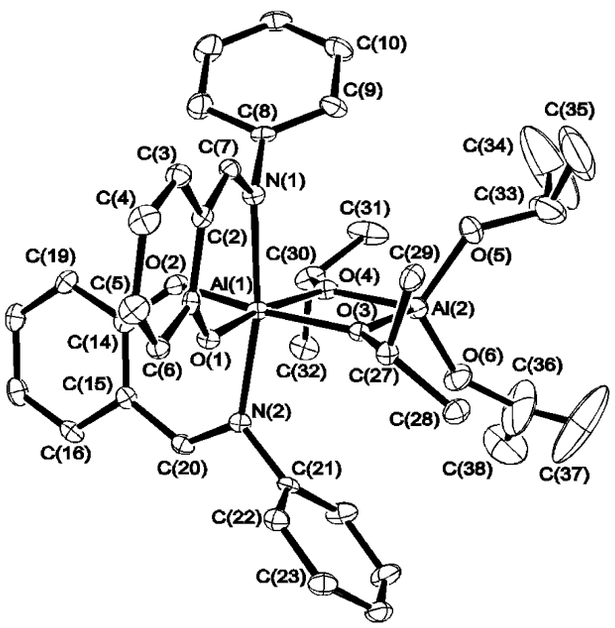


Fig. 2 ORTEP plot[31] of the molecule $[C_6H_4O\{CH{=}N(C_6H_5)\}]_2Al(\mu\text{-}OPr^i)_2Al(OPr^i)_2$. The atoms are drawn with 25% probability ellipsoids. Hydrogen atoms are omitted for clarity.

to two *N*-phenylsalicylideneimine chelate moieties, the tetra-coordinated aluminium is bound to two terminal isopropoxide ligands, and bridging isopropoxide groups join the metal centers. The Al–O bond lengths (Table 3) involving the isopropoxide groups fall into three categories: (i) 1.932(3)–1.909(3) Å found in the bridging isopropoxy groups bound to the hexa-coordinated aluminium sites, (ii) 1.792(3)–1.799(3) Å found in the same bridging isopropoxy groups bound to the tetra-coordinated aluminium sites and (iii) 1.704(3)–1.685(3) Å found in the terminal isopropoxy groups which occupy tetra-coordinated positions. For the bridging isopropoxy group, the Al–O bond length involving the hexa-coordinated aluminium atom is greater than that involving the tetra-coordinated aluminium atom, arising from the steric crowding imposed by the neighbouring salicylidene imine ligand. Both the Al–O bond lengths to salicylideneimine are essentially the same as are those for Al–N.

Experimental

All manipulations were carried out under anhydrous conditions. Solvents were purified and dried according to standard procedures.[23] The Schiff base, *N*-phenylsalicylideneimine, was prepared according to a published procedure.[24] Aluminium[16] and isopropanol[25] were estimated as reported earlier.

Infrared spectra were recorded as Nujol mulls on a Nicolet Magna 550 spectrophotometer in the range 4000–400 cm^{-1}. ^1H and ^{13}C NMR spectra were recorded on a JEOL FX90Q spectrometer using TMS as an internal reference in $CDCl_3$ and $CHCl_3$, respectively. ^{27}Al NMR spectral study was carried out in toluene using aluminium nitrate as an external reference in aqueous solution. Molecular weight measurements were carried out by the elevation in boiling point method using a Beckmann thermometer (Einstellthermometer n-Beckmann, Labortherm-N, Skalenwert, 0.01K, made in GDR) fitted in a glass assembly (supplied by JSGW, India) in anhydrous benzene. All manipulations were carried out under anhydrous conditions using anhydrous $CaCl_2$ guard/side tubes. FAB mass spectra were recorded on a JEOL SX 102/DA-6000 mass spectrometer/data system using argon/xenon (6 kV, 10 mA) as the FAB gas and *m*-nitrobenzyl alcohol as the matrix.

Preparation of $[C_6H_4O\{CH{=}N(C_6H_5)\}]_2Al(\mu\text{-}OPr^i)_2Al(OPr^i)_2$ 1

To a benzene solution (~30 mL) of aluminium isopropoxide (4.18 g) was added $C_6H_4(OH)CH{=}NC_6H_5$ (4.07 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 the removal of the solvent under reduced pressure, a yellow solid was obtained. A concentrated solution of the complex in benzene at room temperature gave yellow crystals (98.7% yield; mp. 142 °C).

Reactions of **1** with alkoxyalkanols in 1 : 1 and 1 : 2 molar ratios in refluxing anhydrous benzene gave binuclear complexes of the type $[C_6H_4O\{CH{=}N(C_6H_5)\}]_2Al(\mu\text{-}OPr^i)_2Al(OCH_2CH_2OR)_n(OPr^i)_{2-n}$ (R = CH_3, C_2H_5, $C_4H_9^n$; n = 1 or 2). Since all of these compounds were synthesized by a similar route, the synthesis of only one representative compound is described in detail below.

Synthesis of $[C_6H_4O\{CH{=}N(C_6H_5)\}]_2Al(\mu\text{-}OPr^i)_2Al(OCH_2CH_2OCH_3)(OPr^i)$

Methoxyethanol (0.23 g) was added to a benzene solution (~40 mL) of **1**. (2.08 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 an 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. Syntheses of the other derivatives and analytical data are summarized in Table 1.

X-Ray diffraction analysis

A pale yellow block crystal of $[C_6H_4O\{CH{=}N(C_6H_5)\}]_2Al(\mu\text{-}OPr^i)_2Al(OPr^i)_2{\cdot}0.5C_6H_6$ was mounted on a glass fibre. Data was collected on an Enraf Nonius KappaCCD area detector (ϕ and ω scans chosen to give a complete asymmetric unit) at the University of Southampton EPSRC National Crystallography Service. Data collection and cell refinement[26] gave cell constants corresponding to a triclinic cell whose dimensions are given in Table 2 along with other experimental parameters. An absorption correction was applied.[27]

The structure was solved by direct methods,[28] and the structure was refined using the WinGX version[29] of SHELX-97.[30] All of the non-hydrogen atoms were treated anisotropically. All hydrogen atoms were included in idealized positions with C–H set at 0.95 Å and with isotropic thermal parameters set at 1.2 times that of the carbon atom to which they were attached. The thermal paramaters are relatively large for the carbon atoms of the isopropyl groups, particularly and not surprisingly, for those in the terminal positions. However, attempts to model the disorder gave no significant improvement to refinement. Selected bond distances and bond angles are given in Table 3. The complete molecule is displayed in the ORTEP diagram in Fig. 2.

Table 2 Crystal data and structure refinement for $[C_6H_4O\{CH{=}N(C_6H_5)\}]_2Al(OPr^i)_2Al(OPr^i)_2$

Empirical formula	$C_{41}H_{51}N_2O_6Al_2$
Formula weight	721.80
Temperature/°C	−120(2)
Wavelength/Å	0.71073
Crystal system	Triclinic
Space group	$P\bar{1}$
a/Å	9.701(2)
b/Å	10.291(2)
c/Å	21.301(4)
α/°	102.51(3)
β/°	91.21(3)
γ/°	108.88(3)
V/Å^{-3}	1954.7(7)
Z	2
D_c/g cm^{-3}	1.226
μ/mm^{-1}	0.122
F(000)	770
Crystal size/mm	0.25 × 0.15 × 0.10
θ range for data collection/°	3.02 to 25.03
Limiting indices	$-11 \leqslant h \leqslant 11$, $-12 \leqslant k \leqslant 12$, $-25 \leqslant l \leqslant 25$
Reflections collected	18969
Independent reflections	5873 [$R_{int} = 0.1010$] (3667 for $F^2 > 4\sigma(F^2)$)
Max. and min. transmissions	0.9879 and 0.9701
Refinement method	Full-matrix least squares on F^2
Data/restraints/parameters	5873/0/481
Goodness-of-fit on F^2	1.040
Final R indices [$F^2 > 4\sigma(F^2)$]	$R_1 = 0.0669$, $wR_2 = 0.1598$
R indices (all data)	$R_1 = 0.1204$, $wR_2 = 0.1865$
Extinction	0.002(2)
Largest diff. peak and hole/e Å^{-3}	0.505 and −0.449

Table 3 Selected bond lengths [Å] and angles [°] for $[C_6H_4O\{CH{=}N(C_6H_5)\}]_2Al\{O(i\text{-}Pr)\}_2Al\{O(i\text{-}Pr)\}_2$

Al(1)–O(1)	1.813(3)	Al(1)–O(2)	1.818(3)
Al(1)–O(3)	1.932(3)	Al(1)–O(4)	1.909(3)
Al(1)–N(1)	2.079(3)	Al(1)–N(2)	2.075(3)
Al(2)–O(3)	1.792(3)	Al(2)–O(4)	1.799(3)
Al(2)–O(5)	1.704(3)	Al(2)–O(6)	1.685(3)
Al(1)—Al(2)	2.887(2)		
O(3)–Al(1)–O(4)	74.9(1)	O(1)–Al(1)–O(2)	99.8(1)
O(1)–Al(1)–O(4)	167.1(1)	O(2)–Al(1)–O(3)	168.0(1)
O(1)–Al(1)–O(3)	92.2(1)	O(2)–Al(1)–O(4)	93.1(1)
O(1)–Al(1)–N(1)	89.5(1)	O(1)–Al(1)–N(2)	84.3(1)
O(2)–Al(1)–N(1)	83.8(1)	O(2)–Al(1)–N(2)	88.7(1)
O(4)–Al(1)–N(1)	92.9(1)	O(4)–Al(1)–N(2)	95.1(1)
O(3)–Al(1)–N(1)	95.6(1)	O(3)–Al(1)–N(2)	93.2(1)
N(1)–Al(1)–N(2)	169.4(1)		
O(3)–Al(2)–O(4)	81.2(1)	O(5)–Al(2)–O(6)	116.4(2)
O(3)–Al(2)–O(5)	109.9(1)	O(3)–Al(2)–O(6)	118.5(1)
O(4)–Al(2)–O(5)	115.6(1)	O(4)–Al(2)–O(6)	110.5(2)
Al(1)–O(3)–Al(2)	101.6(1)	Al(1)–O(4)–Al(2)	102.2(1)
Al(1)–O(1)–C(1)	134.5(2)	Al(1)–O(2)–C(14)	135.6(2)
C(7)–N(1)–Al(1)	123.6(3)	C(20)–N(2)–Al(1)	124.4(3)

CCDC reference number 171510.

See http://www.rsc.org/suppdata/dt/b1/b109729f/ for crystallographic data in CIF or other electronic format.

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