

Synthesis, characterization and photoluminescence of aluminum *N*-aryloxo functionalized β -ketoiminate complexes

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The synthesis, characterization and luminescent properties of aluminum complexes containing a dianionic *N*-aryloxo functionalized β -ketoiminate ligand are presented. 4-(2-Hydroxy-5-*R*-phenyl)imino-2-pentanone (*R* = Me, L¹H₂; *R* = *tert*-butyl, L²H₂) ligands reacted with AlEt₃ in tetrahydrofuran to give the aluminum complexes (L¹AlEt)₂ (**1**) and (L²AlEt)₂ (**2**) in reasonable isolated yields. X-ray diffraction revealed that complexes **1** and **2** have solvent-free centrosymmetric dimeric structures, and each aluminum center has distorted trigonal bipyramidal geometry. At room temperature, complexes **1** and **2** exhibit blue photoluminescence in acetonitrile with maximum emission wavelengths of 419 and 413 nm, respectively.

aluminum, β -ketoiminate ligand, synthesis, structure, photoluminescence

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Over the past few years, β -ketoiminate ligands have become among the most attractive chelating systems in main group and transition metal coordination chemistry because of their simple preparation from inexpensive and readily available starting materials and easily modified steric and/or electronic properties. Metal complexes containing these ligand systems have been used in a variety of applications, including as precursors for metal-organic chemical vapor deposition for the growth of thin films [1] and as active catalysts in homogeneous catalysis [2–9]. However, *N*-aryl-oxo functionalized β -ketoimine, a derivative of β -ketoiminate containing a pendant phenol functionality has seldom been employed in main group and transition-metal coordination chemistry [10].

Recently, we began studying the synthesis and reactivity of rare earth metal complexes containing *N*-aryloxo func-

tionalized β -ketoiminate ligands. In our earlier work, a series of rare earth metal amides and aryloxides based on these ligand systems were synthesized and these complexes were shown to be active initiators for the ring-opening polymerization of *L*-lactide and ϵ -caprolactone [11–13]. In a continuation of our study in this area, herein two aluminum complexes containing *N*-aryloxo functionalized β -ketoiminate ligands are synthesized and their photoluminescent properties examined.

1 Experimental

Because aluminum complexes are sensitive to moisture and air, all manipulations were performed under pure argon with rigorous exclusion of air and moisture using standard Schlenk techniques.

(i) Materials. Tetrahydrofuran (THF), toluene and ace-

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tonitrile (MeCN) were degassed and distilled from sodium benzophenone ketyl under argon prior to use. The ligands 4-(2-hydroxy-5-R-phenyl)imino-2-pentanone (R = Me, L¹H₂; R = *tert*-butyl, L²H₂) were prepared according to our reported procedure [11].

(ii) Synthesis. Synthesis of complex **1**: A solution of AlEt₃ (8.0 mmol) in dry toluene (20 mL) was added to a stirred solution of L¹H₂ (1.64 g, 8.0 mmol) in dry THF (20 mL) at -10°C. The color of the solution immediately changed from colorless to bright yellow. The mixture was stirred at room temperature overnight, and then the solvent was evaporated under vacuum. Toluene (15 mL) was added to extract the product, giving complex **1** as pale yellow crystals after the solution was left undisturbed at room temperature for a few days (1.08 g, 42%). Mp: 180–182°C. Anal. Calcd for C₂₈H₃₆Al₂N₂O₄: C, 64.86; H, 6.95; N, 5.41. Found: C, 64.91; H, 6.86; N, 5.35. ¹H NMR (CDCl₃) δ: -0.41 (q, 2H, *J* = 8.3 Hz, CH₂), 0.69 (t, 3H, *J* = 8.3 Hz, CH₃CH₂), 2.14 (s, 3H, CH₃C=N), 2.20 (s, 3H, CH₃ (arene ring)), 2.31 (s, 3H, CH₃C=O), 5.29 (s, 1H, CH), 6.90–7.57 (3H, Ar). ¹³C(¹H) NMR (CDCl₃) δ: 178.83 (C=O), 169.90 (C=N), 103.20 (CH), 25.65 (CH₃), 25.04 (CH₃), 24.15 (CH₃), 22.07 (CH₃), 21.19 (CH₂CH₃). IR (KBr, cm⁻¹): 2933 (m), 2894 (m), 2856 (m), 2794 (w), 1590 (s), 1513 (s), 1405 (s), 1297 (m), 1266 (s), 1127 (w), 1027 (m), 950 (m), 849 (s), 764 (w), 556 (w).

Synthesis of complex **2**: Complex **2** was synthesized in the same manner as that described for complex **1** using L²H₂ (1.69 g, 6.86 mmol) instead of L¹H₂. Pale yellow crystals were obtained (1.25 g, 61%). Mp: 172–174°C. Anal. Calcd for C₃₄H₄₈Al₂N₂O₄: C, 67.55; H, 8.28; N, 4.64. Found: C, 67.62; H, 8.17; N, 4.59. ¹H NMR (CDCl₃) δ: -0.25 (q, 2H, *J* = 8.1 Hz, CH₂), 0.83 (t, 3H, *J* = 8.1 Hz, CH₃CH₂), 1.31 (s, 9H, (C(CH₃)₃)), 2.00 (s, 3H, CH₃C=N), 2.33 (s, 3H, CH₃C=O), 5.22 (s, 1H, CH), 7.11–7.27 (3H, Ar). ¹³C(¹H) NMR (CDCl₃) δ: 178.26 (CO), 169.30 (CN), 103.20 (CH), 34.56 (CH₃), 32.30 (CH₃), 31.37 (CH₃), 26.38 (CH₃), 23.88 (CH₂). IR (KBr, cm⁻¹): 2964 (m), 2902 (m), 2863 (m), 2794

(w), 1598 (s), 1513(s), 1405 (s), 1297 (m), 1266 (s), 1134 (w), 1027 (m), 949 (m), 857 (m), 787 (w), 556 (w).

(iii) Analyses. ¹H and ¹³C NMR spectra of complexes **1** and **2** were recorded in CDCl₃ at room temperature using a Unity Varian-400 spectrometer. Melting points were determined in a sealed argon-filled capillary and are uncorrected. Carbon, hydrogen and nitrogen analyses were performed by direct combustion on an EA-1110 analyzer (CE instruments), and quoted data are the average of at least two independent determinations. Infrared (IR) spectra were recorded on a Nicolet-550 FTIR spectrometer using KBr pellets. UV-Vis absorption and emission spectra were recorded on a Perkin-Elmer Lambda 35 UV-Vis spectrophotometer and a Perkin-Elmer LS 50B fluorescence spectrophotometer, respectively.

(iv) Crystal structure determination. Single crystals of complexes **1** and **2** suitable for X-ray determination were sealed in a thin-walled glass capillary for determining their molecular structure. Intensity data were collected with a Rigaku Mercury CCD area detector in ω scan mode using Mo K α radiation (λ = 0.07107 nm). The diffracted intensity was corrected for Lorentz polarization effects and empirical absorption corrections were applied. Details of the data collection and crystal data are given in Table 1. The structure was solved using direct methods and refined by full-matrix least-squares procedures based on $|F|^2$. All of the non-hydrogen atoms were refined anisotropically. The hydrogen atoms were all generated geometrically (C—H bond lengths fixed at 0.098 nm for methylene, 0.097 nm for methyl and 0.094 nm for aromatic rings). The structures were solved and refined using SHELXL-97 [14].

2 Results and discussion

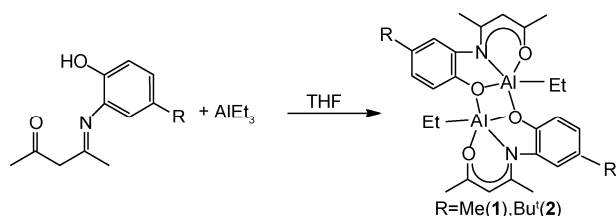
Alkane elimination of *N*-aryloxo functionalized β -ketoimine with alkylaluminum is a convenient method for the synthesis of *N*-aryloxo functionalized β -ketoiminate aluminum

Table 1 Crystallographic data for complexes **1** and **2**

Complex	1	2	Complex	1	2
Formula	C ₂₈ H ₃₆ Al ₂ N ₂ O ₄	C ₃₄ H ₄₈ Al ₂ N ₂ O ₄	Z	1	4
M _w	518.55	602.70	D _c (g cm ⁻³)	1.300	1.193
T (K)	173(2)	173(2)	μ (mm ⁻¹)	0.147	0.125
Crystal system	triclinic	monoclinic	F(000)	276	1296
Space group	P $\bar{1}$	P2 ₁ /n	θ_{\max} (deg)	25.34	27.48
a (nm)	0.7953(1)	0.9703(1)	Collected reflections	6387	36714
b (nm)	0.8470(1)	2.3014(3)	Unique reflections	2411	7658
c (nm)	1.0248(2)	1.5320(2)	Observed reflections [<i>I</i> >2.0 σ (<i>I</i>)]	2245	6740
α (deg)	85.477(10)		No. of variables	168	392
β (deg)	83.121(9)	101.197(2)	GOF	1.041	1.112
γ (deg)	75.450(8)		R [<i>I</i> >2.0 σ (<i>I</i>)]	0.0358	0.0546
V (nm ³)	0.6625(2)	3.3560(6)	wR [<i>I</i> >2.0 σ (<i>I</i>)]	0.0944	0.1279

complexes. Reaction of L^1H_2 or L^2H_2 with $AlEt_3$ in toluene in a 1:1 molar ratio, afforded the monoalkyl β -ketoiminate aluminum complexes **1** and **2** in good isolated yields, as shown in Scheme 1. These complexes were characterized by elemental analysis, and by 1H and ^{13}C NMR and IR spectra. Elemental analysis revealed that complexes **1** and **2** consist of one β -ketoiminate ligand, one ethyl group and an aluminum atom. In the 1H NMR spectra of these complexes, resonances from the coordinating N–H and O–H groups disappeared and resonances from $AlCH_2CH_3$ were observed at high field. X-ray structure determination revealed that complexes **1** and **2** possess dimeric structures. Unexpectedly, crystals of complexes **1** and **2** are stable in air, and can be handled in air without decomposition. No apparent deterioration was observed even when the crystals were immersed in water for 10 min. However, solutions of these complexes in THF are sensitive to moisture, and the color of these solutions changed gradually when they are exposed to air.

The molecular structures of complexes **1** and **2** are shown in Figures 1 and 2, respectively, and selected bond lengths and angles are listed in Table 2. The overall molecular structures of complexes **1** and **2** are similar, but they crystallize in different crystal systems. Complex **1** crystallizes in a triclinic crystal system, and has a solvent-free centrosymmetric dimeric structure. In contrast, complex **2** crystallizes in a monoclinic crystal system, and the molecule has no symmetry. Complexes **1** and **2** possess bridging phenoxo oxygen atoms, which are similar to those observed in



Scheme 1 Synthesis of complexes **1** and **2**.

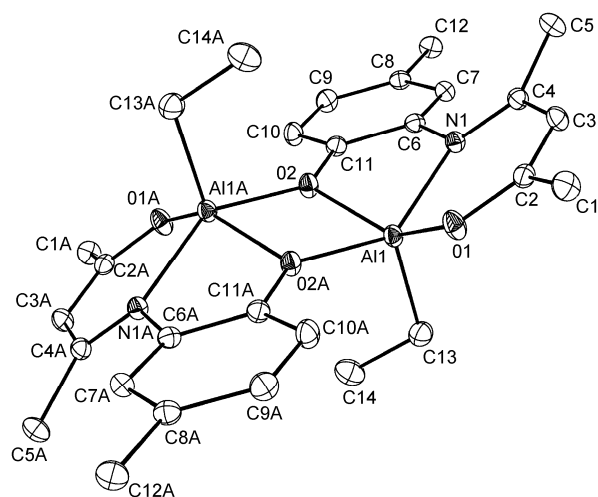


Figure 1 ORTEP diagram of complex **1** showing atom numbering. Thermal ellipsoids are drawn at the 30% probability level. Hydrogen atoms are omitted for clarity.

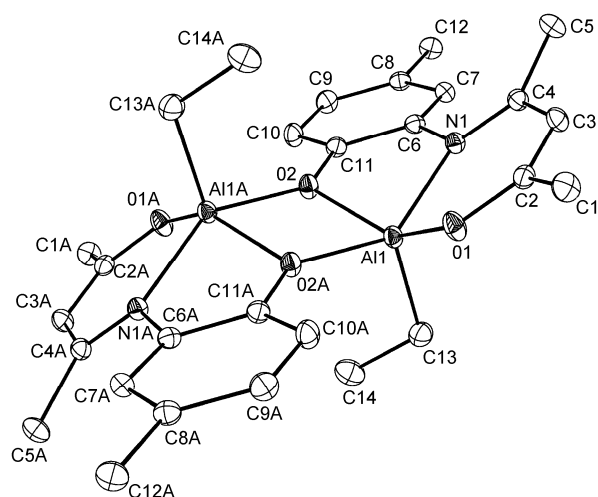


Figure 2 ORTEP diagram of complex **2** showing atom numbering. Thermal ellipsoids are drawn at the 30% probability level. Hydrogen atoms are omitted for clarity.

Table 2 Selected bond lengths (nm) and bond angles ($^\circ$) for complexes **1** and **2**

	Bond lengths (nm)		Bond angles ($^\circ$)	
	1	2	1	2
Al(1)–O(1)	0.1802(1)	0.1792(1)	O(2)–Al(1)–O(4)	73.66(6)
Al(1)–O(2)	0.1891(1)	0.1903(1)	O(4)–Al(1)–O(1)	92.12(6)
Al(1)–O(2A)	0.1897(1)		O(2)–Al(1)–O(2A)	74.32(5)
Al(1)–N(1)	0.2014(1)	0.1998(2)	O(1)–Al(1)–O(2A)	91.81(5)
Al(1)–C(13)	0.1970(2)		O(1)–Al(1)–N(1)	90.71(5)
Al(1)–C(31)		0.1967(2)	O(2)–Al(1)–N(1)	80.43(5)
Al(2)–O(2)		0.1891(1)	Al(1)–O(2)–Al(1A)	105.68(5)
Al(2)–O(3)		0.1803(1)	Al(1)–O(2)–C(11)	113.58(9)
Al(2)–O(4)		0.1900(1)	Al(1A)–O(2)–C(11)	140.73(9)
Al(2)–N(2)		0.2003(2)	Al(1)–N(1)–C(4)	126.59(10)
Al(2)–C(33)		0.1970(2)	Al(1)–N(1)–C(6)	108.76(9)
				108.21(11)

N-aryloxo functionalized β -ketoiminate rare earth metal derivatives [11], and might be caused by the lack of a substituent at the *ortho* position of the arene ring.

In complex **1**, each aluminum atom is five-coordinate with two oxygen atoms and one nitrogen atom from one β -ketoiminate ligand, one carbon atom from an ethyl group, and one oxygen atom from a second β -ketoiminate ligand. The coordination geometry around the aluminum center can be described as a distorted trigonal bipyramid, in which O(1), O(2) and C(13) are considered to occupy the equatorial plane, and O(2A) and N(1) to occupy the apical positions. Compared with a related amine-bridged bis(phenolate) aluminum methyl complex [15], the bridging Al–O(Ar) bond lengths are longer (0.1891(1) and 0.1897(1) nm *versus* 0.17516(15) and 0.17573(14) nm) and the Al–C and Al–N bond lengths are similar. The terminal Al–O(alkoxo) bond length of 0.1802(1) nm is comparable with those found in dimeric β -ketoiminate aluminum chlorides [16].

Each molecule of complex **2** has approximate C_2 symmetry (rotation axis perpendicular to the $Al_2(\mu-O)_2$ plane). The overall molecular structure is fairly similar to that of complex **1**, which also possesses a $Al_2(\mu-O)_2$ core with bridging phenoxo groups. The bond lengths and angles about the aluminum centers in complex **2** are consistent with the corresponding values in complex **1**.

The synthesis and characterization of luminescent aluminum-based coordination complexes has received considerable attention because of their wide range of potential applications. For example, aluminum tris(8-hydroxyquinolate) (Alq_3) and related derivatives exhibit excellent luminescent properties [17–19]. The emission wavelengths of aluminum complexes can be tuned easily by simple modification of the ligands or the coordination environments around the metal centers [19]. Mu et al. [20] reported that aluminum β -diketiminato complexes are efficient fluorescent materials. However, there is no report on the luminescent properties of aluminum complexes containing β -ketoiminate ligands, even though these ligands are also conjugated systems. The photophysical properties of complexes **1** and **2** were measured, and the solution UV-Vis absorption and emission results are summarized in Figures 3 and 4, respectively. The two complexes exhibit absorption bands with similar shape because of the identical conjugation system. The bands at high energy (223, 236, 278 and 314 nm) arise from π - π^* transitions of the phenyl ring in the ligands and the band at low energy (*ca.* 370 nm) is attributed to a π - π^* transition of the whole conjugated skeleton bound to an Al center.

Complexes **1** and **2** exhibit deep blue fluorescence with emission maxima of 419 and 413 nm, respectively, while no emission was observed from the free ligands. The emission peak of complex **2** is slightly blue-shifted because of the increase in the size of the substituents at the meta-position

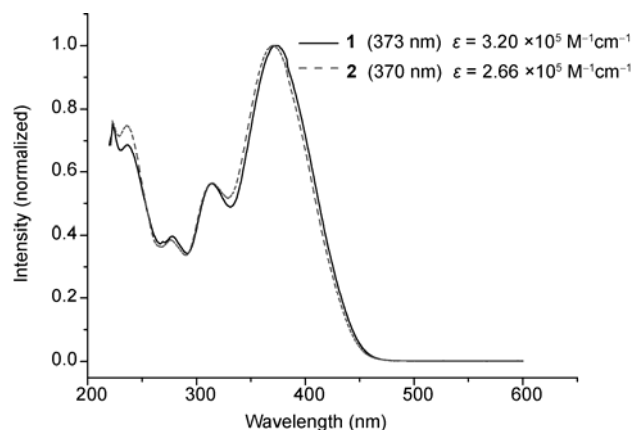


Figure 3 UV-Vis absorption spectra of complexes **1** and **2** in MeCN.

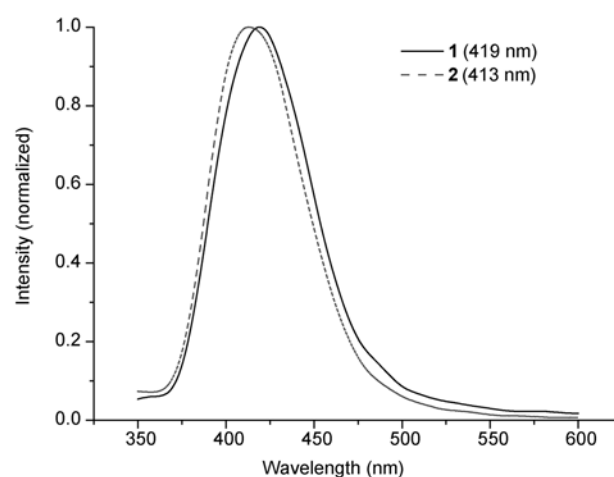


Figure 4 Emission spectra of complexes **1** and **2** in MeCN.

of the aryl ring. Compared with Alq_3 and Al complexes reported in the literature [17–20], the absorption bands and emission peaks of the two complexes appear remarkably blue-shifted because of the small size of the conjugated system.

3 Conclusion

Two new aluminum complexes containing dianionic *N*-aryloxo-functionalized β -ketoiminate ligands were synthesized via simple alkane elimination reactions, and their structural features were characterized by X-ray diffraction. The absorption bands and emission peaks of these aluminum complexes are significantly blue-shifted relative to those of Alq_3 because the conjugated system is smaller.

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