Synthesis, characterization and photoluminescence of aluminum \(N\)-aryloxo functionalized \(\beta\)-ketooiminate complexes

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The synthesis, characterization and luminescent properties of aluminum complexes containing a dianionic \(N\)-aryloxo functionalized \(\beta\)-ketooiminate ligand are presented. \(4-(2\text{-Hydroxy-5-R-phenyl})\text{imino-2-pentanone (R = Me, } L_1\text{; R = tert-butyl, } L_2)\) ligands reacted with \(\text{AlEt}_3\) in tetrahydrofuran to give the aluminum complexes \((L_1\text{AlEt})_2 (1)\) and \((L_2\text{AlEt})_2 (2)\) 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, \(\beta\)-ketooiminate ligand, synthesis, structure, photoluminescence

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Over the past few years, \(\beta\)-ketooiminate 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 \(\beta\)-ketooimine, a derivative of \(\beta\)-ketooiminate 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 functionalized \(\beta\)-ketooiminate 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 \(\varepsilon\)-caprolactone [11–13]. In a continuation of our study in this area, herein two aluminum complexes containing \(N\)-aryloxo functionalized \(\beta\)-ketooiminate 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-
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. 1H NMR (CDCl3) δ: 0.25 (q, 2H, J = 8.1 Hz, C(CH3)2), 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, CH3CH3=C==N), 5.22 (s, 1H, CH2), 6.90 (s), 764 (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 Kα radiation (λ = 0.07107 nm). The diffraction 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 |
|---------|---|---|
| Formula | C28H36Al2N2O4 | C34H48Al2N2O4 |
| Mw (g) | 518.55 | 602.70 |
| T (K) | 173(2) | 173(2) |
| Crystal system | triclinic | monoclinic |
| Space group | P1 | P2_1/n |
| a (nm) | 0.7953(1) | 0.9703(1) |
| b (nm) | 0.8470(1) | 2.3014(3) |
| c (nm) | 1.0248(2) | 1.5320(2) |
| α (deg) | 85.477(10) |  |
| β (deg) | 83.121(9) | 101.197(2) |
| γ (deg) | 75.450(8) |  |
| V (nm^3) | 0.6625(2) | 3.3560(6) |

| Complex | 1 | 2 |
|---------|---|---|
| Z | 1 | 4 |
| D(0) (g cm^−3) | 1.300 | 1.193 |
| μ (mm^−1) | 0.147 | 0.125 |
| F(000) | 276 | 1296 |
| θmax (deg) | 25.34 | 27.48 |
| Collected reflections | 6387 | 36714 |
| Unique reflections | 2411 | 7658 |
| Observed reflections [I>2.0σ(I)] | 2245 | 6740 |
| No. of variables | 168 | 392 |
| GOF | 1.041 | 1.112 |
| R [I>2.0σ(I)] | 0.0358 | 0.0546 |
| wR [I>2.0σ(I)] | 0.0944 | 0.1279 |
complexes. Reaction of $\mathrm{L}^1\mathrm{H}_2$ or $\mathrm{L}^2\mathrm{H}_2$ with $\mathrm{AlEt}_3$ in toluene in a 1:1 molar ratio, afforded the monoalkyl $\beta$-ketoiminate aluminum complexes 1 and 2 in good isolated yields, as shown in Scheme 1. These complexes were characterized by elemental analysis, and by $^1\mathrm{H}$ and $^{13}\mathrm{C}$ NMR and IR spectra. Elemental analysis revealed that complexes 1 and 2 consist of one $\beta$-ketoiminate ligand, one ethyl group and an aluminum atom. In the $^1\mathrm{H}$ NMR spectra of these complexes, resonances from the coordinating N–H and O–H groups disappeared and resonances from AlCH$_2$CH$_3$ 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 phenoxy oxygen atoms, which are similar to those observed in

![Scheme 1](image1.png)  
**Scheme 1** Synthesis of complexes 1 and 2.

| Bond lengths (nm) | 1        | 2        | Bond angles (%) | 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)        | 0.2041(1)| 0.1998(2)| O(1)–Al(1)–O(2A)| 74.32(5)| |
| Al(1)–C(13)       | 0.1970(2)|          | O(1)–Al(1)–N(1)| 91.81(5)| |
| Al(1)–C(31)       | 0.1967(2)|          | O(1)–Al(1)–N(1)| 91.81(5)| |
| Al(2)–O(2)        | 0.1891(1)|          | O(2)–Al(2)–O(3)| 80.43(5)| |
| Al(2)–O(3)        | 0.1803(1)|          | O(2)–Al(2)–O(4)| 80.43(5)| |
| Al(2)–O(4)        | 0.1900(1)|          | O(2)–Al(2)–O(3)| 79.93(6)| |
| Al(2)–N(2)        | 0.2003(2)|          | O(2)–Al(2)–(C11)| 105.62(6)| |
| Al(2)–C(33)       | 0.1970(2)|          | O(2)–Al(2)–C(11)| 105.62(6)| |

![Figure 1](image2.png)  
**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](image3.png)  
**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.
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 C2 symmetry (rotation axis perpendicular to the Al2(μ-O)2 plane). The overall molecular structure is fairly similar to that of complex 1, which also possesses a Al2(μ-O)2 core with bridging phenoxy 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-hydroxyquinolinate) (Alq3) 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-diketiminate 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 of the aryl ring. Compared with Alq3 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 Alq3 because the conjugated system is smaller.

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