Syntheses and Crystal Structures of Homoleptic Lanthanide Complexes \([C_6H_5COCHC(CH_3)N-(p-ClC_6H_4)]_3Ln(THF)_n\) (Ln = Yb, Y, Nd)

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ABSTRACT  Three homoleptic lanthanide complexes, \([C_6H_5COCHC(CH_3)N-(p-ClC_6H_4)]_3Ln(THF)_n\) (n = 0, Ln = Yb (1); n = 0, Ln = Y (2); n = 1, Ln = Nd (3)), were synthesized by amine elimination reaction of \(\text{Ln}[\text{N(SiMe}_3)_2]\) with 1-phenyl-3-N-(p-chlorophenylimino)-1-butanone. These complexes crystallize in triclinic, space group \(P\overline{1}\) with \(a = 9.805(3), b = 14.831(6), c = 16.075(6)\) Å, \(\alpha = 111.996(9), \beta = 91.570(7), \gamma = 93.744(6)\)°, \(V = 2159.4(13)\) Å\(^3\), \(Z = 2, D_c = 1.515\) g/cm\(^3\), \(F(000) = 986, \mu(\text{MoK}\alpha) = 2.396\) mm\(^{-1}\), \(R = 0.0360\) and \(wR = 0.0850\) for 9548 observed reflections with \(I > 2\sigma(I)\) for complex 1; \(a = 9.861(5), b = 14.852(9), c = 16.111(9)\) Å, \(\alpha = 112.362(13), \beta = 91.949(11), \gamma = 93.678(14)\)°, \(V = 2173(2)\) Å\(^3\), \(Z = 2, D_c = 1.377\) g/cm\(^3\), \(F(000) = 924, \mu(\text{MoK}\alpha) = 1.570\) mm\(^{-1}\), \(R = 0.0735\) and \(wR = 0.1389\) for 8015 observed reflections with \(I > 2\sigma(I)\) for complex 2; and \(a = 9.308(3), b = 15.357(3), c = 17.419(4)\) Å, \(\alpha = 66.493(13), \beta = 88.61(2), \gamma = 86.664(19)\)°, \(V = 2279.4(9)\) Å\(^3\), \(Z = 2, D_c = 1.499\) g/cm\(^3\), \(F(000) = 1046, \mu(\text{MoK}\alpha) = 1.364\) mm\(^{-1}\), \(R = 0.0843\) and \(wR = 0.2280\) for 8433 observed reflections with \(I > 2\sigma(I)\) for complex 3. Each central metal in complexes 1 and 2 is six-coordinated by three nitrogen and three oxygen atoms from three \(\beta\)-ketooiminate ligands to give a distorted octahedral geometry, while the central metal in 3 is seven-coordinated by three nitrogen and three oxygen atoms from three \(\beta\)-ketooiminate ligands and one oxygen atom from the solvated THF molecule to complete a distorted monocapped trigonal prism.

Keywords: organolanthanide, \(\beta\)-ketooiminate ligand, crystal structure

1 INTRODUCTION

The application of \(\beta\)-ketooiminate ligands in organolanthanide chemistry has attracted considerable attention because of their hard donor-atom frameworks, good coordination ability and easy preparation from inexpensive and readily available starting materials. Moreover, some \(\beta\)-ketooiminate lanthanide complexes can be used as potential precursors for metal-organic chemical vapor deposition (MOCVD) for the growth of thin films\(^{[1]}\) as homogeneous catalysts for the expoxidation of trans-chalcone\(^{[2]}\) and the ring-opening polymerization of \(\varepsilon\)-caprolactone and related cyclic esters\(^{[3]}\). However, most of the ancillary ligands used in these complexes are tetradentate Schiff bases \([R_1(\text{NC}=(\text{Me})\text{CHC}(R_2)=\text{O})_2]_2\)

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(R₁ = (CH₂)₂, (CH₃)₃, CH₂CMe₂CH₂; R₂ = Bu, Ph)³,⁴  
tridentate N-aryloxo-functionalized β-ketoiminate ligands³⁻⁴ and ether-functionalized β-ketoiminate ligands¹¹, and only one type of bidentate β-ketoiminate ligand [BuCOCH(Bu)N(n-Pr)] was reported to be utilized in ytterbium coordination chemistry⁵. In this article, we report the syntheses and crystal structures of three homoleptic lanthanide complexes containing a bidentate 1-phenyl-3-N-(p-chlorophenylimino)-1-butanonato ligand.

2 EXPERIMENTAL

2.1 General procedures

The organolanthanide complexes described in this paper are sensitive to air and moisture. Consequently, all of the manipulations described below were performed under an argon atmosphere, using the standard Schlenk techniques. The solvents were degassed and distilled from sodium benzophenone ketyl under argon prior to use. Ln[N(SiMe₃)₂]₃ [⁶] and 1-phenyl-3-N-(p-chlorophenylimino)-1-butanone [⁷] were prepared according to the literature methods. The elemental analyses were performed by direct combustion using a Carlo Erba-1110 instrument. IR spectra were recorded on a Nicolet-550 FTIR spectrometer as KBr pellets. ¹H NMR spectrum for the yttrium complex 2 was obtained on an INOVA-300 MHz apparatus.

2.2 Synthesis of

[C₆H₅COCHC(CH₃)N(p-ClC₆H₄)]₃Yb (1)

A solution of Yb[N(SiMe₃)₂]₃ (1.67 g, 2.1 mmol) in THF was injected quickly to a solution of the ligand C₆H₅COCHC(CH₃)N(p-ClC₆H₄) (1.02 g, 3.7 mmol) in THF, and the mixture was stirred overnight at room temperature. The solvent was removed completely under reduced pressure. The resultant yellow solids were crystallized with a mixture of toluene and n-hexane at room temperature to afford yellow crystals (Yield 0.44 g, 36%). Anal. Calcd. (%) for C₄₈H₃₉Cl₃N₃O₃Yb: C, 58.52; H, 3.99; N, 4.26. Found (%): C, 58.01; H, 3.99; N, 4.29. IR (KBr, cm⁻¹): 3524(w), 3055(w), 2963(w), 1866(w), 1577(s), 1492(s), 1403(s), 1300(m), 1192(m), 1091(m), 946(w), 847(m), 760(m), 704(m).

2.3 Synthesis of

[C₆H₅COCHC(CH₃)N(p-ClC₆H₄)]₃Y (2)

A solution of Y[N(SiMe₃)₂]₃ (1.50 g, 2.1 mmol) in n-hexane was injected quickly to a slurry of the ligand C₆H₅COCHC(CH₃)N(p-ClC₆H₄) (1.01 g, 3.7 mmol) in n-hexane, and then the mixture was stirred overnight at 50 °C to give a yellow suspension. Removing the n-hexane solution by centrifugation led to yellow solids. The solids were crystallized from a mixture of toluene and n-hexane at room temperature to afford yellow crystals after several days (Yield 0.42 g, 42%). Anal. Calcd. (%) for C₄₇H₃₇Cl₃N₃O₃Y: C, 63.98; H, 4.36; N, 4.66. Found (%): C, 63.33; H, 4.26; N, 4.51. IR (KBr, cm⁻¹): 3438(w), 3053(w), 1891(w), 1570(s), 1488(s), 1400(s), 1323(m), 1288(m), 1187(m), 1088(m), 1011(m), 943(w), 847(m), 763(m), 702(m). ¹H NMR(300 MHz, C₆D₆): δ = 7.61 (d, 6H, Ar), 7.15 (m, 9H, Ar), 6.95 (d, 6H, Ar), 6.48 (d, 6H, Ar), 5.65 (m, 3H, CH), 1.43 (m, 9H, CH₃).

2.4 Synthesis of [C₆H₅COCHC(CH₃)N(p-ClC₆H₄)]₃Nd(THF) (3)

The synthesis of complex 3 was carried out in a similar way as that described for complex 1, except that C₆H₅COCHC(CH₃)N(p-ClC₆H₄) (0.77 g, 2.8 mmol) and Nd[N(SiMe₃)₂]₃ (1.07 g, 1.4 mmol) were used. The blue crystals were obtained at room temperature (Yield 0.29 g, 32%). Anal. Calcd. (%) for C₵₂H₄₇Cl₃NdO₄: C, 60.72; H, 4.61; N, 4.09. Found (%): C, 59.67; H, 4.66; N, 4.17. IR (KBr, cm⁻¹): 3060(w), 2967(w), 2879(w), 1903(w), 1623(s), 1593(s), 1552(s), 1515(s), 1479(s), 1442(m), 1402(m), 1322(s), 1280(m), 1191(m), 1087(m), 1012(m), 846(m), 765(s), 711(m), 651(w), 508(w), 501(w).

2.5 Crystal structure determination

Single crystals with approximate dimensions of 0.80 mm × 0.30 mm × 0.15 mm for 1, 0.70 mm × 0.50 mm × 0.40 mm for 2 and 0.50 mm × 0.30 mm × 0.20 mm for 3 were selected and
RESULTS AND DISCUSSION

We have previously reported that the amine elimination reaction of \(N\)-aryloxal-functionalized \(\beta\)-ketoiminate ligands with \(Ln[N(SiMe_3)2]_3\) is a straightforward method for the synthesis of monoa-
mido lanthanide complexes\(^{3f-3h}\). Thus, this reaction was used to see if lanthanide amides stabilized by bidentate \(\beta\)-ketoiminate ligands could be synthesized.

Reactions of \(Ln[N(SiMe_3)2]_3\) \((Ln = Yb, Y, Nd)\) with 1-phenyl-3-\(N\)-(p-chlorophenylimino)-1-butanone \([C_6H_5COCHC(CH_3)NH(p-ClC_6H_4)]\) in a 1:2 molar ratio did not give the desired \(\beta\)-ketoiminato lanthanide amido complexes, but instead afforded the homoleptic \(\beta\)-ketoiminate lanthanide complexes \([C_6H_5COCHC(CH_3)N(p-ClC_6H_4)]Ln(THF)_n\) \((n = 0, Ln = Yb (1); n = 0, Ln = Y (2); n = 1, Ln = Nd (3))\), as shown in Scheme 1. Changing the reaction conditions (temperature, nature of solvent and ratios of ingredients) did not affect the outcome of these reactions, which is similar to the formation of homodinuclear lanthanide complexes bearing a salen-type Schiff-base ligand\(^{10}\). The infrared spectra show characteristic CO, CC and CN stretching bands at 1577, 1492 and 1403 cm\(^{-1}\) for complex 1, 1570, 1488 and 1400 cm\(^{-1}\) for complex 2 and 1593, 1515 and 1402 cm\(^{-1}\) for complex 3, which are similar to those previously reported\(^{5, 11}\). The compositions of complexes 1–3 were confirmed by elemental analysis and \(^1\)H NMR spectroscopy in the case of complex 2, and their definitive molecular structures were determined by single-crystal structure analysis. Complexes 1–3 are sensitive to air and moisture. The crystals turn to powder slowly when exposed to air. All complexes are soluble in THF and toluene, but insoluble in \(n\)-hexane.

Scheme 1

![Scheme 1](Image)
All crystals suitable for X-ray structure determination were obtained from concentrated toluene solutions. X-ray diffraction analyses displayed that complexes 1 and 2 are isostructural and have an unsolvated monomeric structure, while complex 3 has a THF-solvated monomeric structure. The ORTEP diagrams of complexes 1 and 3 are shown in Figs. 1 and 2, respectively. The selected bond distances and bond angles for complexes 1~3 are listed in Table 1. Each central metal in complexes 1 and 2 is ligated by three nitrogen and three oxygen atoms from three \( \beta \)-ketoiminate ligands in distorted octahedral coordination geometry. Four atoms, O(1), O(2), O(3) and N(3), can be considered to occupy the equatorial positions with the sum of the bond angles around the metal to be 359.92(11)\(^\circ\) for 1 and 359.87(15)\(^\circ\) for 2 and N(1) and N(2) occupy two sites of the axis (the angle N(1)–Ln(1)–N(2) is 163.97(11)\(^\circ\) for 1 and 163.19(14)\(^\circ\) for 2), as shown in Fig. 1. The bond lengths for the \( \beta \)-ketoiminate backbones O–C, C–C and C–N fall in the 1.274(6)~1.431(5) Å range, confirming \( \pi \)-electron delocalization present within the chelating ring. A similar trend has been observed in [Bu'COCHC(Bu')N(n-Pr)]\( _3 \)Yb\(^{[5]} \) and other non- lanthanide \( \beta \)-ketoiminato complexes\(^{[11b, 12]} \). The Yb–N distances of 2.395(3) and 2.384(3) Å and the Yb–O bond lengths of 2.142(3), 2.145(3) and 2.159(3) Å in complex 1 compare well with the corresponding bond lengths in [Bu'COCHC(Bu')N(n-Pr)]\( _3 \)Yb (ave 2.158(2) Å and 2.422(3) Å\(^{[5]} \) and \( \pi \)-aryloxo-functionalized \( \beta \)-ketoiminato ytterbium complexes (2.138~2.158 Å and 2.371~2.399 Å\(^{[3d-3h]} \), and these values are also consistent with those found in complex 2 when considering the difference in ionic radii between Yb and Y.

![Fig. 1. Crystal structure of complex 1. Complex 2 is isomorphous with complex 1](image1)

![Fig. 2. Crystal structure of complex 3](image2)
The neodymium atom in complex 3 is seven-coordinated by three nitrogen and three oxygen atoms from three \(\beta\)-ketoiminate ligands together with one oxygen atom from one THF molecule. The different structures between complex 3 and complexes 1~2 are likely related to small difference in the ionic radii, for the slightly larger Nd\(^{3+}\) presumably permits the incorporation of THF molecule into the metal coordination sphere. The coordination arrangement around the neodymium atom in complex 3 can be described as a distorted capped trigonal prismatic environment, in which O(1), O(4), N(1) and O(2), N(2), N(3) can be considered to constitute the two triangular faces of the prism with the dihedral angle of 2.99(23)\(^\circ\) and O(3) to occupy the capping position. The bite angles of the \(\beta\)-ketoiminate ligands with the neodymium atom vary from 69.7(3)\(^\circ\) to 72.0(3)\(^\circ\), with an average of 70.6(3)\(^\circ\), which are obviously smaller than those in complexes 1 (75.31(10), 76.61(11), 78.17(11)\(^\circ\)) and 2 (74.13(15), 74.57(15), 76.25(17)\(^\circ\)), reflecting the increase in steric congestion around the central metal atom due to coordination of THF molecule. The average Nd–N and Nd–O bond distances of 2.603(8) and 2.289(7) Å, respectively are comparable with the corresponding distances in complex 1 when the difference in ionic radii is considered and other homoleptic \(\beta\)-ketoiminate neodymium complexes\[1\].

In summary, three homoleptic lanthanide complexes \([C_{6}H_{5}COCHC(CH_{3})N(p-ClC_{6}H_{4})]_{3}Ln(THF)_{n}\) (\(n = 0, Ln = Yb (1); n = 0, Ln = Y (2); n = 1, Ln = Nd (3)) were synthesized and structurally characterized. X-ray diffraction analyses showed that complexes 1 and 2 are isostructural and have an unsolvated monomeric structure, while complex 3 has a THF-solvated monomeric structure.
REFERENCES


