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Lanthanum Complex with Mono- and Dideprotonated Diketoimine

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Abstract—The reaction of $LaCl_3$ with β-diketoimine potassium salt $K^{Dipp,Me}$Nacnac (KL) affords the molecular complex [LaLL'] with singly and doubly deprotonated diketoimine. The complex is characterized by single-crystal X-ray diffraction analysis (CIF file CCDC 1528658). The structure of [LaLL'] in solution is studied by 1D and 2D ^{1}H and ^{13}C NMR spectroscopy.

Keywords: lanthanum, rare-earth elements, diketoimines, X-ray diffraction analysis, NMR spectroscopy

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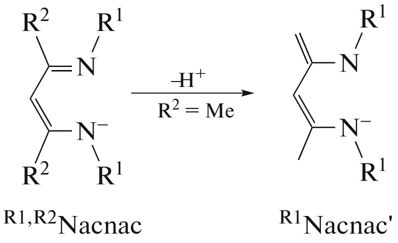
INTRODUCTION

β-Diketoiminates (^{R1,R2}Nacnac; Scheme 1) are especially important in the modern coordination chemistry. Owing to the variation of substituents, these ligands possess wide possibilities of modifying steric and electronic properties. They are also capable of stabilizing both high and low oxidation states of metal-complexing agents and have diverse coordination modes to the metal ion [1, 2]. For a long time, Nacnac were considered as inert ligands, but much experimental data on the transformations of Nacnac in the coordination sphere of the metal were accumulated to the present time [3]. In particular, proton detachment from the methyl group (R^2 = Me) can occur under the action of strong bases to form diamide ligand ^{R1}Nacnac' (Scheme 1) [4–7], and the process is reversible in some cases. Similar complexes are known for metals of different nature (*s*-, *p*-, *d*-, and *f*-), including several rare-earth elements. The reaction of $TmI_3(Thf)_{3.5}$ with KNacnac (3 equiv) gave heteroligand complex [Tm(^{Dipp,Me}Nacnac)(^{Dipp}Nacnac')] (Dipp = 2,6-$iPr_2C_6H_3$), which was characterized by X-ray diffraction analysis [8]. This work is devoted to the synthesis and characterization of its diamagnetic analog, lanthanum complex [LaLL'] (**I**) with the coordinated mono- (L^-) and dianion (L'^{2-}) of sterically hindered β-diketoimine $H^{Dipp,Me}$Nacnac (HL) (Scheme 2).



Scheme 1.

EXPERIMENTAL

All procedures on the synthesis, purification, and characterization of complex **I** were carried out in an inert atmosphere using a standard Schlenk technique. Solvents for the syntheses were dehydrated and degassed by reflux and distillation in an inert gas atmosphere using the corresponding drying agents [9]. The starting salt KL was synthesized according to a known procedure [10]. NMR spectra were recorded on a Bruker Avance III 500 spectrometer with the working frequency 500.03 MHz for ^{1}H and 125.73 MHz for ^{13}C. The signals of the $-CD_2-O$ group of the solvent were used as standards: δ = 3.58 ppm for residual protons in the ^{1}H NMR spectra (CHD group) and δ = 67.21 ppm for the ^{13}C NMR spectra [11]. Signal assignment was performed on the basis of homonuclear ^{1}H,^{1}H-COSY and heteronuclear ^{1}H,^{13}C-HMBC and ^{1}H,^{13}C-HSQC 2D correlations. The IR spectrum in a KBr pellet was recorded on a SCIMITAR FTS 2000 instrument.

Table 1. Crystallographic data and refinement parameters for structure **I**

Parameter	Value
Empirical formula	$C_{58}H_{81}N_4La$
Molecular weight	973.18
Crystal system, space group	Triclinic, $P\bar{1}$
Temperature, K	150
a, Å	11.3003(2)
b, Å	11.6567(2)
c, Å	22.4243(4)
α, deg	80.455(1)
β, deg	80.922(1)
γ, deg	65.152(1)
V, Å^3	2630.43(8)
Z	2
F(000)	1028
μ, mm^{-1}	0.851
Crystal size, mm	0.38 × 0.20 × 0.18
Range of data collection over θ, deg	0.93–26.37
Range of indices h, k, l	$-13 \le h \le 14$, $-13 \le k \le 14$, $-27 \le l \le 28$
Number of measured/ independent/ observed ($I > 2\sigma(I)$) reflections	24366/10725/10275
R_{int}	0.018
R_1, wR_2 ($I > 2\sigma(I)$)	0.0224, 0.0609
R_1, wR_2 (all reflections)	0.0237, 0.0616
GOOF	1.101
Number of refined parameters	586
Number of constraints	0
$\Delta\rho_{\max}/\Delta\rho_{\min}$, e Å^{-3}	0.68/–0.48

Synthesis of complex I. A mixture of solid $LaCl_3$ (144 mg, 0.587 mmol) and KL (800 mg, 1.751 mmol) was placed in a Schlenk flask, cooled to –196°C, and evacuated. Toluene (40 mL) was condensed to the flask. The temperature of the mixture was brought to room temperature, and the obtained suspension was refluxed for 48 h, evaporated to dryness, and extracted with hexane. The yellow extract was filtered through a glass frit (G4) from a white precipitate and evaporated, and the residue was recrystallized consequently from toluene and hexane. The yield was 400 mg (70%). Yellow crystals of compound **I** suitable for X-ray diffraction analysis were obtained by the slow evaporation of the solution in toluene.

For $C_{58}H_{81}LaN_4$

Anal. calcd., %:	C, 71.58;	H, 8.39;	N, 5.76.
Found, %:	C, 71.05;	H, 8.70;	N, 5.85.

IR (KBr), ν, cm^{-1}: 3061 m, 2961 s, 2925 s, 2865 s, 1623 m, 1550 s, 1521 m, 1457 m, 1430 m, 1399 s, 1363 s, 1314 s, 1248 s, 1170 s, 1106 s, 1054 m, 1040 m, 1019 m, 927 m, 902 m, 877 m, 835 m, 786 s, 754 s, 719 w, 625 s, 590 w.

^{1}H NMR (Thf-d_8), δ, ppm: 7.32–6.73 (m, 12H, Ar–H), 5.43 (s, 2H, =CH–), 3.47 (m, 1H, $C\underline{H}Me_2$), 3.13 (s, 1H, $=CH_2$), 3.11 (m, 1H, $C\underline{H}Me_2$), 2.94 (m, 1H, $C\underline{H}Me_2$), 2.76 (m, 1H, $C\underline{H}Me_2$), 2.75 (m, 1H, $C\underline{H}Me_2$), 2.67 (m, 1H, $C\underline{H}Me_2$), 2.65 (m, 1H, $C\underline{H}Me_2$), 2.48 (m, 1H, $C\underline{H}Me_2$), 2.47 (s, 1H, $=CH_2$), 1.94 (s, 3H, $NCCH_3$), 1.81 (s, 6H, $NCCH_3$), 1.67 (d, 3H, $CH\underline{Me_2}$), 1.48 (d, 3H, $CH\underline{Me_2}$), 1.29 (d, 3H, $CH\underline{Me_2}$), 1.22 (d, 3H, $CH\underline{Me_2}$), 1.17 (d, 3H, $CH\underline{Me_2}$), 1.15 (d, 3H, $CH\underline{Me_2}$), 1.09 (d, 3H, $CH\underline{Me_2}$), 1.02 (d, 3H, $CH\underline{Me_2}$), 1.01 (d, 3H, $CH\underline{Me_2}$), 0.99 (d, 3H, $CH\underline{Me_2}$), 0.91 (d, 3H, $CH\underline{Me_2}$), 0.88 (d, 3H, $CH\underline{Me_2}$), 0.64 (d, 3H, $CH\underline{Me_2}$), 0.39 (d, 3H, $CH\underline{Me_2}$), 0.39 (d, 3H, $CH\underline{Me_2}$), 0.23 (d, 3H, $CH\underline{Me_2}$).

^{13}C NMR (Thf-d_8), δ, ppm: 166.67, 152.33 (=C–N), 165.25, 149.27 (–C=N), 151.02, 148.31, 144.68, 143.84, 143.48, 142.34, 141.76, 141.47, 139.89, 139.76 ($C_{i,\,o}$), 126.31, 125.35, 125.19, 124.61, 124.57, 123.95, 123.83, 123.61, 123.32, 123.30, 123.05, 122.72 ($C_{m,\,p}$), 98.05, 91.38 (=CH–), 81.47 ($=CH_2$), 33.88, 33.88, 28.88, 28.73, 28.54, 28.54, 28.02, 27.32 ($C\underline{H}Me_2$), 26.81, 26.80, 24.27 ($NC\underline{C}H_3$), 27.33, 26.32, 26.05, 24.97, 24.67, 24.79, 24.79, 24.47, 24.22, 24.20, 24.09, 24.02, 23.44, 23.32, 23.25, 23.14 ($CH\underline{Me_2}$).

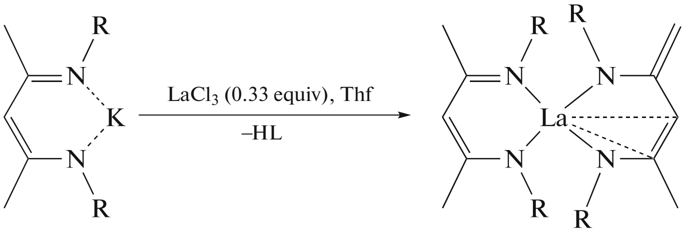
The NMR spectra of compound **I** contain signals of a minor (~5%) impurity of HL identified by a comparison with the authentic sample. ^{1}H NMR (Thf-d_8), δ, ppm: 12.07 (s, 1H, NH), 7.11–7.05 (m, 6H, Ar–H), 4.91 (s, 1H, =CH–), 3.15 (m, 4H, $C\underline{H}(CH_3)_2$), 1.70 (s, 6H, $NCCH_3$), 1.21 (d, $J_{\mathrm{H-H}}$ = 7 Hz, 12H, $CH(C\underline{H}_3)_2$), 1.12 (d, $J_{\mathrm{H-H}}$ = 7 Hz, 12H, $CH(C\underline{H}_3)_2$). ^{13}C NMR (Thf-d_8), δ, ppm: 161.7 (N=C), 142.9 (C_i), 141.5 (C_o), 125.9 (C_p), 123.6 (C_m), 94.3 (=CH–), 28.9 ($\underline{C}HMe_2$), 24.5, 23.4 ($CH(\underline{C}H_3)_2$), 21.0 ($NC\underline{C}H_3$).

X-ray diffraction analysis. Crystallographic and X-ray diffraction data were obtained on a Bruker Duo automated diffractometer (graphite monochromator, $\lambda(\mathrm{Mo}K_\alpha)$ = 0.71073 Å). An absorption correction was applied semiempirically (SADABS) [12]. The structure was solved by a direct method and refined by least squares in the anisotropic approximation (SHELXTL) [13]. Hydrogen atoms were localized geometrically and refined in the rigid body approximation. The crystallographic data and refinement parameters for the structure of compound **I** are presented in the Table 1.

The full tables of atomic coordinates, bond lengths, and bond angles were deposited with the Cambridge Crystallographic Data Centre (CIF file CCDC 1528658; deposit@ccdc.cam.ac.uk or http://www.ccdc.cam.ac.uk) and can be available from the authors.

RESULTS AND DISCUSSION

The reaction of β-diketoimine potassium salt (3 equiv) with $LaCl_3$ in tetrahydrofuran (Thf) followed by the recrystallization of the product from toluene affords a yellow crystalline product of the composition [LaLL'] (**I**). According to the X-ray diffraction data, the complex contains both singly and doubly deprotonated β-diketoimine (L and L', respectively) in the coordination sphere of La. During the reaction, L (1 equiv) is protonated and eliminated in the form of free β-diketoimine HL.



KL R = 2,6-$iPr_2C_6H_3$ LaLL' (**I**)

Scheme 2.

A molecule of complex **I** is a pseudotetrahedral complex (figure 1), and the dihedral angle between the planes La(1)N(1)N(2) and La(1)N(3)N(4) is 90.6°. The La–N distances vary within 2.3175(14)–2.5075(14) Å. As in complex [Al(^{Ph,Me}Nacnac)(^{Ph}Nacnac')] [14], the pair of shorter distances in complex **I** corresponds to diamide ligand L'. The metallocycle La(1)N(1)C(2)C(3)C(4)N(2) has a bath conformation typical of lanthanide β-diketoiminate complexes. The C(3) and La(1) atoms deviate from the plane of the N(1)C(2)C(4)N(2) central fragment by 0.179 and 1.413 Å, respectively. On the contrary, dianionic ligand L' consists of two nearly planar fragments C(30)C(31)N(3)C(32) and C(32)C(33)N(4)C(34), the dihedral angle between which is 45.5°. In addition to the La–N bonds, ligand L' also forms contacts of La with the C=C bond of the metallocycle (La(1)–C(33) 2.8998(17), La(1)–C(32) 2.9797(17) Å). These distances are comparable, for example, to the La–C distances in the complexes with sterically hindered cyclopentadienyl ligands ($La(\eta^5\text{-}C_5Me_5)_3$, 2.8732(2)–2.975(3) Å; $La(\eta^5\text{-}C_5Me_4Et)_3$, 2.857(3)–2.973(3)) Å; $La(\eta^5\text{-}C_5Me_4iPr)_3$, 2.874(3)–2.971(3) Å; $La(\eta^5\text{-}C_5Me_4SiMe_3)_3$, 2.890(2)–3.029(2) Å [15]) or to intermolecular contacts in the structure of polymer $[La(\eta^5\text{-}C_5H_5)_3]_\infty$ (3.032(6)–3.034(6) [16]).

An additional binding of the metal with the C=C fragment inside the metallocycle is also observed in the [TmLL'] complex [8]. The Tm–C distances (2.717(3) and 2.826(3) Å) are close to those in complex **I** taking into account the difference in ionic radii of La and Tm (0.16 Å) [17]. Similar contacts are observed in complexes $[LnL'(Thf)(N(SiMe_3)_2)]$ (Ln = Y, Yb, Gd, Sm) [18]. The short distance C(30)–C(31) (1.346(3) Å) confirms the formation of the C=C double bond due to deprotonation. In addition, the structure of complex **I** contains contacts between La and CH fragments of two isopropyl groups (La(1)–H(27) 2.8513, La(1)–H(56) 2.8026 Å).

The structure of compound **I** determined by X-ray diffraction analysis was confirmed by the ^1H and ^{13}C NMR data in solution. An analysis of the spectrum is impeded by many nonequivalent groups with close chemical shifts and the presence in the solution of a minor (about 5%) impurity of the protonated species HL. This species can be formed in the reaction of $LaCl_3$ and KL and can exist as an impurity even after the double recrystallization of the product. It is also possible that HL is formed by the hydrolysis of complex **I** with traces of water that exists in Thf-d_8. For this reason, the assignment of all groups in molecule **I** required to use heteronuclear 2D NMR spectroscopy. The $=CH_2$ fragment appears in the ^1H NMR spectrum as two singlets at 3.13 and 2.48 ppm, which are partially overlapped with the multiplet signals of the isopropyl groups. The $=CH_2$ group is observed in the ^{13}C NMR spectrum as a signal at 81.47 ppm. For similar complexes $[YL'(Thf)(N(SiMe_3)_2)]$ [18] and $[K(Thf)_4][LaL'_2]$ [19], the signals of the $C=CH_2$ group have close values of δ_C (98.0 and 77.0 ppm in C_6D_6 and Thf-d_8, respectively). The chemical shifts of the signals of diketoiminate ligand L are characteristic of ligands of this type.

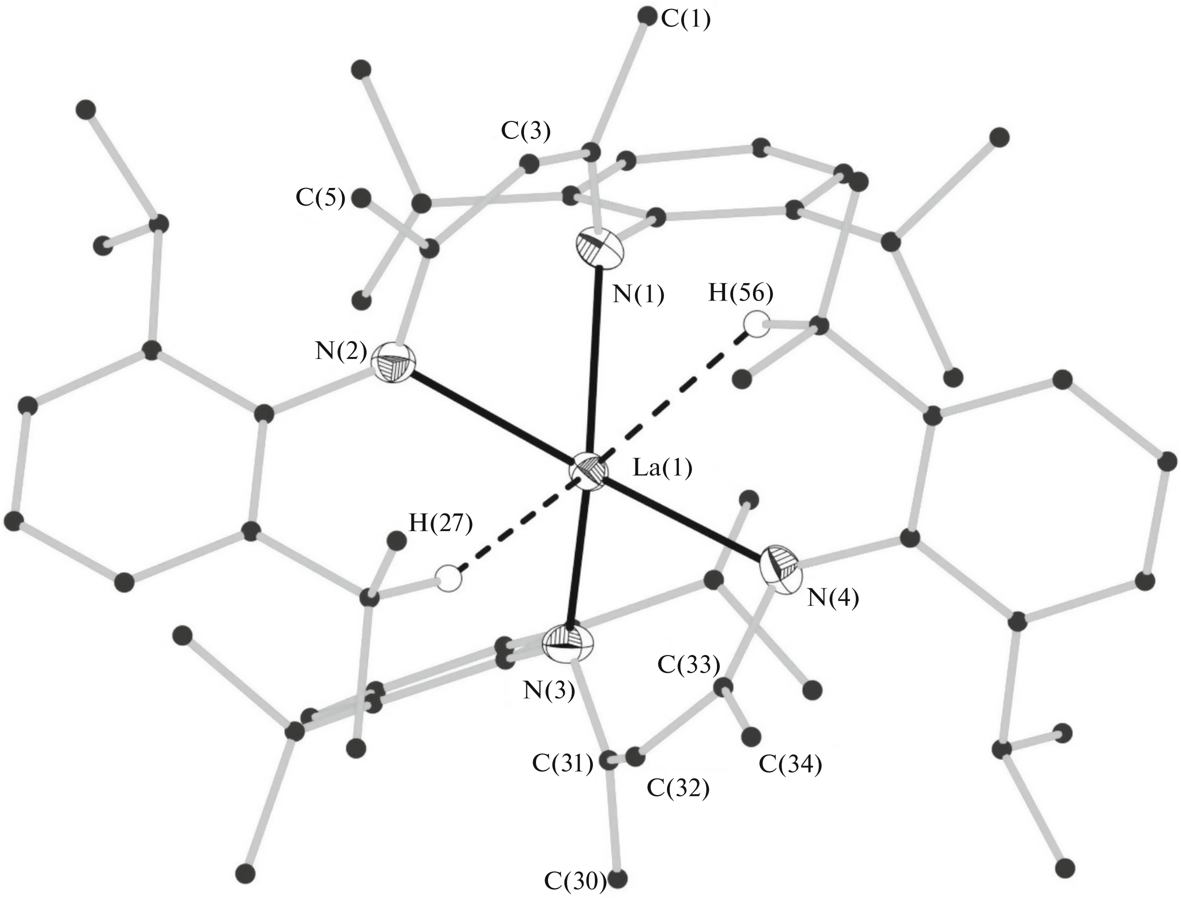


Fig. 1. Structure of complex **I**. Selected bond lengths and angles: La(1)–N(1) 2.4701(14), La(1)–N(2) 2.5075(14), La(1)–N(3) 2.3175(14), La(1)–N(4) 2.3750(14), La(1)–C(32) 2.9797(17), La(1)–C(33) 2.8998(17), La(1)–H(27) 2.8513, La(1)–H(56) 2.8026 Å and N(1)La(1)N(2) 78.97(5)°, N(3)La(1)N(4) 90.90(5)°. Hydrogen atoms (except H(27) and H(56)) are omitted.

To conclude, molecular complex [LaLL'] with singly and doubly deprotonated diketoimine was isolated and characterized by X-ray diffraction analysis and ^{1}H and ^{13}C NMR spectroscopy.

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