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Oxidation and coupling of β-diketiminate ligand in lanthanide complexes: Novel eight-nuclear lanthanide clusters with μ-, μ_3-Cl, and μ_4-O bridge†

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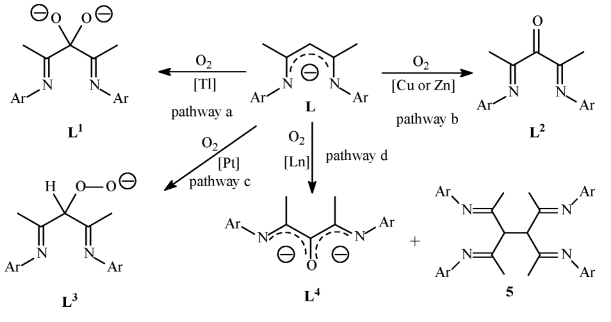
Two novel eight-nuclear lanthanide oxide and chloride clusters $Ln_8(\mu\text{-}\eta^2\text{-}L^4)_2(\mu_3\text{-}Cl)_4(\mu\text{-}Cl)_{10}(\mu_4\text{-}O)_3(THF)_8$ (Ln = Er(3), Dy(4); $L^4 = [OC\{(Me)CN\text{-}2,6\text{-}{}^iPrC_6H_3\}_2]^{2-}$) have been synthesized by the reaction of β-diketiminate rare-earth metal chlorides with oxygen, providing a new oxidation and coupling reaction of the β-diketiminate ligand.

β-diketiminate ligands continue to be a focus in organometallic and coordination chemistry,[1,2] and are capable of exhibiting a variety of coordination modes and a range of donor properties leading to compatibility with a wide range of metal ions from all parts of the periodic table.[1–3] Furthermore, ligands with bulky aromatic groups as an *N*-substituent can stabilise low valent and/or coordinatively unsaturated metal complexes.[4] Such a ligand backbone is usually stable enough for the synthesis of these complexes. A few ligand modifications based on the reactive centre carbon in the β-diketiminate backbone have been known.[5] However, little attention has been paid to the ligand-oxidation of the β-diketiminate metal complexes, only some examples of β-diketiminate ligand oxidation in p- and d-block metal complexes have been reported so far, and provided three oxidation routes to form a dianionic ligand L^1,[6a] a neutral ketone diimine L^2,[6b] and a peroxo intermediate L^3 (Scheme 1, pathway a–c)[6c] To our knowledge, no example of the β-diketiminate ligand oxidation in lanthanide complexes is reported.

It is well-known that organolanthanide complexes are sensitive to oxygen in most cases, and ligand oxygenation is one of the most common reactions during the manipulation of these complexes. However, little is known about the reaction details and the final products. It should be pointed out that the oxidation processes are usually complicated, and yield some mixed products with the difficulty in the purification and characterization. Emerging from the study of O_2 transport *via* metalloenzymes and other proteins, reactions of transition-metal complexes with oxygen have been extensively investigated.[7] However, the exploration on the reactivity of organolanthanides with oxygen are very limited.[8] In this contribution, we would like to report an unusual oxidation and coupling of β-diketiminate ligand in lanthanide complexes by controlling oxidation to construct two eight-nuclear lanthanide clusters $Ln_8(\mu\text{-}\eta^2\text{-}L^3)_2(\mu_3\text{-}Cl)_4(\mu\text{-}Cl)_{10}(\mu_4\text{-}O)_3(THF)_8$ ($L^4 = [OC\{(Me)CN\text{-}2,6\text{-}{}^iPrC_6H_3\}_2]^{2-}$; Ln = Er, Dy), in which the β-diketiminate ligand L is oxidized to form a dianionic ligand L^4 and a C–C coupling product **5** (Scheme 1, pathway d).



Scheme 1 Different oxidation modes of the β-diketiminate ligand in metal complexes.

Treatment of $LLnCl_2(THF)_2$ (Ln = Er(**1**), Dy(**2**); L = $CH\{(Me)C{=}N\text{-}2,6\text{-}{}^iPrC_6H_3\}_2$), prepared from the reaction of $LnCl_3$ with KL,[9] in THF at room temperature under aerobic conditions for one week,[10] after workup, produces the novel eight-nuclear lanthanide clusters $Ln_8(\mu\text{-}\eta^2\text{-}L^4)_2(\mu_3\text{-}Cl)_4(\mu\text{-}Cl)_{10}(\mu_4\text{-}O)_3(THF)_8$ in moderate yields (Ln = Er(**3**), 43%; Dy(**4**), 34% isolated yield). The β-diketiminate ligand coupling product **5**·0.5 hexane is obtained through further crystallization of the n-hexane solution in about 40% isolated yields (see supporting information). The solid-state structures of **3**–**5** were confirmed by X-ray single crystal diffraction.‡[10] Structural determination results of **3** and **4** show that a novel oxidative β-diketiminate ligand L^4 is formed and carries two metal ions Ln^{3+} in a bridging tridentate bonding-mode to construct an unprecedented eight-nuclear lanthanide oxide and chloride clusters (Fig. 1a). The ^{1}H NMR spectra of **5**·0.5C_6H_{14} shows a single peak of 13.38 ppm, attributable to the characteristic resonance of the N*H* bonds, and indicates that an imine-to-enamine isomerization occurs in solution.[11]

Fig. 1a shows that **3** and **4** are eight-nuclear clusters with four μ-Cl, ten μ_3-Cl and three μ_4-O atoms. Five oxygen atoms O2, O1, O3, O1A, and O2A form a pseudo molecular axis. The eight lanthanide atoms arranged in pairs, cross the axis (Fig. 1b). Such a distribution of the metal core is rather rare, and has never been described for lanthanide clusters, though lanthanide oxide clusters

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† Electronic supplementary information (ESI) available: Full procedures and characterization data of complexes **3**–**6**. CCDC reference numbers 819597–819600. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/c1dt11383f

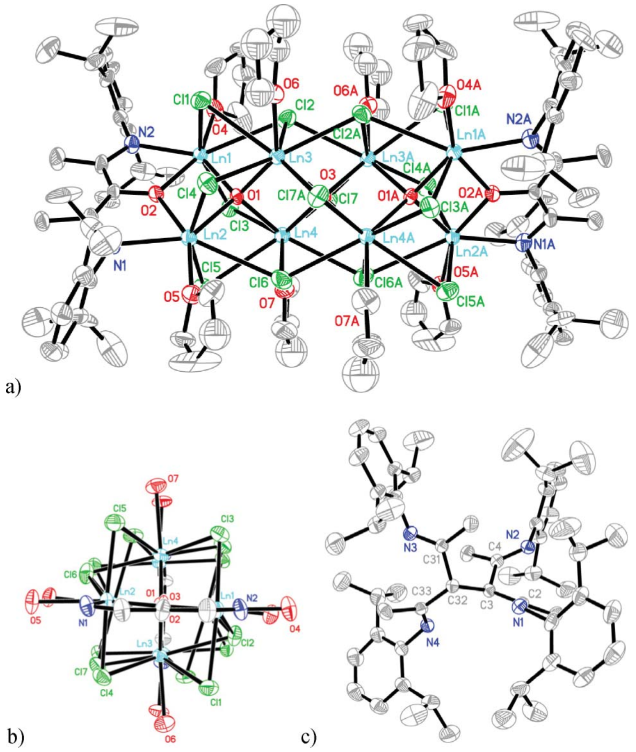


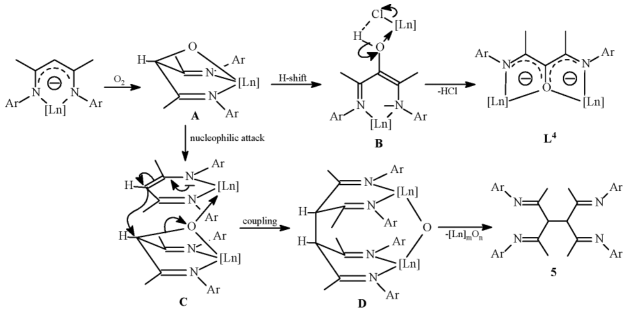
Fig. 1 Molecular structures (30% thermal ellipsoids): a) the clusters of **3** (Ln = Er) and **4** (Ln = Dy); b) view of the core of **3** and **4** from the orientation of the oxygen axis; c) **5**·0.5 hexane. Hydrogen atoms and *n*-hexane molecules in the lattices omitted for clarity. Selected bond lengths (Å) and angles (°): for **3**, Er1–N2 2.377(9), Er1–O2 2.152(7), Er2–N1 2.392(9), Er2–O2 2.189(7), N1–C2 1.323(14), N2–C4 1.376(14), C3–C2 1.353(15), C3–C4 1.401(15), C3–O2 1.417(13); N1–C2–C3 118.0(10), N1–C2–C1 119.2(10), C3–C2–C1 122.8(11), C2–C3–O2 114.4(9), C2–C3–C4 132.9(11), O2–C3–C4 112.7(9), N2–C4–C3 115.5(9), N2–C4–C5 121.4(10), C3–C4–C5 123.0(11). Symmetry transformations used to generate equivalent atoms: $-x + 1, -y, z$.

are common.[12] In **3**, each four adjacent erbium atoms form a tetrahedron, and an interstitial μ^4-oxygen atom contacts with the four apexes. Four μ^3-bridging and ten μ-bridging chlorine atoms symmetrically arrange around the eight-erbium cores. One exotic oxygen atom comes into contact with the central carbon of the *β*-diketiminate ligand and two erbium ions Er^{3+} to form two coplanar five-membered rings. The planarity in the C3N2OEr2 skeleton and nearly equivalent bond distances of the C–C, C–N, and C–O bonds indiacte the existence of a resonance stabilization in the C3N2OEr2 skeleton due to the completely delocalized π-electrons of the C═N double bond. Consistent with this observation, the Er1–N2, Er2–N1, Er1–O2, and Er2–O2 distances (2.377(9), 2.392(9), 2.152(7), and 2.189(7) Å) are intermediate between the values observed for a Er–N, Er–O σ-bond and a Er–N, Er–O donor bond.[13]

5 is not a new compound, but its solid-state structure has not been reported.[14] The crystal structure of **5** is shown in Fig. 1c, a newly-formed C–C bond connects with two β-diketiminate ligands in a crossing arrangement (62.0°). The bond lengths of the C–N and C–C bonds suggested that the π-electrons of the C═N double bonds are localized and proton migration from the central carbon of β-diketiminate frameworks to the nitrogen atom, *viz*. imine-to-enamine isomerization, does not occur in its solid-state.[11] This result is different from the observation in its ^{1}H NMR spectrum in solution. So we speculate that this isomerization might be reversible in solution.

Seen from Scheme 1, the oxidation modes of the anionic *β*-diketiminate ligand (L) depend strongly on the characters of the central metal ions. The neutral ketone diimine L^2 is formed through the oxidative degradation of the *β*-diketiminate ligand in Zn(II)- and Cu(II)-complexes,[6a] possibly undergoing a peroxo intermediate.[6c] During the oxidation of the *β*-diketiminate ligand in Tl(I)-complex, the electron transfer process occurs from metal to ligand through the metal oxidation (Tl(I) to Tl(III)).[6b] However, L^4 and **5** cannot be formed through the above processes. In order to explore the process for the formation of L^4 and **5** in our system, we also investigated the reaction of **1** with ketone diimine **6** (Ar = 2,6-^{i}PrC$_6$H$_3$), prepared by literature method.[6b] But we cannot obtain products **3** and **5**, only isolate the original materials **1** and **6**. This result may suggest that L^4 and **5** is not formed by the nucleophilic attack of **6** to L. On the other hand, reaction of $LLnCl_2(THF)_2$ with O_2 does not yield the intermediate **6**.

On the base of the aforementioned experimental results, a proposed process for the formation of the ligand L^4 and **5** is illustrated in Scheme 2, though the detailed mechanism needs further study. At first, the addition of a single oxygen atom to the central carbon of the *β*-diketiminate ligand framework affords intermediate **A**.[15] Then the oxygen atom is coordinated with another central metal to produce **B**, accompanied by hydrogen migration from the central carbon atom to the oxygen atom. The dianionic ligand L^4 is constructed through the HCl-elimination and ligand rearrangement. **C** is formed by the nucleophilic attack of one anionic *β*-diketiminate ligand from another metal with the center carbon of **A**. A C–C bond coupling reaction affords **D** with the cleavage of the C–O bond. Finally the coupling product **5** is dissociated from the cluster framework. Apparently, this *β*-diketiminate ligand oxidation and C–C bond coupling occuring in two metal centers is key to the formation of the ligand L^4 and **5**, and the later is different from the radical C–C bond coupling process in the β-diketiminate Ag(I)-complexes.[10]



Scheme 2 Plausible mechanism for the formation of the ligand L^4 and **5**.

In conclusion, an oxidation and coupling reaction of the β-diketiminate ligand (L) in lanthanide complexes *via* controlling oxidation has been achieved for the first time, and constructs two novel eight-nuclear lanthanide chloride and oxide clusters with the dianionic oxy-diketiminate ligand L^4.

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Notes and references

‡ *Crystallographic Data* for **3**: $C_{90}H_{144}C_{114}Er_8N_4O_{13}$, $T = 293(2)$ K, $M_w = 3324.47$, orthorhombic, space group *A*ba2, $a = 28.632(4)$, $b = 31.254(5)$, $c = 16.142(2)$ Å, $V = 14444(4)$ Å^3, $Z = 4$, $D_c = 1.529$ g cm^{-3}, μ(Mo-K$_\alpha$) = 4.894 mm^{-1}, F(000) = 6392, 12 510 reflections measured, 6617 unique ($R_{int} = 0.0405$) which was used in all calculations. Final $R_1 = 0.0325$ and w$R_2 = 0.0717$ (I > 2σ). CCDC 819597. For **4**: $C_{90}H_{144}C_{114}Dy_8N_4O_{13}$, $T = 293(2)$ K, $M_w = 3286.39$, orthorhombic, space group *A*ba2, $a = 28.668(6)$, $b = 31.282(6)$, $c = 16.199(3)$ Å, $V = 14527(5)$ Å^3, $Z = 4$, $D_c = 1.503$ g cm^{-3}, μ(Mo-K$_\alpha$) = 4.359 mm^{-1}, F(000) = 6328, 12 652 reflections measured, 6650 unique ($R_{int} = 0.0819$) which was used in all calculations. Final $R_1 = 0.0490$ and w$R_2 = 0.1078$ ($I > 2\sigma$). CCDC 819598. For **5**: $C_{61}H_{89}N_4$, $T = 293(2)$ K, $M_w = 878.36$, triclinic, space group $P\bar{1}$, $a = 12.937(4)$, $b = 13.424(4)$, $c = 17.464(6)$ Å, $\alpha = 86.122(5)$, $\beta = 75.906(5)$, $\gamma = 71.960(5)°$, $V = 2796.9(16)$ Å^3, $Z = 2$, $D_c = 1.043$ g cm^{-3}, μ(Mo-K$_\alpha$) = 0.060 mm^{-1}, F(000) = 966, 11 658 reflections measured, 9683 unique ($R_{int} = 0.0346$) which was used in all calculations. Final $R_1 = 0.0555$ and w$R_2 = 0.1372$ ($I > 2\sigma$). CCDC 819599. For **6**: $C_{29}H_{40}N_2O$, $T = 293(2)$ K, $M_w = 432.63$, triclinic, space group $P\bar{1}$, $a = 9.177(5)$, $b = 10.603(5)$, $c = 15.394(8)$ Å, $\alpha = 85.265(7)°$, $\beta = 73.552(7)°$, $\gamma = 66.988(6)°$, $V = 1321.5(11)$ Å^3, $Z = 2$, $D_c = 1.087$ g cm^{-3}, μ(Mo-K$_\alpha$) = 0.065 mm^{-1}, F(000) = 472, 5497 reflections measured, 4578 unique ($R_{int} = 0.0651$) which was used in all calculations. Final $R_1 = 0.0932$ and w$R_2 = 0.2381$ ($I > 2\sigma$). CCDC 819590.

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