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Communication

Oxidative Degradation of β-Diketiminate Ligand in Copper(II) and Zinc(II) Complexes

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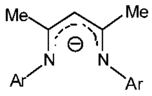
Copper(II) and zinc(II) complexes supported by a popular β-diketiminate ligand ($\mathbf{1}^-$, 2-mesitylamino-4-mesitylimino-2-pentene), $[Cu^{II}(\mathbf{1})(AcO)]$ and $[\{Zn^{II}(\mathbf{1})\}_2(\mu\text{-}MeO)(\mu\text{-}AcO)]$, have been demonstrated to undergo an oxidative degradation to give a ketone diimine derivative (**2**) under aerobic conditions. The crystal structures of the mononuclear copper(II) and dinuclear zinc(II) complexes of the β-diketiminate ligand as well as the copper(II) complex of the modified ligand have been determined by X-ray crystallographic analysis. Mechanism for the oxidative degradation reaction of the β-diketiminate ligand is also discussed.

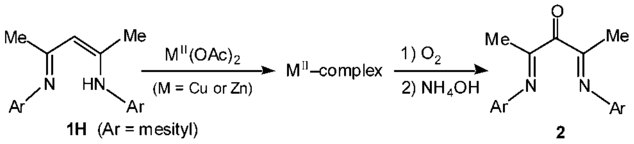
There is an increasing interest in the coordination chemistry of β-diketiminate derivatives carrying bulky aromatic groups as the *N*-substituent. They are monoanionic bidentate ligands allowing us to isolate and characterize coordinatively unsaturated mononuclear and/or dinuclear metal complexes of a wide variety of transition metal, main group element, and lanthanide ions.[1] Particular attention has recently been focused on the roles of such complexes as polymerization catalysts and novel organometallic compounds[1] as well as models for active sites of metalloenzymes.[2]

The majority of β-diketiminate ligands so far reported consist of the carbon framework shown in Chart 1, because they are commonly prepared by the reaction of acetylacetone and anilines.[3] Such a ligand backbone is stable enough for the synthesis and characterization of the wide variety of metal complexes,[1,2] but some ligand modification may occur during the catalytic reactions of β-diketiminate complexes. However, little attention has been paid to the ligand degradation of the β-diketiminate complexes.[4] We herein report that copper(II) and zinc(II) complexes of a popular β-diketiminate ligand ($\mathbf{1}^-$, Ar = mesityl) easily undergo an oxidative degradation to afford ketone diimine **2** (Scheme 1), providing further insight into the reactivity of β-diketiminate complexes.[5]

Chart 1



Scheme 1



Copper(II) and zinc(II) complexes employed in this study, $[Cu^{II}(\mathbf{1})(AcO)]$ and $[\{Zn^{II}(\mathbf{1})\}_2(\mu\text{-}MeO)(\mu\text{-}AcO)]$, have been prepared by treating the ligand precursor (**1H**) and copper(II) acetate or zinc(II) acetate in $CH_3OH-CH_2Cl_2$ at room temperature.[6,7] The crystal structures of them are shown in Figures 1 and 2, respectively.[8-10] The copper(II) complex exhibits a mononuclear metal center with a distorted square

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[1] Complete information about the metal complexes of β-diketiminate ligands has been cited in the following papers: (a) Cheng, M.; Moore, D. R.; Reczek, J. J.; Chamberlain, B. M.; Lobkovsky, E. B.; Coates, G. W. *J. Am. Chem. Soc.* **2001**, *123*, 8738–8749. (b) Stender, M.; Eichler, B. E.; Hardman, N. J.; Power, P. P. *Inorg. Chem.* **2001**, *40*, 2794–2799.

[2] (a) Holland, P. L.; Tolman, W. B. *J. Am. Chem. Soc.* **1999**, *121*, 7270–7271. (b) Holland, P. L.; Tolman, W. B. *J. Am. Chem. Soc.* **2000**, *122*, 6331–6332. (c) Dai, X.; Warren, T. H. *Chem. Commun.* **2001**, 1998–1999. (d) Smith, J. M.; Lachicotte, R. J.; Pittard, K. A.; Cundari, T. R.; Lukat-Rodgers, G.; Rodgers, K. R.; Holland, P. L. *J. Am. Chem. Soc.* **2001**, *123*, 9222–9223.

[3] Recently, β-diketiminate ligands having different substituent patterns of the carbon framework have also been developed: (a) Yokota, S.; Tachi, Y.; Nishiwaki, N.; Ariga, M.; Itoh, S. *Inorg. Chem.* **2001**, *40*, 5316–5317. (b) Jazdzewski, B. A.; Holland, P. L.; Pink, M.; Young, Jr., V. G.; Spencer, D. J. E.; Tolman, W. B. *Inorg. Chem.* **2001**, *40*, 6097–6107. (c) Budzelaar, P. H. M.; van Oort, A. B.; Orpen, A. G. *Eur. J. Inorg. Chem.* **1998**, 1485–1494.

[4] Derivatizations at the center carbon of β-diketiminate ligand backbone have been reported in ref 3b and in the following papers: (a) Radzewich, C. E.; Coles, M. P.; Jordan, R. F. *J. Am. Chem. Soc.* **1998**, *120*, 9384–9385. (b) Fekl, U.; Kaminsky, W.; Goldberg, K. I. *J. Am. Chem. Soc.* **2001**, *123*, 6423–6424.

[5] A similar ligand oxygenation reaction was reported in Co(II) complexes of tetraaza macrocyclic dianion ligand (dibenzotetramethyltetraaza-[14]annulene dianion): Weis, M. C.; Goedken, V. L. *J. Am. Chem. Soc.* **1976**, *98*, 3389–3392.

[6] Analytical data for $[Cu^{II}(\mathbf{1})(AcO)]$: IR (KBr) 1556, 1532, 1473, 1397 cm^{-1}; UV–vis (CH_3CN) $\lambda_{max} = 319$ ($\epsilon = 25500$), 342 (21800), 407 (1090), ~550 (sh) nm (230 M^{-1} cm^{-1}); ESR (9.219 GHz, −150 °C, in CH_2Cl_2) $g_1 = 2.186$, $A_1 = 175$ G, $g_2 = 2.053$, $A_2 = 11$ G, $g_3 = 1.971$, $A_3 = 12$ G (see Figure S1). Anal. Calcd for $C_{25}H_{32}N_2O_2Cu$: C, 65.84; H, 7.07; N, 6.14. Found: C, 65.86; H, 7.12; N, 6.11.

10.1021/ic0156238 CCC: $22.00

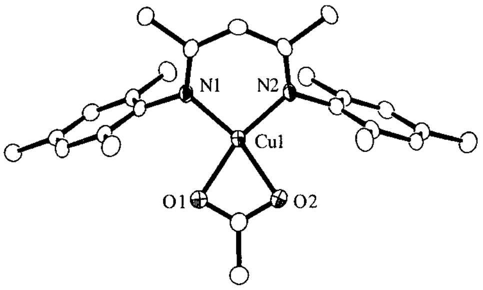

Figure 1. ORTEP drawing of [Cu^{II}(**1**)(AcO)] showing 50% probability thermal ellipsoid. Hydrogen atoms are omitted for clarity. Selected bond distances: Cu(1)−O(1) 2.027(2) Å, Cu(1)−O(2) 2.029(2) Å, Cu(1)−N(1) 1.913(3) Å, Cu(1)−N(2) 1.917(3) Å.

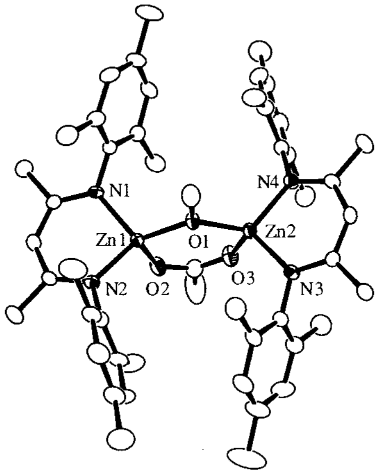

Figure 2. ORTEP drawing of [{Zn^{II}(**1**)}$_2$(μ-MeO)(μ-AcO)] showing 50% probability thermal ellipsoid. Hydrogen atoms are omitted for clarity. Selected bond distances: Zn(1)−O(1) 1.927(3) Å, Zn(1)−O(2) 2.001(3) Å, Zn(1)−N(1) 1.969(3) Å, Zn(1)−N(2) 1.962(3) Å, Zn(2)−O(1) 1.959(3) Å, Zn(2)−O(3) 1.972(3) Å, Zn(2)−N(3) 1.966(3) Å, Zn(2)−N(4) 1.970(3) Å.

planar structure in which both **1**$^-$ and acetate ion act as bidentate ligands (Figure 1). On the other hand, the zinc(II) complex exists as a dinuclear metal complex where methoxide and acetate ions bridge the two zinc ions (Figure 2). In this case, both metal ions exhibit four-coordinate tetrahedral geometry.

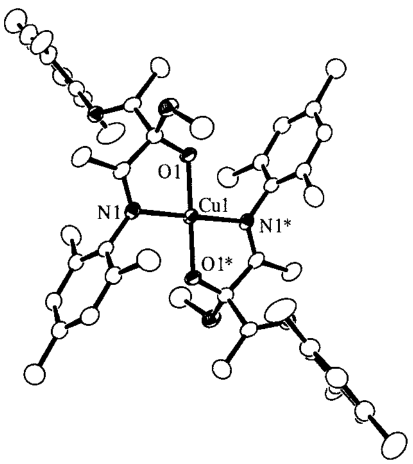

Figure 3. ORTEP drawing of complex **3** showing 50% probability thermal ellipsoid. Hydrogen atoms are omitted for clarity. Selected bond distances: Cu(1)−O(1) 1.875(2) Å, Cu(1)−N(1) 1.970(2) Å.

Treatment of the copper(II) complex in methanol at 50 °C under *aerobic* conditions for 12 h resulted in color change from brown to dark green, and from the final reaction mixture, ketone diimine **2** was obtained quantitatively after the workup treatment with aqueous ammonia.[11] When the reaction mixture was allowed to stand for a few days, single crystals of a copper(II) complex of the modified ligand (**3**) were obtained, for which X-ray crystallographic analysis has also been done as shown in Figure 3.[8,12,13] In this complex, compound **2** is converted into a hemiacetal derivative by the addition of solvent methanol to the carbonyl group and coordinates to copper(II) ion at its one of the imine functions and the hydroxide group of the hemiacetal function (Figure 3). The copper(II) center exhibits a square planar geometry with a N_2O_2 donor set which is provided from the two molecules of the modified ligand. Demetalation of this complex by treating it with aqueous ammonia generated ketone diimine **2**.

Compound **2** also formed in a similar treatment of the zinc(II) complex in methanol at 50 °C under aerobic conditions, demonstrating that the conversion of **1**$^-$ to **2** commonly occurs both in the redox-active (Cu^{II}) and redox-inactive (Zn^{II}) metal complexes. Such an oxidative degradation of **1**$^-$ did not proceed when the reaction was carried out under *anaerobic* conditions (under Ar). An isotope labeling experiment using $^{18}O_2$ instead of $^{16}O_2$ gave the ^{18}O-labeled product. These results unambiguously confirmed that the oxygen atom in **2** was originated from molecular oxygen.

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(7) Analytical data for [{Zn^{II}(**1**)}$_2$(μ-MeO)(μ-AcO)]: IR (KBr) 1625, 1588, 1546, 1523, 1456, 1400 cm^{-1}; UV−vis (CH_3CN) λ_{max} = 338 nm (ϵ = 37800 M^{-1} cm^{-1}); FAB-MS m/z = 887.5 ([{Zn^{II}(**1**)}$_2$(μ-MeO)(μ-AcO)] + H$^+$). Anal. Calcd for $C_{49}H_{64}N_4O_3Zn_2\cdot{}^1/_2H_2O$: C, 65.62; H, 7.31; N, 6.25. Found: C, 65.71; H, 7.24; N, 6.22.

(8) X-ray diffraction data were collected by a Rigaku RAXIS-RAPID imaging plate two-dimensional area detector using graphite-monochromated Mo Kα radiation (λ = 0.71070 Å) at T = 158 K. The crystal structure was solved by the direct methods and refined by the full-matrix least squares using SIR-92.

(9) Crystallographic data for [Cu^{II}(**1**)(AcO)]: triclinic, space group $P\bar{1}$ (No. 2), a = 6.8661(2) Å, b = 13.5471(2) Å, c = 13.6614(3) Å, α = 66.262(2)°, β = 77.410(6)°, γ = 86.357(5)°, V = 1134.83(6) Å^3, Z = 2, ρ_{calcd} = 1.335 g/cm^3, 2θ_{max} = 55.0°, R = 0.065 and R_w = 0.102 for 3563 independent reflection with $I > 3\sigma(I)$ and 304 parameters.

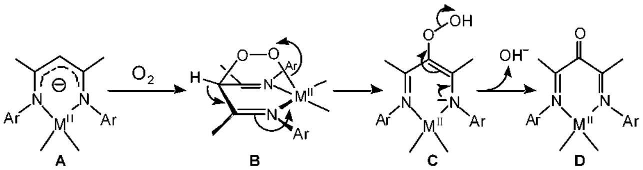
(10) Crystallographic data for [{Zn^{II}(**1**)}$_2$(μ-MeO)(μ-AcO)]: triclinic, space group $P\bar{1}$ (No. 2), a = 10.5615(8) Å, b = 13.586(1) Å, c = 18.431(1) Å, α = 75.287(5)°, β = 74.153(2)°, γ = 67.332(2)°, V = 2314.4(3) Å^3, Z = 2, ρ_{calcd} = 1.274 g/cm^3, 2θ_{max} = 54.8°, R = 0.048 and R_w = 0.067 for 6796 independent reflection with $I > 2\sigma(I)$ and 588 parameters.

(11) Analytical data for **2**: IR (KBr) 1704, (C═O), 1667 cm^{-1} (C═N); UV−vis (CH_2Cl_2) λ_{max} = 270 (ϵ = 2300), ~380 (sh) nm (470 M^{-1} cm^{-1}); ^{1}H NMR (300 MHz, $CDCl_3$): δ 1.94 (s, 6H, CH_3), 2.00 (s, 12H, CH_3), 2.27 (s, 6H, CH_3), 6.87 (s, 4H, aromatic H of mesityl); ^{13}C NMR ($CDCl_3$); 16.5 (CH_3), 17.7 (CH_3), 20.6 (CH_3), 124.8, 128.6, 133.0, 144.5 (aromatic carbons), 168.3 (imine carbon), 193.6 ppm (ketone carbon); HRMS (FAB, pos) m/z 349.2302, calcd for [$C_{23}H_{28}N_2O$ + H$^+$] 349.2280.

(12) Analytical data for **3**: IR (KBr) 1553, 1533, 1455, 1405 cm^{-1}; UV−vis (CH_2Cl_2) λ_{max} = 342 (ϵ = 35000), 421 (2600) and ~530 (sh) nm (360 M^{-1} cm^{-1}); ESR (9.221 GHz, −150 °C, in toluene) g_1 = 2.194, A_1 = 174 G, g_2= 2.045, A_2 = 12 G, g_3= 1.971, A_3 = 14 G (see Figure S2); FAB-MS m/z = 411.3 ([Cu(**2**)]), 884.5 ([Cu$_2$(**2**·OMe)$_2$]). Anal. Calcd for $C_{48}H_{62}N_4O_4Cu\cdot{}^1/_2H_2O$: C, 69.33; H, 7.64; N, 6.74. Found: C, 69.57; H, 7.68; N, 6.76.

(13) Crystallographic data for **3**: monoclinic, space group $P2_1/c$ (No. 14), a = 10.8954(3) Å, b = 13.4599(6) Å, c = 15.5743(5) Å, β = 86.977(1)°, V = 2280.8(1) Å^3, Z = 2, ρ_{calcd} = 1.198 g/cm^3, 2θ_{max} = 54.9°, R = 0.048 and R_w = 0.055 for 4319 independent reflection with $I > 0.5\sigma(I)$ and 291 parameters.

Scheme 2



Although further study remains to disclose the mechanistic details for the formation of **2** from the copper(II) and zinc(II) complexes, one can assume a reaction pathway illustrated in Scheme 2. Addition of dioxygen to the center carbon of the ligand framework of **A** affords intermediate **B**,[5] which may easily rearrange to hydroperoxo intermediate **C**. Heterolytic cleavage of the O−O bond in **C** will produce product **D**. The first step (**A** to **B**) may involve electron transfer from the anionic ligand $\mathbf{1}^-$ to O_2, generating a ligand radical $\mathbf{1}^\bullet$ and superoxide ion O_2^-; the recombination of them produces the intermediate **B**. In the copper case, such an electron transfer from $\mathbf{1}^-$ to O_2 could occur through the redox active metal center. Namely, inner-sphere electron transfer from $\mathbf{1}^-$ to Cu(II) in the complex will produce $\mathbf{1}^\bullet$ and Cu(I), and then O_2 is reductively activated at the reduced metal center. On the other hand, Fukuzumi et al. have recently demonstrated that the electron transfer reduction of O_2 to superoxide ion is significantly enhanced by *redox-inactive* Lewis acids such as Li^+, Mg^{2+}, Ca^{2+}, Sc^{3+}, and so forth. This has been ascribed to the coordinative interaction between the Lewis acid and generated O_2^-.[14] Such a mechanism could be adopted to the reaction of redox-inactive zinc complex.

In conclusion, the β-diketiminate ligand in Cu(II)- and Zn(II)-complexes has been shown to undergo the oxidative degradation quite easily to afford the ketone diimine derivative. Such a ligand modification could occur during the catalytic reactions of β-diketiminate complexes.

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Supporting Information Available: Experimental details including synthesis and characterization of the products. ESR spectra of copper(II) complexes (Figures S1, S2). X-ray structural determination and details of the crystallographic data (CIF). This material is available free of charge via the Internet at http://pubs.acs.org.

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(14) Fukuzumi, S.; Ohkubo, K. *Chem.*−*Eur. J.* **2000**, *6*, 4532−4535.