A New β-Diketiminate Ligand Carrying a Functional Group on the Carbon Framework. Synthesis and Characterization of a Linear Polymeric Copper(I) Complex

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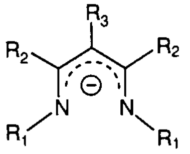
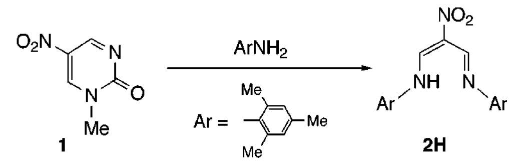
β-Diketiminate derivatives function as monoanionic bidentate ligands, which have been applied for synthesis of a wide variety of transition metal,[1] main group element,[2] and lanthanide complexes.[3] Particular attention has recently been focused on the roles of such complexes as polymerization catalysts,[1a,f,g,k,2j] novel organometallic compounds,[1d,2a,b,d,g,h] and models for active sites of metalloenzymes.[1j,m] In most cases, sterically encumbered β-diketiminate derivatives (R_1 = ortho-substituted aryl group in Chart 1) have been employed to make the complexes as mononuclear and coordinatively unsaturated. However, variation of substituents on the carbon framework of the ligand is rather limited (mostly R_2 = Me and R_3 = H).[1−3] Thus, modification of the ligand skeleton will provide further opportunity to add more function to the metal complexes and to modulate their coordination chemistry.

We report herein a new β-diketiminate ligand ($\mathbf{2}^-$) carrying a nitro group on the carbon framework (R_1 = mesityl; R_2 = H; R_3 = NO_2).[4] Complexation of the ligand with cuprous ion resulted in formation of a linear polymeric copper(I) complex, demonstrating a possible application of the β-diketiminate ligand to the supramolecular chemistry.

Chart 1



Scheme 1



Nishiwaki and co-workers have demonstrated that aminolysis of 1-methyl-5-nitropyrimidin-2(1*H*)-one (**1**) affords a series of diimine derivatives of nitromalonaldehyde.[5] This reaction was applied for the preparation of ligand precursor **2H**. Thus, the reaction of **1** (3.2 mmol) and 2,4,6-trimethylaniline (6.9 mmol) in refluxing methanol (40 mL) for 4 days gave **2H**, which was isolated by flash column chromatography in 27% (Scheme 1).[6] Structural refinement of **2H** in the X-ray analysis (Figure 1) has indicated that the compound exists as a 3-imino-2-nitropropenylamine derivative as shown in Scheme 1.[7] Thus, the bond distances of C(1)−C(3) (1.454(3) Å) and C(2)−N(1) (1.314(3) Å) are longer than those of C(1)−C(2) (1.416(3) Å) and C(3)−N(2) (1.286(3) Å), respectively.

Treatment of **2H** (0.1 mmol) with an equimolar amount of $[Cu^I(MeCN)_4]PF_6$ in the presence of Et_3N (0.3 mmol) in dry methanol (5 mL) under anaerobic conditions resulted in the formation of dark purple microcrystals of complex **3** in 70%

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(6) Analytical data for **2H**: IR (KBr) 1637 (C═N), 1573, 1311, 1289, 1270 cm^{-1} (NO_2); ^1H NMR ($CDCl_3$, 300 MHz) δ 2.22 (s, 12H, CH_3), 2.29 (s, 6H, CH_3), 6.93 (s, 4H, aromatic H of Ar group), 8.75 (s, 2H, C*H*), 12.77 (br, 1H, N*H*); HRMS *m*/*z* 351.1957, calcd for $C_{21}H_{25}N_3O_2$ 351.1947. Anal. Calcd for $C_{21}H_{25}N_3O_2$: C, 71.77; H, 7.17; N, 11.96. Found: C, 71.79; H, 7.21; N, 11.75.

(7) Crystal data for **2H**: $M = 351.45$, $C_{21}H_{25}N_3O_2$, crystal dimensions 0.30 × 0.30 × 0.30 mm, triclinic, space group $P\bar{1}$ (No. 2), $a = 8.954\ (2)$ Å, $b = 14.536(4)$ Å, $c = 8.220(2)$ Å, $\alpha = 105.55(1)°$, $\beta = 109.61(1)°$, $\gamma = 77.70(2)°$, $V = 961.9(5)$ Å^3, $Z = 2$, $\rho_{calcd} = 1.213$ g/cm^3, $2\theta_{max} = 55.0°$, Mo Kα = radiation ($\lambda = 0.71069$ Å), $T = 158$ K. Data were collected using the Rigaku RAXIS rapid imaging plate system, and the structure was solved via direct methods. Full-matrix least-squares refinement on *F* using SIR92 converged with final $R = 0.080$ and $R_w = 0.103$ for 5226 independent reflection with $I > 1\sigma(I)$ and 3859 parameters.

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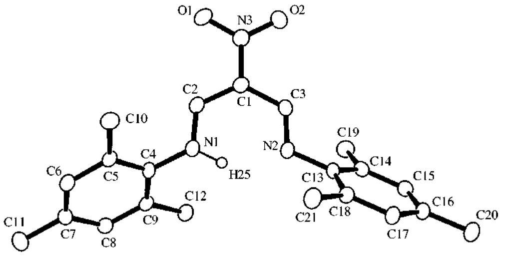

Figure 1. ORTEP drawing of **2H** showing 50% probability thermal ellipsoids. Hydrogen atoms except H(25) are omitted for clarity. Selected bond distances (Å) and angles of least-squares planes (deg): O(1)−N(3) 1.261(2), O(2)−N(3) 1.257(2), N(1)−C(2) 1.314(3), N(1)−C(4) 1.444(3), N(2)−C(3) 1.286(3), N(2)−C(13) 1.451(3), N(3)−C(1) 1.424(3), C(1)−C(2) 1.416(3), C(1)−C(3) 1.454(3); plane 1 and plane 2, 49.10°; plane 1 and plane 3, 65.24°; plane 2 and plane 3, 100.64°. (Plane 1: N(1), N(2), C(1), C(2), C(3). Plane 2: C(4), C(5), C(6), C(7), C(8), C(9). Plane 3: C(13), C(14), C(15), C(16), C(17), C(18)).

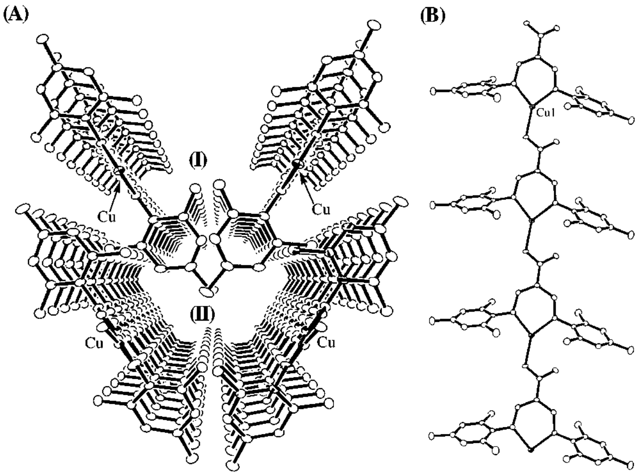

Figure 2. A top view of the crystal packing of **3** (A) and a side view of the linear chain of **3** (B) with 50% probability thermal ellipsoids. Hydrogen atoms are omitted for clarity. Selected bond distances (Å) and angles of least squares planes (deg): Cu(1)−N(1) 1.992(2), Cu(1)−N(2) 1.991(2), Cu(1)−O(1)′ 1.986(1), O(1)−N(3) 1.290(2), O(2)−N(3) 1.237(2), N(1)−C(2) 1.295(2), N(1)−C(4) 1.438(2), N(2)−C(3) 1.291(2), N(2)−C(13) 1.445(2), N(3)−C(1) 1.393(2), C(1)−C(2) 1.430(3), C(1)−C(3) 1.435(3); plane 1 and plane 2, 68.0; plane 1 and plane 3, 67.0. (Plane 1: N(1), N(2), C(3), C(1), C(2). Plane 2: C(4), C(5), C(6), C(7), C(8), C(9). Plane 3: C(13), C(14), C(15), C(16), C(17), C(18)). Atom numbering of the ligand is the same as that indicated in Figure 1.

yield.[8] When the complexation was carried out slowly at an interface between a CH_3OH solution containing $[Cu^I(MeCN)_4]PF_6$ and a CH_2Cl_2 solution containing **2H**, single crystals of **3** were obtained, for which X-ray crystallographic analysis has been performed (Figure 2).[9,10] The neutral copper(I) unit, $[Cu^I(\mathbf{2}^-)]$, associates each other to form a head-to-tail (Cu-to-NO_2) linear chain, where the cuprous ion adopts a trigonal planar structure and the nitro group acts as a monodentate ligand to link the mononuclear copper(I) units (Figure 2B). The dark purple color of **3** in the solid state may be due to the extended $d-p_\pi$ interaction through the $Cu-NO_2$ linkage.[11] In fact, the color turns to pale yellow, when the polymer complex is converted into a monomeric copper(I) complex such as $[Cu^I(\mathbf{2}^-)(PPh_3)]$.[12]

There seems to be no specific interaction between the neighboring linear chains other than van der Waals interaction between the aryl substituents; the mesityl groups on the polymer chain are arranged alternately with the mesityl groups of other neighboring polymer chains.[13] As a result of this arrangement, there is a long V-shaped column along with the polymer chain. Direction of the head-to-tail vector is the same in one column (indicated as (I) or (II) in Figure 2A), while that in the neighboring column is opposite; from the bottom to the top in column (I) and from the top to the bottom in column (II). Although a great number of self-assembled supramolecules based on copper(I) and silver(I) complexes are known,[14] the completely linear polymer complex containing a 3-coordinate planar copper(I) complex is rare.

In summary, a new β-diketiminate ligand containing a nitro group on the carbon framework has been developed, complexation of which with cuprous ion provided a novel linear polymer copper(I) complex with an extended $d-p_\pi$ system. Further studies are now in progress to evaluate the electronic communication between the monomer units in $[Cu^I(\mathbf{2}^-)]_n$.

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Supporting Information Available: Experimental details including synthetic procedures of the ligand and the copper complexes and X-ray structural determination. Details of the crystallographic data supplied as a CIF file. This material is available free of charge via the Internet at http://pubs.acs.org.

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(8) In the reaction of cuprous ion and other nitro-diketiminate ligands (L) carrying different types of *N*-substituents such as R_1 = phenyl, 3,5-di-*tert*-butylphenyl, or *o*-methoxyphenyl, disproportionation reaction mainly occurred to give $[Cu^{II}(L)_2]$ and Cu^0, but no linear copper(I)−polymer complex was obtained. A 2,6-disubstituted aromatic group such as mesityl in **2H** may prevent the formation of the copper(II) complex of type $[Cu^{II}(L)_2]$ and stabilize the copper(I) state in the polymer complex. The copper(I) complex of a diketiminate ligand without the nitro group on the carbon framework (R_1 = mesityl, R_2 = methyl, R_3 = H) is significantly air-sensitive, leading to an oxidative ligand degradation. This clearly indicates that the electron-withdrawing nature of the nitro group is also important for stabilization of the copper(I) complex.

(9) Analytical data for **3**: IR (KBr): 1598 (C=N), 1542, 1297, 1262 cm^{-1} (NO_2). FAB-MS: *m/z* = 414 ($[Cu(\mathbf{2}^-)]$), 828 ($[Cu(\mathbf{2}^-)]_2$). Anal. Calcd for $C_{21}H_{24}N_3O_2Cu$: C, 60.93; H, 5.84; N, 10.15. Found: C, 61.02; H, 5.85; N, 10.18.

(10) Crystal data for **3**: $M = 413.99$, $C_{21}H_{24}N_3O_2Cu$, crystal dimensions 0.30 × 0.30 × 0.30 mm, monoclinic, space group $P2_1/a$ (No. 14), a = 7.2949(2) Å, b = 15.7167(5) Å, c = 16.6267(4) Å, β = 100.0625(7)°, V = 1876.96(8) Å^3, $Z = 4$, ρ_{calcd} = 1.465 g/cm^3, $2\theta_{max}$ = 55.0°, Mo Kα = radiation (λ = 0.71069 Å), T = 93 K. Data were collected using the Rigaku RAXIS rapid imaging plate system, and the structure was solved via direct methods. Full-matrix least-squares refinement on F using SIR92 converged with final R = 0.031 and R_w = 0.046 for 8476 independent reflection with $I > 3\sigma(I)$ and 3367 parameters.

(11) The solid sample of **3** exhibited a very broad absorption band in the visible region (400−650 nm) in the reflectance UV−vis spectrum.

(12) $[Cu^I(\mathbf{2}^-)(PPh_3)]$ was obtained by treating the polymer complex **3** with an equimolar amount of PPh_3 based on the copper ion in CH_2Cl_2. λ_{max} = 365 nm (ϵ = 23500 M^{-1} cm^{-1}). ^1H NMR (600 MHz, $CDCl_3$): δ 2.01 (s, 12H, CH_3), 2.27 (s, 6H, CH_3), 6.74 (s, 4H, aromatic H of Ar group), 6.79 (dd, J = 8.0, 10.7 Hz, 6H, H_o), 7.11 (dd, J = 7.0, 7.0 Hz, 6H, H_m), 7.30 (t, J = 7.1 Hz, 3H, H_p), 8.89 (s, 2H, CH). HRMS (FAB, positive): *m/z* 676.2170 ($M^+ + 1$), calcd for $C_{39}H_{40}N_3O_2PCu$ 676.2154. Anal. Calcd for $C_{39}H_{39}N_3O_2PCu$: C, 69.27; H, 5.81; N, 6.21. Found: C, 69.24; H, 5.82; N, 6.03.

(13) The free ligand **2H** itself adopts a rather similar chain structure in the crystal, although the distance between the neighboring ligands [C(1)−C(1)′ = 8.22 Å] is significantly longer than that in the polymer complex (7.29 Å). The ligand skeleton itself may promote formation of this type of structure even in the absence of intermolecular interactions.

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