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The First β-Diketiminate–Ag(I) Complexes. Macrocyclic Dinuclear and Tetranuclear Ag(I)-Complexes and Linear Coordination Polymer Ag(I)-Complex

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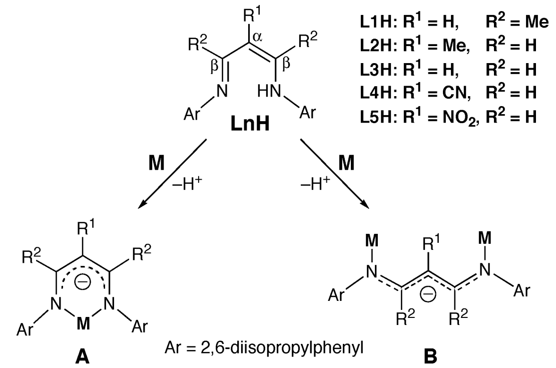
Reactions of Ag(I) and a series of β-diketiminate ligands have been investigated to demonstrate that unique macrocyclic dinuclear and tetranuclear Ag(I)-complexes and a linear coordination polymer Ag(I)-complex as well as oxidative C–C coupling dimer products of the ligands were obtained depending on the substituents on the carbon framework of β-diketiminate ligands.

β-Diketiminate derivatives function as essentially monoanionic didentate ligands, which have been widely adopted for the syntheses of transition metal, main group element, and lanthanide complexes.[1] In most cases, β-diketiminate ligands are adapted to take a closed conformation (type-**A**), affording a six-membered metallacyclic ring as a minimum structural unit of the complexes (Scheme 1). However, β-diketiminatometal complexes with an open conformation (type-**B**) are very rare.[1−5]

We herein report our investigation of the reactions of Ag(I) and a series of β-diketiminate ligands (**L1**$^-$ − **L5**$^-$; deprotonated forms of **L1H** − **L5H**, Scheme 1) which found that the ligands behave quite differently toward the metal ion depending on the substituents on the carbon framework (R^1 and R^2). It should be noted that nothing is known about coordination chemistry of silver in β-diketiminate ligand systems.[1,6] Thus, the present study provides the first examples of β-diketiminate−silver(I) complex.

L1$^-$ (R^1 = H, R^2 = Me) is one of the most popular β-diketiminate ligands so far investigated, since it can be easily obtained by the condensation reaction between acetylacetone and 2,6-diisopropylaniline.[1,7] Thus, the reaction of **L1**$^-$ and Ag(I) was first examined. Treatment of **L1H** with an equimolar amount of $AgPF_6$ in the presence of triethylamine in methanol at room temperature under anaerobic and dark conditions resulted in precipitation of silver metal Ag(0) and organic materials. From the mixture was isolated an organic product in a 58% yield, the structure of which was determined as a dimer of the original ligand **(L1)$_2$** (Scheme 2).[8] One-electron oxidation of **L1**$^-$ by Ag(I) may occur to give a radical species **L1**$^\bullet$ and Ag(0), the former of which is converted into the dimer product **(L1)$_2$** by C_α−C_α radical coupling and following proton migration from the α-carbon to the nitrogen atom (imine-to-enamine isomerization, see Scheme 2).

Scheme 1



A similar C_α−C_α coupling reaction took place in the same treatment of **L2H** and $AgPF_6$ to give **(L2)$_2$** in a 79% yield (Scheme 3). In this case, imine-to-enamine isomerization does not occur, since there is no proton on the α-carbon of **L2H**. Figure 1 shows the crystal structure of **(L2)$_2$** that unambiguously confirms the C_α−C_α bond formation reaction.[9] The bond lengths of N−C_β (1.251(1) Å), C_α−C_β

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(5) Hitchcock, P. B.; Lappert, M. F.; Wei, X.-H. *J. Organomet. Chem.* **2004**, *689*, 1342−1349.
(6) Silver(I)-complexes of closely related triazapentadienyl ligands with fluorinated alkyl substituents were reported recently. Dias, H. V. R.; Singh, S. *Inorg. Chem.* **2004**, *43*, 7396−7402.
(7) Feldman, J.; McLain, S. J.; Parthasarathy, A.; Marshall, W. J.; Calabrese, J. C.; Arthur, S. D. *Organometallics* **1997**, *16*, 1514−1516.
(8) Details of the experimental procedures and the analytical data of the products are presented in Supporting Information.

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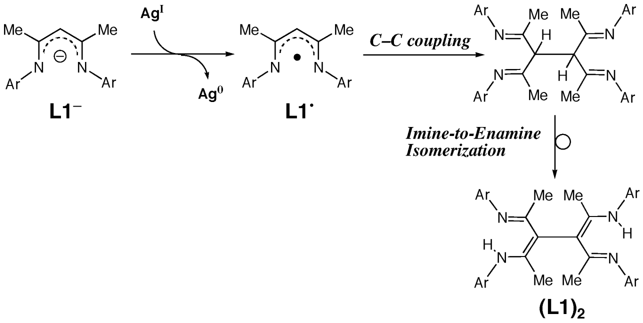
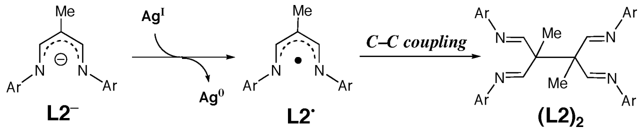
Scheme 2



Scheme 3



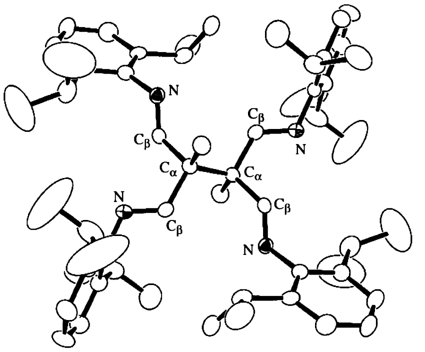


Figure 1. ORTEP drawing of **(L2)$_2$** with 50% probability thermal-ellipsoids. Hydrogen atoms are omitted for clarity.

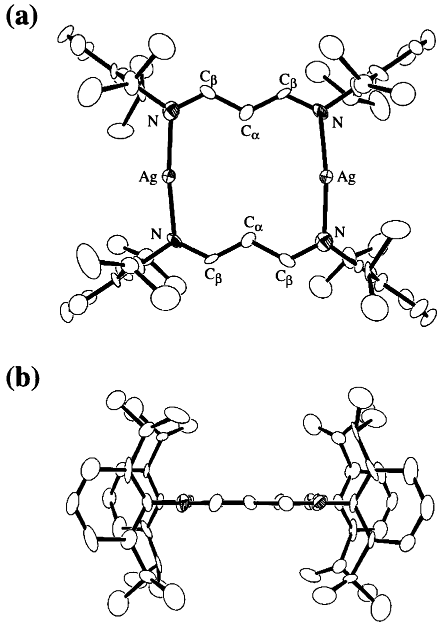


Figure 2. ORTEP drawings [(a) top view and (b) a side view] of $[Ag^I_2(\mathbf{L3}^-)_2](CH_2Cl_2)_2$ with 50% probability thermal-ellipsoids. Hydrogen atoms and the solvent molecules (CH_2Cl_2) in the crystal lattice are omitted for clarity.

(1.530(1) Å), and $C_\alpha-C_\alpha$ (1.578(2) Å) also confirm the structure of **(L2)$_2$** indicated in Scheme 3. Occurrence of such a $C_\alpha-C_\alpha$ coupling reaction with *β*-diketiminate ligands carrying alkyl substituent(s) on the carbon framework may be a reason for the lack of *β*-diketiminate−silver coordination chemistry.

Notably, the same treatment of $AgPF_6$ with **L3H** carrying no substituent on the carbon framework ($R^1 = R^2 = H$)[10] gave a dinuclear Ag(I)-complex $[Ag^I_2(\mathbf{L3}^-)_2](CH_2Cl_2)_2$ in 96% as shown in Figure 2. In this complex, *β*-diketiminate ligand **L3**$^-$ exhibits the open conformation (type-**B**), acting as a didentate bridging ligand to afford the 12-membered macrocyclic compound as shown in Figure 2a. The silver(I) ion exhibits two-coordinate nearly linear structure (bond angle of N−Ag−N is 173°), and the distance between the two Ag(I) ions is about 5.0 Å. The 12-membered macrocyclic ring is perfectly flat and the aromatic ring of 2,6-diisopropylphenyl substituent is almost perpendicular to the macrocyclic plane (Figure 2b). In the cases of **L1**$^-$ and **L2**$^-$, such a linear conformation of Ag(I) may not be stable due to steric repulsion between the ligand substituents (R^1, R^2, and Ar), thus causing the oxidative degradation ($C_\alpha-C_\alpha$ coupling) reaction.

More interestingly, the treatment of $AgPF_6$ with cyano-ligand **L4H**[11] gave a much larger macrocyclic tetranuclear Ag(I)-complex shown in Figure 3 in 84% yield.[12] As in the case of the dinuclear Ag(I)-complex (Figure 2), the ligand is adapted to take the open conformation and acts as a didentate bridging ligand, producing the large 24-membered ring. The silver(I) ions also exhibit a two-coordinate structure, but the N−Ag−N angles of 154−158° are smaller than that in the dinuclear Ag(I)-complex (173°). The molecule exhibits a saddle-shape structure, in which one molecule of CH_2Cl_2 is entrapped in the cavity (Figure 3b). There seems to be hydrogen-bonding interaction between the hydrogen atoms of CH_2Cl_2 and the nitrogen atoms of −CN groups, but the distance between the carbon atom of the incorporated CH_2Cl_2 molecule and the nitrogen atom of −CN (4.97 Å) seems to be too long for the formation of hydrogen-bonding interaction.

On the other hand, another electron-deficient nitro-ligand **L5H** afforded a totally different *β*-diketiminatosilver(I) complex as shown in Figure 4a (72% isolated yield). The product was a coordination polymer Ag(I)-complex with **L5**$^-$ exhibiting the closed conformation (type-**A**), where the neutral $[Ag^I(\mathbf{L5}^-)]$ units associate with each other to form a head-to-tail ($Ag\text{-to-}NO_2$) linear polymer chain. The Ag(I)

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(9) Crystallographic data as well as the selected bond lengths and angles are presented in Supporting Information.

(10) 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.

(11) Shimokawa, C.; Yokota, S.; Tachi, Y.; Nishiwaki, N.; Ariga, M.; Itoh, S. *Inorg. Chem.* **2003**, *42*, 8395−8405.

(12) Multinuclear Ag(I) macrocyclic complexes with a two-coordinate linear coordination geometry have also been reported in other ligand systems. (a) Munakata, M.; Wu, L. P.; Kuroda-Sowa, T. In *Advances in Inorganic Chemistry*; Sykes, A. G., Ed.; Academic Press: San Diego, CA, 1999; Vol. 46, pp 173−303. (b) Gimeno, M. C.; Laguna, A. In *Comprehensive Coordination Chemistry II*; Fenton, D. E., Ed.; Elsevier: Amsterdam, 2004; Vol. 6, pp 911−1145.

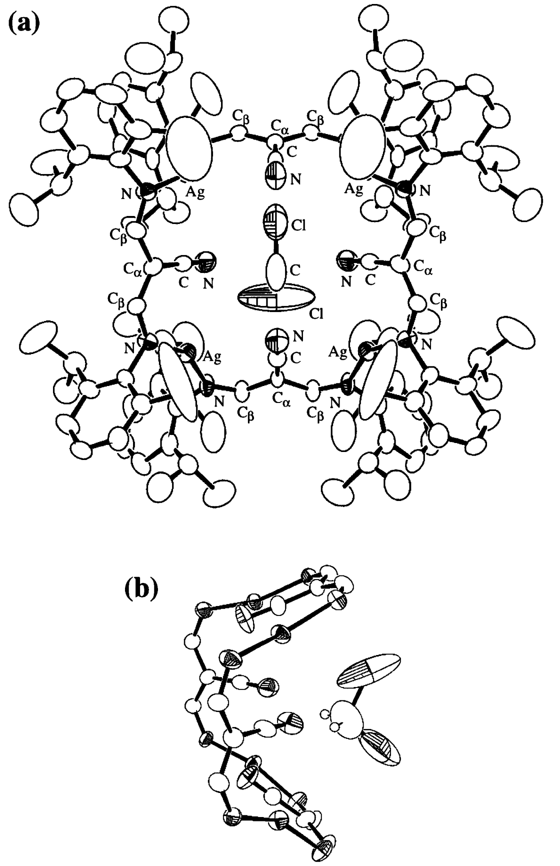

Figure 3. ORTEP drawings [(a) front view and (b) a side view] of $[Ag^I_4(\mathbf{L4}^-)_4(CH_2Cl_2)]$ with 50% probability thermal-ellipsoids. Hydrogen atoms in (a), and hydrogen atoms except those on CH_2Cl_2 and Ar groups in (b), are omitted for clarity.

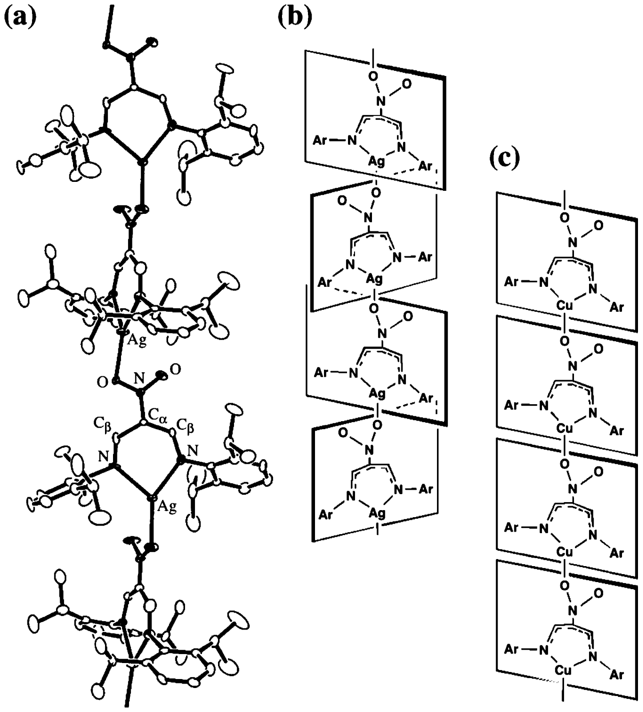

Figure 4. (a) ORTEP drawing of the polymer complex $\{[Ag^I(\mathbf{L5}^-)](CH_2Cl_2)\}_n$ with 50% probability thermal-ellipsoids. Hydrogen atoms and CH_2Cl_2 molecules are omitted for clarity. Schematic drawings of the monomer unit alignment of (b) the silver(I)−polymer complex and (c) the copper(I)−polymer complex.

ion exhibits a distorted trigonal planar structure and the nitro group acts as a monodentate ligand to link the monomer units.

We previously reported a linear copper(I)−polymer complex supported by a similar α-nitro β-diketiminate ligand (Ar = mesityl).[13] The coordination geometry of the metal center of the Ag(I)−polymer complex is fairly close to that of the Cu(I)−polymer complex, but the alignment of monomer units is largely different between the two systems. Namely, in the copper(I)-system, the six-membered chelate rings of all the monomer units are parallel to each other, making a flat wall of the one-dimensional polymer chain (Figure 4c), whereas the chelate ring of the silver(I)-complex is perpendicular to that of the neighboring monomer units as illustrated in Figure 4b. Thus, the copper(I)−polymer complex exhibits a dark purple color probably due to an extended $d-p_\pi$ interaction through the $Cu-NO_2$ linkage,[13] but such an extended conjugative interaction is absent in the silver system due to the perpendicular monomer alignment. Thus, the color of the Ag(I)−polymer complex is yellow.

In summary, unique behavior of β-diketiminate ligands has been found in the reaction with $AgPF_6$. With the ordinary alkyl substituted ligands ($\mathbf{L1}^-$ and $\mathbf{L2}^-$), one-electron oxidation of the ligand occurred to induce the $C_\alpha-C_\alpha$ radical coupling reaction. This may be a reason for the lack of coordination chemistry in the β-diketiminate−silver system. Less hindered β-diketiminate ligand $\mathbf{L3}^-$, on the other hand, provided the dinuclear silver(I) complex $[Ag^I_2(\mathbf{L3}^-)_2]$ with the open conformation of the supporting ligand. The Ag(I) oxidation state may be stabilized in the linear coordination geometry, prohibiting the one-electron oxidation of ligand by Ag(I). The β-diketiminate ligands involving a strong electron-withdrawing group such as −CN in $\mathbf{L4}^-$ and $-NO_2$ in $\mathbf{L5}^-$ can also stabilize the silver(I) oxidation state to give a unique macrocyclic tetranuclear Ag(I)-complex with the open conformation (type-**B**) and the linear polymer−Ag(I)-complex with a trigonal planar geometry supported by the ligand with the closed conformation (type-**A**). Thus, control of the oxidation state of silver by the ligand is very important for the development of β-diketiminato−silver complexes.

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Supporting Information Available: Details of the experimental procedures and analytical data of the products (pdf), and 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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