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Syntheses and Structures of a Macrocyclic *β*-Diketimine and Its Zinc and Copper Complexes

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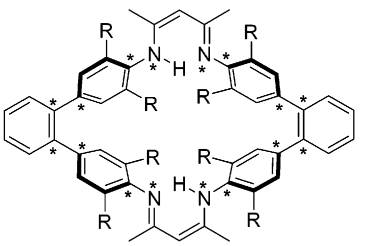
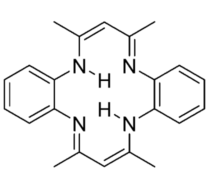
Summary: A macrocyclic compound containing two β-diketimine units is synthesized from 4,4″-diamino-o-terphenyl. Complexations with zinc and copper are achieved, and their X-ray structures are elucidated.

Recently, *β*-diketiminato complexes and their applications to catalysis have drawn extensive attention.[1] Examples are the zinc complexes for epoxide/CO_2 copolymerization[2,3] and the copper complexes for O_2 activation.[4,5] We have been interested in macrocyclic compounds containing two *β*-diketimine units (**1**). The asterisked carbon and nitrogen atoms in **1** are ideally situated in a plane to form a rigid lozenge-shaped macrocycle. Syntheses of macrocyclic compounds and their use for molecular recognition and materials science are currently a hot research field.[6] The analogous cyclic compounds of relatively small ring size (**2**) have been extensively studied, but they have been used as a tetravalent ligand to coordinate a metal.[7] In the case of **1**, four nitrogen atoms on the ring cannot coordinate simultaneously to a metal by the size of the ring. Instead, complexes containing two metals are expected, in which cooperative actions of the two metals can be expected in some catalysis. Coates recently revealed by kinetic study that two metals are involved in the catalysis of the epoxide/CO_2 copolymerization,[2] and Marks reported some advantages of the two-metal catalysis in the olefin polymerization.[8]



1



2

Cyclization is achieved by reacting an equimolar amount of **4**, which is easily prepared by reacting 4,4″-diamino-*o*-terphenyl (**3**)[9] with excess 2,4-pentanedione, with the HCl salt of **3** in anhydrous ethanol (Scheme 1). Rigorous drying of ethanol with sodium and diethyl phthalate and high dilution (7.7 mM) are required for the success of the cyclization. The deposited HCl salt is deprotonated by treatment with saturated aqueous $NaHCO_3$ solution to afford **5**. The overall yield from **4** is satisfactory (42%). A couple of doublet signals are observed at 7.14 and 6.58 ppm in the ^1H NMR spectrum (C_6D_6), which can be assigned to the two protons on the peripheral benzene rings in the terphenyl fragment, and a typical signal pattern observed for a symmetrically *o*-disubstituted benzene compounds is observed at 7.41 and 7.21 ppm.[10] Signals of CH_3, CH, and N-H are observed at 1.81, 4.75, and 12.95 ppm, respectively, as singlets.

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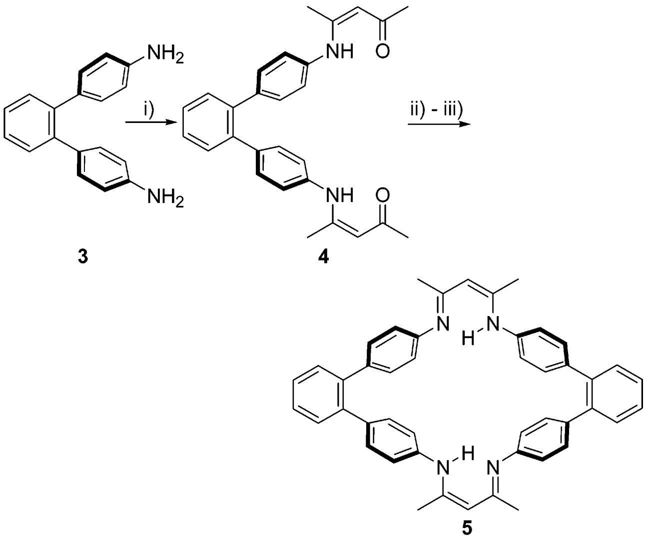
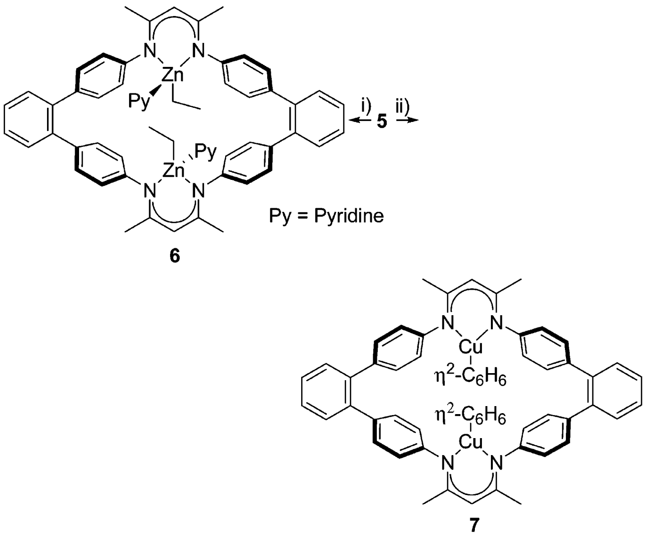
Scheme 1[a]



[a] Legend: (i) 2,4-pentanedione; (ii) HCl salt of **3** in EtOH; (iii) aqueous $NaHCO_3$.

Scheme 2[a]



[a] Legend: (i) Et_2Zn in pyridine and benzene; (ii) Cu(I)O^{t}Bu in benzene.

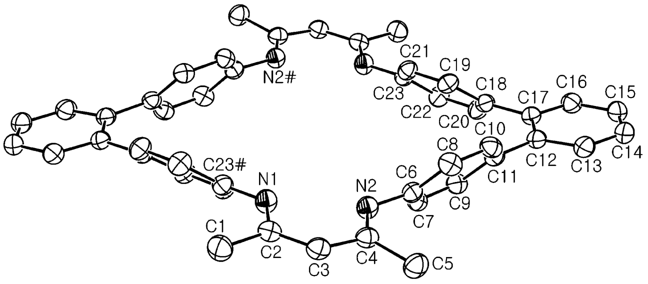


Figure 1. Thermal ellipsoid plot (30% probability level) of **3**. Hydrogen atoms are omitted for clarity. Selected bond distances (Å): N(1)−C(2), 1.354(3); C(2)−C(3), 1.370(3); C(3)−C(4), 1.425(3); N(2)−C(4), 1.302(3); C(1)−C(2), 1.501(3); C(5)−C(4), 1.514(3); N(1)−C(23)#1, 1.407(3); N(2)−C(6), 1.413(3); N(1)−N(2)#, 7.854.

Single crystals of **5** suitable for X-ray crystallography were obtained by vapor-phase diffusion of pentane to a benzene solution, and its molecular structure was unambiguously determined.[11] Figure 1 shows the structure with the selected bond lengths and angles. Amino and imino moieties are not distinguished in the ^{1}H and ^{13}C NMR spectra by rapid exchange of the N-H proton between the two nitrogen atoms, but in the crystal lattice the imino and amino groups are distinguished. The N1−C2 distance is longer than the N2−C4 distance, while the C2−C3 distance is shorter than the C4−C3 distance. The N1−C2−C3−C4−N2 atoms are located in a plane (rms deviation, 0.0117), and the plane is nearly coplanar with the C12−C17 benzene plane (angle between the two planes, 11.14(4)°). The C6−C12 and C18−C23 benzene rings are tilted from the C12−C17 benzene ring by 48.30(8)° and 43.22(8)°, respectively. The distance from a nitrogen to the nitrogen situated on the opposite side on the other β-diketimine (N1−N2# distance) is 7.854 Å.

When a solution of Et_2Zn in pentane is layered onto a solution of **5** in benzene/pyridine (v/v, 10:1), light yellow crystals are deposited overnight that are suitable for X-ray crystallography (Scheme 2). The crystals were isolated in 57% yield. The crystals are not soluble or decompose in common organic solvents, hampering the NMR characterization and further reactions. X-ray crystallography studies reveal the structure, which is shown in Figure 2 with selected bond distances and angles.[12] It shows a severely distorted tetrahedral structure around the zinc center. The sum of N1−Zn−N2, N1−Zn−C24, and C24−Zn1−N2 angles is 346.9°, which is between those expected for an ideal tetrahedral structure (328.5°) and an ideal trigonal planar structure (360°). It may be considered as a flattened tetrahedron formed by the uptake of a pyridine ligand by a trigonal β-diketiminatoZnEt fragment. The Zn−N(pyridine) vector is not parallel to the pyridine plane, and the C28−N3−Zn angle is 157.59°. The Zn−N1 and Zn−N2 distances (2.021(6) and 2.022(6) Å, respectively) are slightly longer than those observed for a monomeric trigonal β-diketiminatoZnEt complex (1.973(3) and 1.943(3) Å).[3b] The bite angle of the β-diketiminato ligand (N1−Zn−N2, 89.8(2)°) is substantially small when compared with those observed for the various previously reported β-diketiminato zinc complexes (97−99°).[2,3] The N1−C2−C3−C4−N2 plane is more tilted from the C12−C17 benzene plane (angle between the two planes,

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(10) Becker, E. D. *High-resolution NMR: Theory and Chemical Application*, 2nd ed.; Academic Press: London, 1980; p 171.

(11) Crystallographic data for $C_{46}H_{40}N_4\cdot 2C_6H_6$: $M = 805.04$, triclinic, $P\bar{1}$, $\lambda = 0.71073$ Å, $T = 293(2)$ K, $a = 7.5586(7)$ Å, $b = 11.0220(9)$ Å, $c = 15.0433(14)$ Å, $\alpha = 98.759(2)°$, $\beta = 102.071(2)°$, $\gamma = 104.454(2)°$, $V = 1158.77(18)$ Å^3, $Z = 1$, $D_{calcd} = 1.154$ Mg/m^3, $\mu = 0.067$ mm^{-1}, $F(000) = 428$, crystal size 0.3 × 0.16 × 0.16 mm, θ range for data collection 1.42−28.32°, index range $-9 \le h \le 10$, $-14 \le k \le 8$, $-20 \le l \le 18$, 8566 reflections collected, 5677 unique data (R(int) = 0.0184), absorption correction SADABS (Sheldrick, 1996), refinement method full-matrix least-squares on F^2, data/restraints/parameters 5677/0/294, goodness-of-fit on F^2 0.996, final R indices ($I > 2\sigma(I)$) R1 = 0.0545, wR2 = 0.1455, largest difference peak and hole 0.300 and −0.242 e·Å^{-3}.

(12) Crystallographic data for $C_{30}H_{29}N_3Zn$: $M = 496.93$, monoclinic, $P2_1/n$, $\lambda = 0.71073$ Å, $T = 293(2)$ K, $a = 8.9360(6)$ Å, $b = 13.9600(9)$ Å, $c = 20.6595(13)$ Å, $\beta = 97.8500(10)°$, $V = 2553.1(3)$ Å^3, $Z = 4$, $D_{calcd} = 1.293$ Mg/m^3, $\mu = 0.984$ mm^{-1}, $F(000) = 1040$, crystal size 0.20 × 0.17 × 0.14 mm, θ range for data collection 1.77−28.31°, index range $-11 \le h \le 11$, $-18 \le k \le 13$, $-27 \le l \le 27$, 18 417 reflections collected, 6334 unique data (R(int) = 0.0756), absorption correction SADABS (Sheldrick, 1996), refinement method full-matrix least-squares on F^2, data/restraints/parameters 6334/0/311, goodness-of-fit on F^2 1.064, final R indices ($I > 2\sigma(I)$) R1 = 0.1005, wR2 = 0.3045, largest difference peak and hole 0.636 and −1.286 e·Å^{-3}.

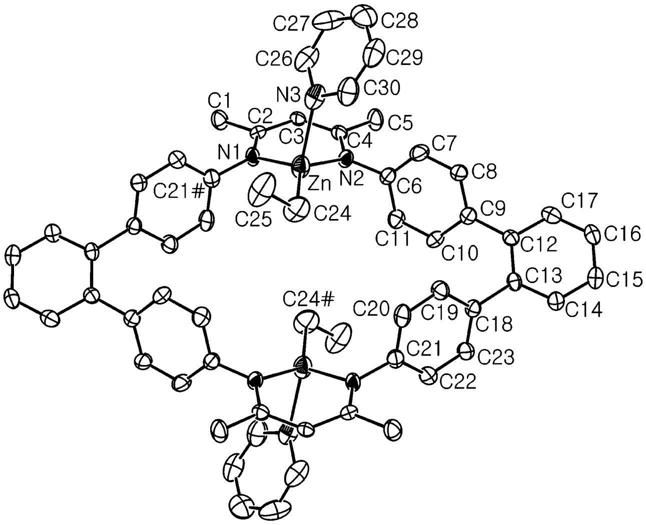

Figure 2. Thermal ellipsoid plot (30% probability level) of **4**. Hydrogen atoms are omitted for clarity. Selected bond distances (Å) and angles (deg): Zn(1)−C(24), 1.949(9); Zn(1)−N(1), 2.021(6); Zn(1)−N(2), 2.022(6); Zn(1)−N(3), 2.267(8); N(1)−C(2), 1.348(8); N(1)−C(21)#, 1.438(9); N(2)−C(4), 1.337(8); N(2)−C(6), 1.422(9); C(2)−C(3), 1.385(9); C(3)−C(4), 1.421(9); C(1)−C(2), 1.505(9); C(4)−C(5), 1.493(9); Zn−Zn, 6.010; C24−C24#, 4.177; C(24)−Zn(1)−N(1), 124.8(4); C(24)−Zn(1)−N(2), 132.2(4); N(1)−Zn(1)−N(2), 89.8(2); C(24)−Zn(1)−N(3), 107.9(4); N(1)−Zn(1)−N(3), 104.2(3); N(2)−Zn(1)−N(3), 91.3(3).

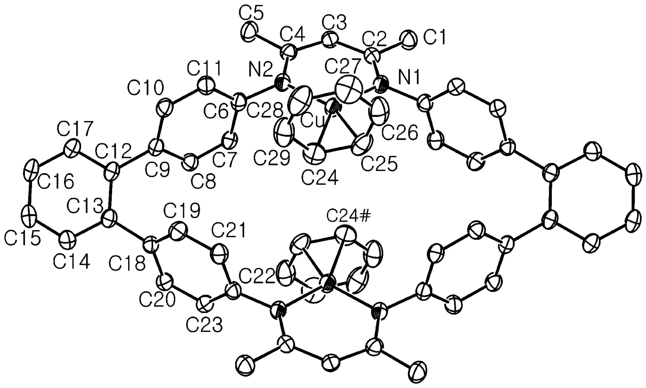

Figure 3. Thermal ellipsoid plot (30% probability level) of **5**. Hydrogen atoms are omitted for clarity. Selected bond distances (Å) and angles (deg): Cu(1)−N(2), 1.925(2); Cu(1)−N(1), 1.935(2); Cu(1)−C(24), 2.112(3); Cu(1)−C(25), 2.078(3); N(1)−C(2), 1.325(4); N(2)−C(4), 1.337(4); C(3)−C(2), 1.406(4); C(3)−C(4), 1.395(4); C(1)−C(2), 1.509(4); C(4)−C(5), 1.509(4); C(24)−C(25), 1.397(5); Cu−Cu, 5.201; C24−C24#, 4.078; N(2)−Cu(1)−N(1), 99.40(10); N(1)−Cu(1)−C(25), 108.98(13); N(2)−Cu(1)−C(24), 113.45(13); C(25)−Cu(1)−C(24), 38.93(14).

29.89(21)°) than the corresponding plane is in **5** (angle between the two planes, 11.14(4)°). The zinc atom is situated slightly above the N1−C2−C3−C4−N2 plane, and the distance between the zinc and the plane is 0.6605(91) Å. Both the tilting and the situation of the zinc atom out of the plane make it possible for the ethyl and the pyridine ligand to be situated in an axial site of the macrocyclic plane (Figure 4). The distance between the two methylene carbons attached on each zinc atoms is 4.177 Å, and the Zn−Zn distance is 6.010 Å. The closest distance between the two hydrogen atoms attached on each methylene carbon is 2.605 Å. Considering the van der Waals radius of the hydrogen atom (1.2 Å), the H−H distance of 2.605 Å implies that the two ethyl groups are situated nearly in the van der Waals contact.

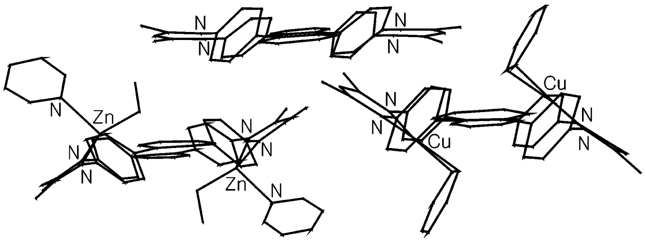

Figure 4. Side views of **3**, **4**, and **5**.

The copper complex **7** is synthesized by reacting **5** with copper(I) *tert*-butoxide[13] in benzene (Scheme 2).[5] The complex is insoluble in benzene, and single crystals are obtained by layer diffusion of the two reactants in benzene. The crystals are not soluble or decompose in common organic solvents, hampering the NMR characterization and further studies. Figure 3 shows its structure, with selected bond distances and angles.[14] It shows a slightly distorted square planar structure, copper being coordinated by a η^2-benzene and a β-diketiminate ligand. Sadighi reported a similar structure with a fluorinated β-diketiminate ligand, and the bond distances and angles are in agreement with those observed for the fluorinated β-diketiminato complex.[5] The N1−C2−C3−C4−N2 plane is tilted further from the C12−C17 benzene plane (angle between the two planes, 35.29(11)°) than the corresponding plane is in **6**, but the deviation of the metal center from the N1−C2−C3−C4−N2 plane is smaller than that observed for the zinc complex **6** (distance between the metal and N1−C2−C3−C4−N2 plane, 0.2151(35) and 0.6605(91) Å for **7** and **6**, respectively). The Cu−Cu distance is 5.201 Å, which is smaller than the Zn−Zn distance observed for **6** (6.010 Å). The η^2-benzene ligands occupy each axial site of the macrocyclic ring (Figure 4), and the benzene ring is not distorted by the coordination. The nearest C−C distance between the two η^2-benzenes is 4.078 Å, and the nearest H−H distance is 2.699 Å, which is slightly out of the van der Waals contact. The η^2-benzene ring is tilted slightly toward copper, and the angle between the Cu−C24−C25 plane and the η^2-benzene plane is 78.79(17)°.

In summary, a macrocyclic compound containing two β-diketimine units and its zinc and copper complexes are synthesized. The N−N distance in the β-diketimine is ~8 Å, and the metal−metal distances vary by 5−6 Å due to the amount of the tilting of the β-diketiminato plane from the macrocyclic plane and the amount of deviation of the metal center from the β-diketiminato plane. We are currently making efforts to synthesize

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[13] Håkansson, M.; Lopes, C.; Jagner, S. *Inorg. Chim. Acta* **2000**, *304*, 178.

[14] Crystallographic data for $C_{29}H_{25}CuN_2{\cdot}C_6H_6$: $M = 543.16$, triclinic, $P\bar{1}$, $\lambda = 0.71073$ Å, $T = 293(2)$ K, $a = 9.6030(10)$ Å, $b = 11.8460(10)$ Å, $c = 12.7940(10)$ Å, $\alpha = 96.216(3)°$, $\beta = 99.775(3)°$, $\gamma = 95.664(3)°$, $V = 1415.6(2)$ Å^3, $Z = 2$, $D_{calcd} = 1.274$ Mg/m^3, $\mu = 0.797$ mm^{-1}, $F(000) = 568$, crystal size 0.20 × 0.20 × 0.20 mm, θ range for data collection 2.94−27.55°, index range $-8 \le h \le 12$, $-15 \le k \le 15$, $-16 \le l \le 16$, 8364 reflections collected, 6335 unique data (R(int) = 0.0258), refinement method full-matrix least-squares on F^2, data/restraints/parameters 6335/0/345, goodness-of-fit on F^2 1.004, final R indices ($I > 2\sigma(I)$) R1 = 0.0527, wR2 = 0.1005, largest difference peak and hole 0.344 and −0.350 e·Å^{-3}.

4,4″-diamino-*o*-terphenyl derivatives having various alkyl or aryl substituents in the 3, 5, 3″, and 5″ positions and macrocyclic compounds derived from them. Metal complexes prepared from the substituted macrocyclic compounds may be soluble in common organic solvents, allowing further reactions and tests as catalysts.

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Supporting Information Available: Complete details for crystallographic studies of **4**, **5**, and **6** and experimental details. This material is available free of charge via the Internet at http://pubs.acs.org.

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