First 'Back-to-back' Shaped Compartmental Ligand; Structural Characterization of a Tetranuclear Zinc(II) Complex in a Highly Flattened Form

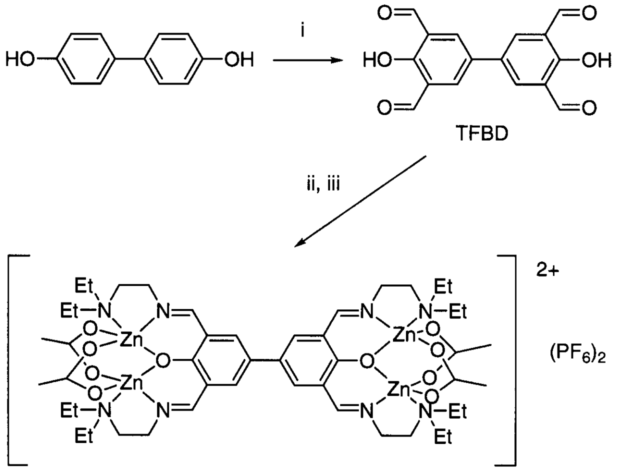
Eiji Asato,* Mitsuyoshi Chinen, Atsushi Yoshino, Yoshiteru Sakata,† and Ken-ichi Sugiura†
Department of Chemistry, Biology and Marine Science, College of Science, University of the Ryukyus, Nishihara, Okinawa 903-0213
†*The Institute of Scientific and Industrial Research (ISIR), Osaka University, 8-1 Mihogaoka, Ibaraki, Osaka 567-0047*

(Received March 8, 2000; CL-000230)

Schiff-base condensation of 3,3',5,5'-tetraformyl-4,4'-biphenyldiol, which was converted from 4,4'-biphenyldiol by a modified Duff reaction, and *N,N*-diethylethylenediamine in the presence of $Zn(CH_3CO_2)_2$ followed by the addition of excess NH_4PF_6 gave a tetrazinc complex $[Zn_4(L)(\mu\text{-}CH_3CO_2)_4](PF_6)_2$ (**1**), where L^{2-} is a new ligand bearing four Schiff-base and two phenoxo-bridging moieties; structure of **1** was fully characterized by X-ray crystallography.

Phenol-based ligands possessing functional coordinating groups at the 2- and 6- positions, namely compartmental ligands, are some of the most powerful tools for inorganic chemists to create dinuclear metal cores. In addition to many examples of these kinds of dinuclear metal complexes, recent elaborated ligand synthesis has generated some multi-phenol-based ligands such as large macrocycles[1-4] into which several metal ions (n > 3) can be incorporated. Similar chemical modification of coordinating groups onto the 3,3',5,5'-positions of 4,4'-biphenyldiol seems to be of great value, because 1) such phenol derivatives should have a high potential as an efficient tetranucleating ligand providing two phenoxo-bridged dinuclear metal cores at the two termini; and 2) the π-conjugated and potentially redox-active property of the biphenyldiol unit make it possible to study the electrochemical and magnetic interactions between the terminal metal pairs. However, to the best of our knowledge, no example of such tetranucleating ligands has been reported thus far, being in contrast with the rapidly increasing number of reports on dinuclear metal complexes where deprotonated biphenyl- or oligophenyldiol units bridge two metal ions in their termini.[5,6] In this communication, we wish to report the first example of the biphenyldiol-based tetranucleating ligand categorized into a new type of compartmental ligand.

A recently reported modified Duff reaction[7] was used for the synthesis of the key compound in this study, i.e., 3,3',5,5'-tetraformyl-4,4'-biphenyldiol (TFBD).[8] Further attempts to convert TFBD into tetra Schiff-base compounds were carried out to prove its high potential as an effective precursor to a variety of tetranucleating ligands. As a representative case, the Schiff-base condensation of TFBD and *N,N*-diethylethylenediamine (Et_2en) in the presence of $Zn(CH_3CO_2)_2{\cdot}2H_2O$ with the mole ratio of 1 : 4 : 4 in ethanol gave a dark brown solution. The addition of excess NH_4PF_6 into the solution immediately gave a yellow crystalline precipitate. Recrystallization of the product from acetonitrile finally gave plate-like yellow crystals formulated as $[Zn_4(L)(CH_3CO_2)_4](PF_6)_2$[9] (**1**) (ca. 80% yield before recrystallization), where L^{2-} is the tetra Schiff-base ligand shown in Scheme 1.



Scheme 1. Reagents and conditions: i, TFA, HMT, reflux, 7d; ii, EtOH, $Zn(CH_3COO)_2$, Et_2en; iii, NH_4PF_6.

The X-Ray structural analysis[10] of **1** revealed that it consists of a discrete dicationic complex $[Zn_4(L)(\mu\text{-}CH_3CO_2)_4]^{2+}$ (Figure 1) and two PF_6^- counter anions. The asymmetric unit of the cation is a dinuclear metal core formed by the phenoxo- and two carboxylato bridges which has a distance of 3.2441(9) Å for the Zn(1)-Zn(2) pair, and related to the other unit by a crystallographically imposed center of symmetry located on the middle point of the C(4)-C(4') bond. Thus, the tetra Schiff-base ligand L^{2-} has a very high planarity in its structure, characterized by the twisted angle of 0° between the two rings. The two zinc ions in each dinuclear core have essentially the same coordination geometry in slightly distorted trigonal-bipyramids formed by the two N and three O donors where the O(1)-N(2) and O(1)-N(4) atoms occupy the apical sites of Zn(1) and Zn(2), respectively. Concerning the bond distances, the Zn-N interaction (av. 2.096 Å) and the Zn-O bonds (av. 2.010 Å) fall well within the range of distances observed for typical Zn(II)-nitrogen and -oxygen coordination compounds with a trigonal-bipyramidal configuration.[4]

Its charge balance consideration clearly indicates that the potentially redox-active ligand is in a reduced form, i.e., deprotonated hydroquinone, because the metal ion is redox inactive Zn(II) rejecting the possibility of electron transfer from the ligand to the metal ions. Thus, the highly flattened form causing a significant π-conjugated character over the ligand should be due to a crystallographical requirement, not to the contribution by the quinoid structure. Although the cyclic voltammogram of **1** in acetonitrile showed no clear oxidation process up to 2.0 V, the hydroquinone form is strongly supported by the following four conclusive observations. First, the C(4)-C(4') distance of 1.512(4) Å is a typical value for a C-C single bond, which is

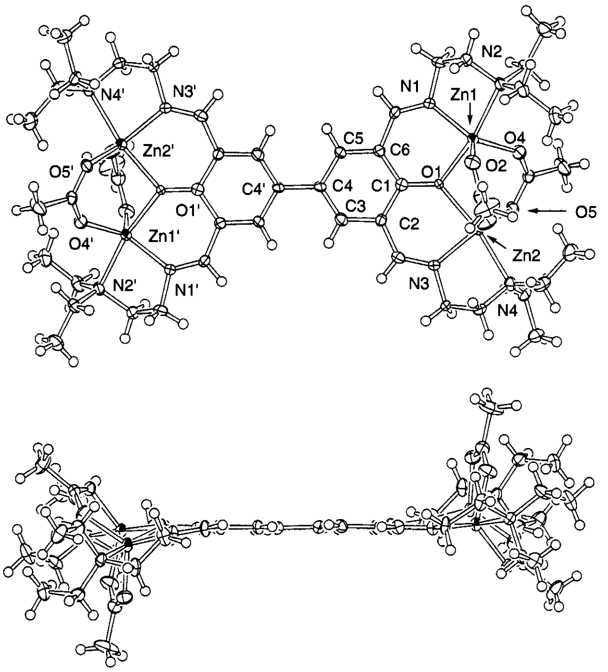


Figure 1. Top and side view of $[Zn_4(L)(\mu\text{-}CH_3CO_2)_4]^{2+}$ cation; Selected distancs (Å) : Zn(1)-Zn(2) = 3.2441(9), Zn(1)-O(1) = 2.154(4), Zn(1)-O(2) = 1.977(4), Zn(1)-O(4) = 1.976(4), Zn(1)-N(1) = 2.014(5), Zn(1)-N(2) = 2.243(5), Zn(2)-O(1) = 2.112(4), Zn(2)-O(3) =1.963(4), Zn(2)-O(5) = 1.973(4), Zn(2)-N(3) = 2.027(5), Zn(2)-N(4) = 2.237(5), C(4)-C(4)' = 1.512(4), C(1)-O(1) = 1.296(7) Å .

more than 0.1 Å longer than that of the corresponding C=C double bond for a biphenoquinone.[12] Second, the C(1)-O(1) distance [1.296(7) Å] is quite normal for that of the metal-bridged phenoxo moiety,[1-4] but significantly longer (ca. 0.07 Å) than that of the C=O double bond in a biphenoquinone.[11] Third, the ^{1}H-NMR chemical shift for the ring protons (7.79 ppm) showed a downfield shift by ca. 0.5 ppm, compared with those for biphenoquinones.[12] Fourth, the UV-vis spectrum of **1** in acetonitrile showed the absorption at λ_{max} = 265 nm (π-π* of the rings) and λ_{max} = 394 nm (π-π * of the imines), the former of which is close to that of biphenyldiol derivatives,[12] but significantly different from that of biphenoquinones.[12]

The molar conductance (263 S cm^2 mol^{-1}) and the strongest peak in the electrospray mass spectrum (*M/z* = 593) of **1** in acetonitrile indicated that it behaves as a 1: 2 electrolyte and that the dicationic structure seen in the solid is essentially maintained even in solutions. However, it is readily expected that the π-conjugated character arising from the planarity of L^{2-} should be reduced to some extend by twisting between the two rings. In fact, the imine protons were less influenced by the ring current from the adjacent unit and appeared at 8.57 ppm in its ^{1}H NMR spectrum, which is close to 8.43 ppm of the corresponding peak reported for a closely related dinuclear zinc(II) core with a non-π-conjugated phenoxo-bridged system.[4]

In conclusion, the tetraformylation of 4,4'-biphenyldiol and the subsequent Schiff-base condensation were proven to be an effective way to obtain a new class of wire-like tetranuclear metal complexes. Current efforts in our laboratory are directed to variation in the chelation moieties, the ligand(s) metal combination and the expansion of the biphenyl unit to the longer π-conjugated systems such as the terphenyl and tetraphenyl units.

This work was supported in part by a Grant-in-Aid for Scientific Research on Priority Area (#11136242 "Metal-assembled Complexes" to E.A.) from the Ministry of Education, Science, Sports and Culture, Japan. We appreciate the analytical assistance provided by the Material Analysis Center of ISIR, Osaka University.

References and Notes

1 a) V. McKee and S. S. Tandon, *Inorg. Chem.*, **28**, 2901 (1989). b) M. Bell, A. J. Edwards, B. F. Hoskins, E. H. Kachab, and R. Robson, *J. Am. Chem. Soc.*, **111**, 3603 (1989). c) K. K. Nanda, K. Venkatsubramanian, D. Majumdar, and K. Nag, *Inorg. Chem.*, **33**, 1581(1994).

2 a) A. J. Edwards, B. F. Hoskins, E. H. Kachab, A. Markiewicz, K. S. Murray, and R. Robson, *Inorg. Chem.*, **31**, 3585(1992). b) S. S. Tandon, L. K. Thompson, J. N. Bridson, and C. Cristiano, *Inorg. Chem.*, **34**, 5507(1995). c) S. Mohanta, K. K. Nanda, R. Werner, W. Haase, A. K. Mukherjee, S. K. Dutta, and K. Nag, *Inorg. Chem.*, **36**, 4656(1997) .

3 a) E. Asato, H. Furutachi, C. Tamanaha, H. Matsudaira, M. Ohba, H. Okawa, and M. Mikuriya, *Chem. Lett.*, **1999**, 647. b) H. Sakiyama, K. Tokuyama, Y. Matsumura, and H. Okawa, *J. Chem. Soc., Dalton Trans.*, **1993**, 591.

4 E. Asato, H. Furutachi, T. Kawahashi, and M. Mikuriya, *J. Chem. Soc., Dalton Trans.*, **1995**, 3897.

5 a) F. S. McQuillan, T. E. Berridge, H. Chen, T. A. Hamor, and C. J. Jones, *Inorg. Chem.*, **37**, 4959(1998). b) N. C. Harden, E. R. Humphrey, J. C. Jeffery, S. Lee, M. Marcaccio, J. A. McCleverty, L. H. Rees, and M. D. Ward, *J. Chem. Soc., Dalton Trans.*, **1999**, 2417. c) V. A. Ung, D. A. Bardwell, D. Gatteschi, J. C. Jeffery, J. P. Masher, J. A. McClererty, M. D. Ward, and A. Williamson, *Inorg. Chem.*, **35**, 5290(1996).

6 a) V. A. Ung, A. M. W. Cargill Thompson, D. A. Bardwell, D. Gatteschi, J. C. Jeffery, J. A. McClererty, F. Totti, and M. S. Ward, *Inorg. Chem.*, **36**, 3447(1997). b) V. A. Ung, S. M. Couchman, J. C. Jeffery, J. A. McClererty, M. D. Ward, F. Totti, and D. Gatteschi, *Inorg. Chem.*, **38**, 365(1999).

7 L. F. Lindon, G. V. Meehan, and N. Svenstrup, *Synthesis*, **1998**, 1029.

8 4,4'-Biphenyldiol reacted with 10 equiv of hexamethylenetetramine (HMT) in absolute trifluoroacetic acid under Ar, and refluxed for 7 days. The mixture was poured into 4 M HCl, and precipitated yellow product was filtered, and then recrystalized from hot DMSO, to give yellow micro-crystals in 65% yield (Scheme 1). Selected data for TFBD: EI-mass, M^+ = 296, ^{1}H NMR (DMSO-d_6), δ10.31 (s, 4H, CHO), 8.24 (s, 4H, Ar-H), phenol protons were not observed because of the exchanging with H_2O in the solvent used. Anal. Found: C, 63.35; H, 3.52%. Calcd for $C_{16}H_{10}O_6\cdot 0.3H_2O$: C, 63.27; H, 3.52%. This compound was previously prepared by a different multi-steps synthesis started from 4,4'-biphenyldiol. (S. Taniguchi, The 37th Symposium of Thermosetting Plastics, Tokyo, October 1987, Abstr., pp. 93–96).

9 Anal. Found: C, 39.13; H, 5.21; N, 7.58 %. Calcd for $C_{48}H_{76}N_8O_{10}Zn_4P_2F_{12}$: C, 39.04; H, 5.19; N, 7.59%. Selected solution data: UV-Vis [MeCN; λ_{max} (ε/dm^3 mol^{-1} cm^{-1})] 265(71,100), 394 (11,100). ^{1}H NMR (CD_3CN, 25 ˚C): δ 8.57 (s, 4H, imine-H), 7.79 (s, 4H, aryl), 3.78 (t, 8H, C=N-C*H*$_2$CH$_2$-NEt$_2$), 2.89 (t, 8H, -C=N-CH$_2$C*H*$_2$-NEt$_2$), 2.7–3.1 (br, 16H, NC*H*$_2$CH$_3$), 2.01 (s, 12H, CH_3CO_2), 1.01 (t, 24H, NCH$_2$C*H*$_3$).

10 Crystal data for $C_{48}H_{76}N_8O_{10}Zn_4P_2F_{12}$ **1**: M = 1476.62, monoclinic, a = 12.968(2), b = 15.156(1), c = 15.883(3) Å, b = 101.98(1)˚, U = 3053.5(6) Å^3, T = 190 K, space group $P2_1/n$ (# 14), Z = 2, μ(Mo-Kα) =17.01 cm^{-1}, Of the 7224 which were collected, 6999 reflections were unique (R_{int} = 0.055). The structure was solved by direct methods and refined using full-matrix least-squares procedures. All hydrogen atoms were located on the calculated positions. Refinement converged with R_1 = 0.057 for 4046 data with $I > 2\sigma(I)$, and R_1 = 0.150 for all the data.

11 M. A. Khan, A. Osman, and D. G. Tuck, *Acta Crystallogr., Sect. C*, **42**, 1399(1986).

12 a) Y. Morita, A. Kashiwagi, and K. Nakasuji, *J. Org. Chem.*, **62**, 7464 (1997). b) W. J. Detroit and H. Hart, *J. Am. Chem. Soc.*, **74**, 5215 (1952).