COMMUNICATION

ChemComm
www.rsc.org/chemcomm

Insertion of a strongly π–π stacked chloranilate pair into an M_4 arrangement preorganized within a large macrocyclic ligand (M = Zn^{2+} and Cu^{2+})†

Atsushi Yoshino,[a] Hideo Matsudaira,[a] Eiji Asato,*[a] Masayuki Koikawa,[b] Takuya Shiga,[c] Masaaki Ohba[c] and Hisashi Okawa[c]

[a] *Department of Chemistry, Biology and Marine Science, College of Science, University of the Ryukyus, Nishihara, Okinawa 903-0213, Japan. E-mail: asato@sci.u-ryukyu.ac.jp*

[b] *Department of Chemistry and Applied Chemistry, Faculty of Science and Engineering, Saga University, Honjo 1, Saga-shi, Saga 840-8502, Japan*

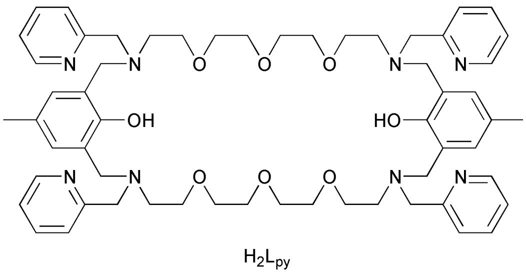
[c] *Department of Chemistry, Faculty of Science, Kyushu University, Hakozaki, Higashiku, Fukuoka 812-8581, Japan*

Received (in Cambridge, UK) 12th March 2002, Accepted 26th April 2002
First published as an Advance Article on the web 13th May 2002

Four Zn(II) ions arranged within a pyridine-modified large phenolate-containing macrocycle L_{py}^{2-} encapsulate two chloranilate ions in a double bis-didentate bridging fashion; the ligands are strongly π–π stacked with each other with a short distance of 3.27 Å and are electrochemically reduced at the same potential of – 1.00 V to produce a reasonably stable biradical species with $T_{1/2}$ = 60 min at 25 °C.

Tetraoxolenes, which have four oxygen donor atoms and are derivatives of benzoquinone (BQ) widely occurring in nature including biological systems,[1] can connect two metal ions as bis-didentate bridging ligands.[2,3] Since these can undergo a one-electron oxidation in addition to a stepwise two-electron reduction process, the bridging ligands have a potential advantage over BQ to create new types of molecules in multi-redox systems. The increase in the number of the redox-active units in polynuclear metal complexes, *i.e.*, metal ions and tetraoxolenes, in principle, make their redox and magnetic chemistry much richer, owing to a variety of formal oxidation states not only for the metal center but also for the ligand. To create such molecular systems with such advanced functionalities, insertion of tetraoxolene bridging ligand(s) into a host cavity preconstructed by several transition metal ions seems likely to be an effective method. While such an established methodology has, as yet, not been reported, we expected that a specially designed macrocyclic ligand would be highly useful to form a *metal-based host cavity* by preorganizing several metal ions within the ligand. Thus, we have started the project approaching to such redox-active molecular systems by using a pyridine-modified large macrocycle H_2L_{py}.[4] We wish to report herein novel tetranuclear metal cores (M = Zn^{2+}, Cu^{2+}) bridged by two redox-active chloranilate ions (CA^{2-} : dianion of chloranilic acid) and two phenoxide moieties derived from the macrocycle.

To a methanol solution containing the macrocycle and $Zn(ClO_4)_2{\cdot}6H_2O$ was added the disodium salt of chloranilic acid (Na_2CA), with the mole ratio adjusted to $H_2L_{py}:Zn^{2+}:CA^{2-}$ = 1:4:2. The reaction mixture immediately gave a dark green precipitate, which was further recrystallized in acetonitrile to give a crystalline product with the formulation $[Zn_4L_{py}(CA)_2](ClO_4)_2{\cdot}3H_2O$ (**1**·$3H_2O$)‡ in 85% yield. A similar reaction using $Cu(ClO_4)_2{\cdot}6H_2O$ instead of the zinc salt under the same conditions gave the brown product $[Cu_4L_{py}(CA)_2](ClO_4)_2$ (**2**)§ in 90% yield. Formation of the tetranuclear species and inclusion of two CA^{2-} units for each complex were confirmed by detecting the strongest peak in electrospray mass spectra for their acetonitrile solutions; *m*/*z* 834.4 for **1** and 839.2 for **2**, respectively, corresponding to their dications. The IR spectra of the two complexes are nearly the same. The carbonyl stretching mode of the two CA^{2-} units in each complex appeared as a very strong band without splitting at 1558 cm^{-1} for **1** and at 1546 cm^{-1} for **2**, respectively, suggesting a bis-didentate bridging mode for both units.[3] Full structural characterization was performed by X-ray crystallography¶ on the zinc(II) complex as the acetonitrile adduct **1**·$4CH_3CN$. As shown in Fig. 1, the macrocycle L_{py}^{2-} binds four Zn(II) ions into the ring to afford two μ-phenoxo zinc pairs [Zn(1)···Zn(4) 3.613(1) Å, Zn(2)···Zn(3) 3.622(1) Å], in between which two strongly π–π stacked CA^{2-} units are inserted in a double bis-didentate fashion leading to two dinuclear cores with distances of 7.802(1) Å for Zn(1)···Zn(2) and 7.528(1) Å for Zn(3)···Zn(4) pairs, respectively. The most remarkable feature is a very short interplanar distance of 3.27 Å with a shortest sparatoin of 3.238(3) Å for C(64)–C(69). This value can be compared to the value of 3.15 Å for TCNQ molecules in conductive crystals[5] and an interplanar separation of 2.67 Å for magnetically coupled semiquinoid-type radicals in $[Mo_4O_{10}(C_6H_2O_4)_2]$.[6] The C–O bond distances in the two CA^{2-} units, ranging from 1.242(3) to 1.272(3) Å, are typical values for a bond order of 1.5,[7] in accord with the bis-didentate coordination. Each Zn(II) ion has a similar five coordination attained by two nitrogens (amine-N and pyridine-N) and three oxygens (two from the CA^{2-} chelation and phenoxy-O) atoms,



H_2L_{py}

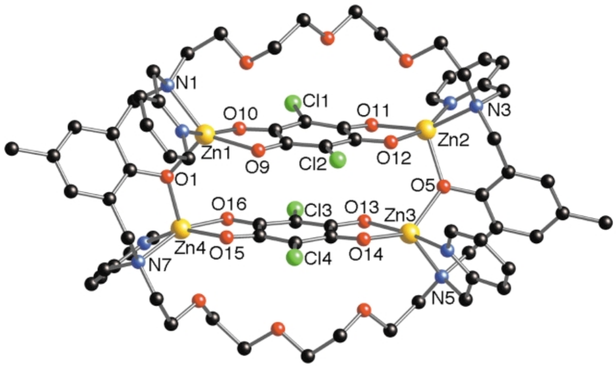


Fig. 1 Perspective view of the complex cation $[Zn_4L_{py}(\mu\text{-}CA)_2]^{2+}$ in **1**.

---

† Electronic supplementary information (ESI) available: Fig S1: variable-temperature EPR spectra. See http://www.rsc.org/suppdata/cc/b2/b202529a/

DOI: 10.1039/b202529a

but in different geometry; the discrimination parameters[8] (ranging from $\tau = 0$ for an ideal square-pyramid to $\tau = 1$ for an ideal trigonal–bipyramid) are 0.023, 0.386, 0.178 and 0.640 for Zn(1), Zn(2), Zn(3) and Zn(4), respectively. Concerning the bond distances, the Zn(II)–N (av. 2.099 Å) and Zn(II)–O (av. 2.042 Å) distances fall well within the range of those observed for typical Zn–nitrogen and –oxygen coordination compounds.[9,10]

Cyclic (CV) and square-wave (SWV) voltammograms of both complexes in acetonitrile solutions (1.0 mM, 0.1 M NEt_4ClO_4) were recorded at a glassy carbon working electrode (Pt counter electrode, Ag/Ag$^+$ reference electrode). The CV and SWV of **1**·3H$_2$O (see Fig. 2(a) and (b)) exhibited two quasi-reversible reduction waves at $E_{1/2} = -0.96$ and -1.93 V, which were assigned by a coulometric experiment to be a two-electron and a one-electron transfer processes, respectively. On the other hand, metal-free chloranilate ion (Na_2CA in DMF) showed its first reduction at -2.00 V in an irreversible form. Because the metal ions in **1** are redox-inactive Zn(II), the redox processes are undoubtedly occurring at the bridging CA^{2-} ligands. Thus, the reduced form present after the first reduction process is expected to be a biradical species characterized by $2 \times [CA^{\cdot 3-}]$. The EPR spectrum of the two-electron reduced form generated by controlled potential electrolysis in DMF showed a sharp signal at $g = 2.0056$ characteristic of an organic radical. The radical species is reasonably stable with a life-time of $T_{1/2} = ca.$ 60 min at 298 K and infinitely stable in frozen solution at < 200 K. Additionally, the signal intensity decreased with decreasing temperature (see ESI†) indicating that the stability was attributed to magnetic coupling between two CA$^{\cdot 3-}$ radicals with short interplanar separation.

From the viewpoint of functional chemistry, the copper(II) derivative **2** may be much more important than **1** because of its potential as a multi-redox and a multi-spin system. Although its detailed magnetic analysis has not yet been completed, weak antiferromagnetic behavior was observed in this complex. The CV of **2** in acetonitrile (Fig. 2(c)) showed an irreversible reduction wave at -1.19 V and a quasi-reversible reduction wave at $E_{1/2} = -0.69$ V, respectively. Unlike the case for **1**, controlled potential electrolysis of **2** at -1.20 V in DMF immediately gave an uncharacterizable black precipitate, probably due to irreversible decomposition to a Cu(I)-based product. Evidently, the quasi-reversible oxidation couple at $E_{1/2} = +0.72$ V is a metal-centered electron transfer process, since the CV of **1** does not show any ligand-centered oxidation wave up to +1.4 V. Although controlled potential electrolysis was applied to identify the oxidized species, no informative EPR signal was obtained from the electrolyzed solution, probably owing to its significant instability.

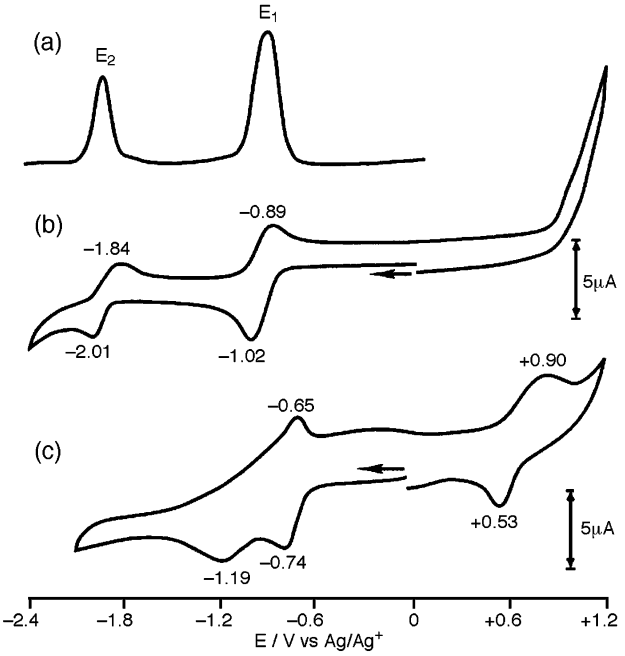


Fig. 2 (a) Square-wave voltammogram of **1** in acetonitrile measured with pulse frequenciy of 15 Hz, pulse height 25 mV. Cyclic voltammograms of **1** (b) and **2** (c) in acetonitrile, scan rate 100 mV s^{-1}.

In conclusion, a chloranilate pair characterized by strong π–π stacking was found to be an effective unit to bridge two phenoxo-bridged metal dimers. To the best of our knowledge, its function as a two-electron acceptor yielding a reasonably stable semiquinone radical pair ($= 2 \times [CA^{\cdot 3-}]$) is the first example, while a two-electron oxidized form of hydroxybenzoquinone ($= 2 \times [HBQ^{\cdot -}]$) has already been reported for a Mo(VI) aggregate.[6] The very short interplanar separation appears to stabilize the reduced biradical species through magnetic coupling. An oxidation process of **2** was found to proceed on the Cu(II) center prior to the $2 \times [CA^{2-}]$ unit, but the electrochemically oxidized species is too unstable to be characterized by spectroscopic methods. If other M(II) ions which are readily oxidized to M(III) form similar complexes, their oxidized forms are expected be more stabilized. Such synthetic studies are now scheduled and in progress in our laboratory.

This work was supported by a Grant-in-Aid for Scientific Research on Priority Ares (#12023243 ″Metal-assembled Complexes″ to E. A.) from the Ministry of Education, Science, Sports and Culture of Japan. A. Y. is thankful for financial support by the Sasagawa Scientific Research Grant from The Japan Science Society.

Notes and references

‡ Complex **1**·3H$_2$O: Anal. for $C_{70}H_{80}N_8O_{27}Cl_6Zn_4$, found (calc.): C, 43.48 (43.35); H, 4.08 (4.16); N, 5.79 (5.78%); ESI-MS [*m/z*, found (calc.)]: 834.4 (834.4). UV–VIS [MeCN; λ_{max}/nm (ε/dm^3 mol^{-1} cm^{-1})]: 327 (75900), 557 (205). Molar conductivity in MeCN, Λ_M/S cm^2 mol^{-1} = 243.

§ Complex **2**: Anal. for $C_{70}H_{74}N_8O_{24}Cl_6Cu_4$, found (calc.): C, 44.56 (44.76); H, 3.99 (3.97); N, 5.97 (5.97%); ESI-MS [*m/z*, found (calc.)]: 839.2 (839.7). UV–VIS [MeCN; λ_{max}/nm (ε/dm^3 mol^{-1} cm^{-1})]: 334 (68700), 754 (930). Molar conductivity in MeCN, Λ_M/S cm^2 mol^{-1} = 264. Variable-temperature magnetic susceptibility data between 1.9 and 300 K were collected for complex **2** by using a SQUID magnetometer. The molar magnetic susceptibility χ_M shows a maximum at about 20 K. The effective magnetic moment decreases monotonically from 3.731 μ_B at 300 K to 0.331 μ_B at 1.9 K.

¶ *Crystal data* for **1**·4CH$_3$CN: $C_{78}H_{86}N_{12}O_{24}Cl_6Zn_4$, $M = 2049.84$, triclinic, space group $P\bar{1}$, $a = 17.744(2)$, $b = 19.093(2)$, $c = 15.701(2)$ Å, $\alpha = 113.796(5)$, $\beta = 96.578(4)$, $\gamma = 102.170(5)°$, $V = 4637.6(9)$ Å^3, $Z = 2$, $D_c = 1.468$ g cm^{-3}, $T = 223$ K, dark green plate (0.20 × 0.10 × 0.10 mm), μ(Mo-Kα) = 12.71 cm^{-1}. 41012 reflections measured, 20672 unique ($R_{int} = 0.056$), $R1 = 0.060$ and $wR2 = 0.117$.

CCDC reference number 181719. See http://www.rsc.org/suppdata/cc/b2/b202529a/ for crystallographic data in CIF or other electronic format.

1 *Principles and Applications of Quinoproteins*, ed.V. L. Davidson, Marcel Dekker Inc., New York, 1992.

2 F. Tinti, M. Verdagure, O. Kahn and J.-M. Savariault, *Inorg. Chem.*, 1987, **26**, 2380; J. V. Folgado, R. Ibanez, E. Coronado, D. Beltran, J. M. Savariault and J. Galy, *Inorg. Chem.*, 1988, **27**, 19; A. Dei, D. Gatteschi and L. Pardi, *Inorg. Chem.*, 1990, **29**, 1442; A. Dei, D. Gatteschi, L. Pardi and U. Russo, *Inorg. Chem.*, 1991, **30**, 2589; M. D. Ward, *Inorg. Chem.*, 1996, **35**, 1712; S. Gallert, T. Weyhermuller, K. Wieghardt and P. Chaudhuri, *Inorg. Chim. Acta*, 1998, **274**, 111.

3 C. G. Pierpont, L. C. Francesconi and D. N. Hendrickson, *Inorg. Chem.*, 1978, **17**, 3470.

4 E. Asato, H. Furutachi, C. Tamanaha, H. Matsudaira, M. Ohba, H. Okawa and M. Mikuriya, *Chem. Lett.*, 1999, 647.

5 A. F. Garito and A. J. Heeger, *Acc. Chem. Res.*, 1974, **7**, 232.

6 S. Liu, S. N. Shaikh and J. Zubieta, *Inorg. Chem.*, 1989, **28**, 723.

7 P. E. Riley, S. F. Haddad and K. N. Raymond, *Inorg. Chem.*, 1983, **22**, 3090.

8 A. W. Addison, T. N. Rao, J. Reedijk, J. van Rijn and G. C. Verschoor, *J. Chem. Soc., Dalton Trans.*, 1984, 1349.

9 M. Bell, A. J. Edwards, B. F. Hoskins, E. H. Kachab and R. Robson, *J. Am. Chem. Soc.*, 1989, **111**, 3603; D. G. McCollum, C. Fraser, R. Ostrander, A. L. Rheingold and B. Bosnish, *Inorg. Chem.*, 1994, **33**, 2383.

10 E. Asato, M. Chinen, A. Yoshino, K. Sugiura and Y. Sakata, *Chem. Lett.*, 2000, 678.