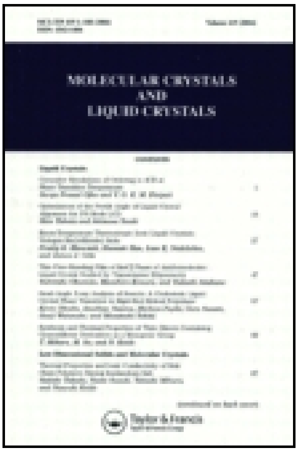

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Insertion of a π-π Stacked Chloranilate Pair into Two Phenoxo-Bridged Dinuclear Metal Cores

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Tetranuclear zinc(II) and nickel(II) complexes formulated as $[M_4(bpmp)_2(CA)_2](ClO_4)_2$ (M = Zn : **1**, Ni : **2**) have been synthesized, where Hbpmp and H_2CA are a multidentate dinucleating ligand and chloranilic acid, respectively. X-ray crystallography of **1**•2BuCN has revealed that the phenoxide moiety from $bpmp^-$ bridges two Zn(II) ions, which are further connected to another μ-phenoxo zinc pair by two π–π stacked CA^{2-} units in a double bis-bidentate fashion. Electrochemical study combined EPR techniques revealed that **1** was reduced at $E_{1/2}$ = –1.10 V in a one-step 2-electron process and the resultant two $CA^{\bullet 3-}$ radicals are antiferromagnetically coupled.

Keywords: tetranuclear metal complexes; phenoxide bridge; chloranilate ion; π–π stacking; X-ray crystallography

INTRODUCTION

Tetraoxolenes are redox-active organic molecules and can connect two metal ions in a bis-bidentate bridging fashion[1,2]. Since these can undergo not only a 1-electron oxidation but also stepwise 2-electron reduction processes, the ligands have the advantage to create a new type of multi-redox system capable of changing their magnetism by generating or disappearing radical(s) on the ligand center(s). Here we report a π–π stacked chloranilate pair as a double bis-bidentate bridging unit, which can connect two phenoxo-bridged dinuclear cores to produce a cyclic frame core characterized by $[M_4(\mu\text{-phenoxo})_2(\mu\text{-CA})_2]^{2+}$, where CA^{2-} is the dianion of chloranilic acid and a derivative of tetraoxolene. To our best knowledge, a π–π stacked chloranilate pair and its ability to bridge two dimetal cores are the first example[3], while a simple bis-bidentat bridging mode of a chloranilate unit has been widely recognized in many dinuclear metal complexes[1]. In this paper electrochemical behavior of the π–π stacked chloranilate pair as well as metal ions in $[M_4(bpmp)_2(CA)_2](ClO_4)_2$ (M = Zn : **1**, Ni : **2**) is also briefly reported.

EXPERIMENTAL

Preparations

Dinucleating ligand 2,6-bis[(2-pyridylmethyl)aminomethyl]-4-methylphenol (Hbpmp) was prepared by the literature method[4]. Other reagents were commercially available and used without further purification. Tetranuclear complexes **1** and **2** were obtained as follows: To a methanol solution containing Hbpmp and $Zn(ClO_4)_2 \cdot 6H_2O$ was added sodium chloranilate (Na_2CA), where their mole ratio was adjusted to be Hbpmp : Zn^{2+} : CA^{2-} = 2 : 4 : 2. The reaction mixture was refluxed for 1h, and the resultant dark green precipitate was collected, washed successively with methanol and ether, and then dried in vacuo. Recrystallization from *n*-butyronitrile gave needle-like crystals as the butyronitrile adduct **1**•2BuCN. Anal. Found: C, 49.60; H, 3.78; N, 9.39 %. Calcd for $C_{86}H_{80}N_{14}O_{18}Cl_6Zn_4$: C, 49.85; H, 3.89; N, 9.46 %. ESI mass [*m/z*]: 867.3 corresponding to $[Zn_4(bpmp)_2(CA)_2]^{2+}$. A similar reaction using $Ni(ClO_4)_2 \cdot 6H_2O$ instead of the zinc salt under the same conditions gave brown crystals **2**•2BuCN. Anal. Found: C, 50.50; H, 3.88; N, 9.56 %. Calcd for $C_{86}H_{80}N_{14}O_{18}Cl_6Ni_4$: C, 50.51; H, 3.94; N, 9.59 %. ESI mass [*m/z*]: 854.1 corresponding to $[Ni_4(bpmp)_2(CA)_2]^{2+}$.

Measurements and Instruments

Elemental analyses (C, H, N contents) were obtained at the Elemental Analysis Service Center of Kyushu University. Infrared (KBr pellets) and X-band EPR spectra were recorded on JASCO FT/IR-800 and JEOL JES-TE 300 spectrometers, respectively. Electrospray ionization (ESI) mass spectra were recorded on a Shimazu LCMS-2010 mass spectrometer. Cyclic voltammograms (CV) were recorded with a BAS CV-50W electrochemical analyzer.

Crystallographic measurement on a single crystal of **1** was made on a Rigaku R-AXIS RAPID at –50 °C. The crystal data and analytical details are as follows: Mo-Kα, λ = 0.71073 Å formula : $C_{86}H_{80}N_{14}O_{18}Cl_6Zn_4$, triclinic, space group $\bar{P}1$ (No. 2), $Z = 2$, a = 19.3581(6) Å, b = 26.1404(9) Å, c = 9.1524(3) Å, α=99.921(1)°, β=99.921(1)°, γ=90.020(1)°, V = 4562.1(2) Å^3, d_{calc} = 1.263 g/cm^3, $2\theta < 55.0°$, 11564 reflections and 5973 observed ($I > 3.00\sigma(I)$), Reflection/parameter ratio = 9.86, R = 0.070, R_w = 0.145. All the calculation was made using the Crystal Structure[5] software package of RIGAKU Corporation.

RESULTS AND DISCUSSION

The infrared spectra of the two complexes are nearly the same. The carbonyl stretching mode of the two CA $^{2-}$ units in each complex was appeared as a very strong band without splitting at 1552 cm^{-1} for **1** and at 1554 cm^{-1} for **2**, respectively, suggesting bis-bidentate bridging fashion for the both units[6]. Full structural characterization on the zinc(II) complex **1** was performed by X-ray crystallography. Figure 1 shows an ORTEP drawing of the cation structure together with the numbering scheme, where a half unit of the cation is crystallographically independent and related into the rest half by the inversion center. The multidentate ligand bpmp$^-$ bridges two zinc(II) ions by its phenoxide moiety with the distance of Zn(1)-Zn(2) = 3.802 Å, which is a typical value for the phenoxide-bridged dimetal cores[7]. One chloranilate unit bridges crystallographically inequivalent two zinc ions in a bis-bidentate fashion [Zn(1)-Zn(2A) = 7.796 Å], and paired to another unit by π–π stacking interaction. The interplanar separation is *ca.* 3.3 Å. The C-O bond distances in the CA^{2-} units, [C(32)–O(2) = 1.246(2) Å, C(33)–O(3) = 1.255(1) Å], are typical values for a bond order of 1.5, being in agreement with the bis-bidentate coordination.

Cyclic voltammograms (CV) of both complexes in degassed 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). As drawn in Figure 2a, complex **1** shows a quasi-reversible redox couple at $E_{1/2} = -1.04$ V with $\Delta E = 110$ mV, which was assigned to a 2-electron transfer process by the coulometric experiment. Because the metal ions in **1** are redox-inactive Zn(II), the redox couple is assigned to occur at the bridging CA^{2-} ligands. The EPR spectrum of the 2-electron reduced form generated by the controlled potential electrolysis in DMF showed a sharp singlet at $g = 2.005$ characteristic of an organic radical. Its life time $T_{1/2}$ was 165 sec at 298 K. The EPR signals for the reduced species were measured over the temperature range 103 ~ 173 K. Upon cooling, the signal intensity at

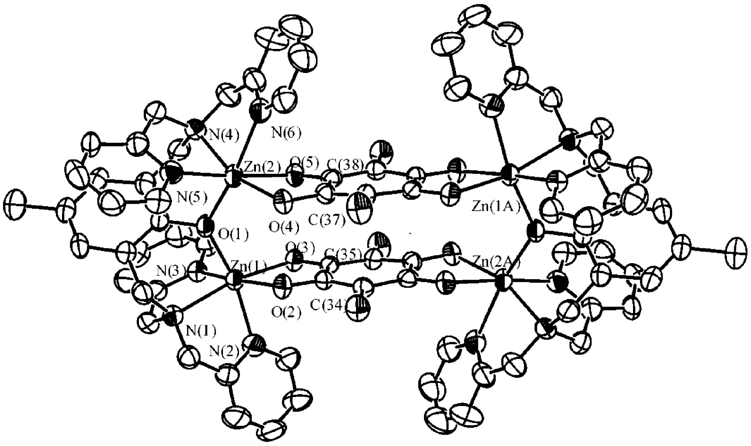

FIGURE 1 ORTEP drawing of $[Zn_4(bpmp)_2(CA)_2]^{2+}$.
Zn(1)–O(1) 2.107(9), Zn(1)–O(2) 2.070(9),
Zn(1)–O(3) 2.067(9), Zn(1)–N(1) 2.189(1),
Zn(1)–N(2) 2.277(1), Zn(1)–N(3) 2.087(7),
Zn(2)–O(1) 2.072(9), Zn(2)–O(4) 2.066(8),
Zn(2)–O(5) 2.054(1), Zn(2)–N(4) 2.168(1),
Zn(2)–N(5) 2.075(4), Zn(2)–N(6) 2.257(3),
Zn(1)–Zn(2) 3.802, Zn(1)–Zn(2A) 7.796 Å.

103 K decreased by 66% compared to that at 173 K. Upon heating to 173 K, the signal intensity recovered and the spectrum perfectly coincided to the original one measured before cooling down. This result clearly indicates that the two $CA\bullet^{3-}$ radicals are antiferromagnetically coupled, probably due to their short interplanar distance.

As shown in Figure 2b, the first reduction wave of **2** appears at $E_{1/2} = -1.14$ V, which is very close to the first reduction potential of **1**, suggesting a ligand-centered redox couple. However, the process was confirmed to be a 1-electron process by the coulometric experiment, and is followed by successive second 1-electron reduction with $E_{1/2} = -1.50$ V, unlike the case of **1**. Furthermore, complex **2** is irreversibly oxidized at +0.73 V and +1.18 V, both of which were confirmed to be 2-electron concerned oxidation. From the viewpoint of magnetochemistry, generating organic radical(s) on the CA unit(s) embedded in paramagnetic species **2** is of significant interest. However, unfortunately, electrochemically generated reduced and oxidized species are too unstable to isolate or measure EPR spectra for the study of its magnetism. In addition to the magnetism of **2**, details on its electrochemistry are now under investigation.

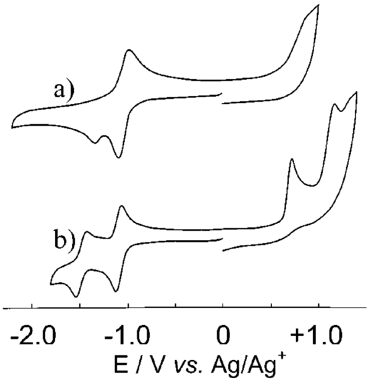

FIGURE 2 Cyclic voltammograms of **1** (a) and **2**(b)

Acknowledgments

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