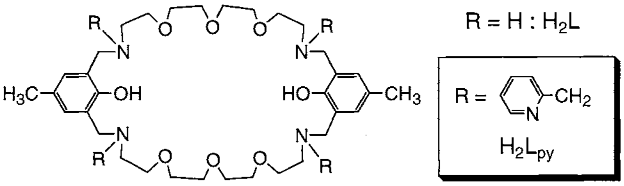
New Pyridine-modified Macrocycle and Its Ability to Encapsulate Four Divalent Metal Ions [Nickel(II), Manganese(II), and Zinc(II)] into the Ring

Eiji Asato,* Hideki Furutachi, Chikahiro Tamanaha, Hideo Matsudaira, Masaaki Ohba,† Hisashi Ōkawa,† and Masahiro Mikuriya††
Department of Chemistry, Biology and Marine Science, College of Science, University of the Ryukyus, Nishihara, Okinawa 903-0213
†*Department of Chemistry, Faculty of Science, Kyushu University, Hakozaki, Fukuoka 812-8581*
††*Department of Chemistry, School of Science, Kwansei Gakuin University, Uegahara, Nishinomiya 662-8501*

(Received March 15, 1999; CL-990171)

A large phenol- and polyether chain-based macrocycle H_2L_{py} possessing four pyridylmethyl groups as pendant donors was prepared and its ability to encapsulate four divalent metal ions [Ni(II), Mn(II), and Zn(II)] was confirmed by IR and NMR spectroscopy and X-ray crystallography.

Tetranuclear metal complexes in which the metal ions are located in close proximity are of current interest,[1] as models of multi-electron redox reactions, such as the oxygen-evolving complex (OEC) of photosystem II of green plants.[2] In an earlier stage of our program to produce tetranuclear metal complexes, we have synthesized a phenol-based large macrocycle H_2L,[3] which had been designed to encapsulate four metal ions into the ring. However, the macrocycle could not give any tetranuclear complexes, instead, functioned as a dinucleating ligand. Thus, with the aim of strengthening metal binding ability to produce tetra- or polynuclear structures, we have designed and synthesized a new functionalized macrocycle H_2L_{py}, which possesses four pyridylmethyl groups onto the secondary amines of the reduced macrocycle. Herein we report its property as a tetranucleating ligand toward divalent metal ions Ni(II), Mn(II), and Zn(II). And, further, structural characterization and magnetic property are described for the isolated complexes $[M_4(L_{py})(CH_3CO_2)_4](ClO_4)_2{\bullet}3H_2O$ (M = Ni : **1**, Mn : **2**, and Zn : **3**). To our best knowledge, H_2L_{py} is the first example as a stable large macrocycle which can be isolated and afford a type of "dimer of dimers" tetranuclear arrangement[4] toward different metal species.



Functionalized ligand H_2L_{py} used in this study

The new macrocyclic ligand was prepared by general N-alkylation of H_2L with 2-(chloromethyl)pyridine.[5] As the representative case, the tetranuclear Ni(II) complex **1** was synthesized as follows: To a solution of 100 mg (0.987 mmol) of H_2L_{py} dissolved in 10 cm^3 of methanol was added 89 mg (3.95 mmol) of nickel(II) acetate dihydrate. The reaction mixture was heated at 50 - 60 °C for 5 min and then an excess of $NaClO_4$ (97.0 mg, 78.9 mmol) was added. The precipitated green microcrystals were collected, washed with methanol, diethyl ether, and then air-dried. Yield: 89 mg (52%).[6] A similar reaction using manganese(II) acetate dihydrate and zinc(II) acetate, instead of the nickel salt, under the same conditions (reaction scale and stoichiometry) gave off-white microcrystals **2** (Yield: 48%)[7] and colorless microcrystals **3** (46%),[8] respectively.

The three complexes on KBr disks show practically the same IR spectral pattern, indicating essentially the same molecular structure in their solid state. The four acetate groups included in each complex show a set of very strong absorption for their ν_{as}(COO) and ν_s(COO) vibrations.[9] The separation between the two vibrations (162 - 175 cm^{-1}) is typical value for that of bridging carboxylate.[10] ^1H NMR spectrum of the metal-free ligand in CD_3CN shows a single doublet at 8.49 ppm for the protons at 6-position of the pyridine units, while it shifted to lower field and separates into two doublets at 8.62 and 8.70 ppm in the spectrum of **3**, indicating that the four pyridyl groups are involved in coordination in the solution. Molar conductance of **1** (290 S cm^2 mol^{-1}), **2** (269 S cm^2 mol^{-1}), **3** (310 S cm^2 mol^{-1}) measured in acetonitrile falls within the range reported for a 1: 2 electrolyte type.[11] All these results suggest that the functionalized macrocycle $(L_{py})^{2-}$ binds four metal ions to form $[M_4(L_{py})(\mu\text{-}CH_3COO)_4]^{2+}$ cation both in solid and solution. In fact, the suggested structure was confirmed by X-ray crystallography to the nickel(II) complex as the acetonitrile adduct $[Ni_4(L_{py})(\mu\text{-}CH_3COO)_4](ClO_4)_2{\bullet}2CH_3CN$ (**1'**).[12]

Figure 1 shows the structure of $[Ni_4(L_{py})(\mu\text{-}CH_3COO)_4]^{2+}$ with the numbering scheme. The compound resides on a crystallographically imposed center of symmetry, relating the primed and unprimed atoms. The macrocycle $(L_{py})^{2-}$ has a planar form and linear conformation with respect to its polyether chains, producing a large cavity in the center of the ring, into which four Ni(II) ions are encapsulated as a pair of μ-phenoxo-bis(μ-carboxylato)dinuclear species. The two nickel ions in each dinuclear core are at a distance of 3.338(1) Å, and crystallo-

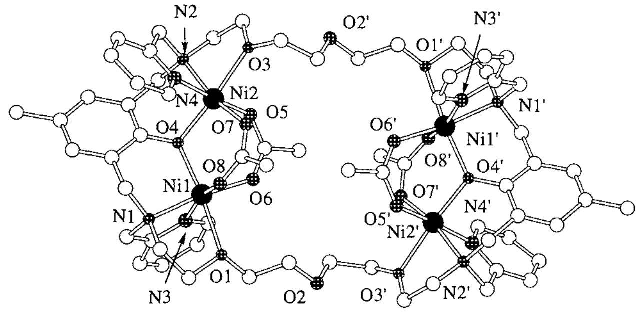


Figure 1. Perspective view and atom-numbering scheme of complex cation in **1** as the acetonitrile adduct. Selected bond distances (Å) and angle (°) around Ni1 and Ni2: Ni1-O1 = 2.140(5), Ni1-O4 = 2.006(4), Ni1-O5 = 2.026(5), Ni1-O7 = 2.013(5), Ni1-N1 = 2.096(7), Ni1-N3 = 2.087(6), Ni2-O3 = 2.256(6), Ni2-O4 = 1.979(5), Ni2-O6 = 2.015(3), Ni2-O8 = 2.023(5), Ni2-N2 = 2.108(4), Ni2-N4 = 2.092(6), Ni1-O4-Ni2 = 113.8(2).

graphically inequivalent. However, the metal ions have essentially the same coordination geometry in distorted octahedron with N_2O_4 donor sets. Concerning bond distances, the Ni(II)-N(amin, py) interaction (average 2.096 Å), and all the Ni(II)-O bonds (average 2.010 Å), except for the ether oxygens, fall well within the range of distances observed for typical Ni(II)-nitrogen and -oxygen coordination compounds. The bond distances between the Ni(II)-O(ether) linkages (average 2.198 Å) are slightly longer than the other Ni(II)-O interactions, probably due to the poorer affinity of the ether oxygen to the metal. The two dinuclear units are far apart with the distances Ni1-Ni1' = 8.846(1) Å, Ni1-Ni2' = 8.163(1) Å, and N2-Ni2'= 8.793(1) Å, respectively.

Magnetic susceptibilities of **1** and **2** were measured in the temperature range 4.2 - 290 K. Their temperature dependences of the magnetic susceptibility (χ_A) and effective magnetic moment (μ_{eff}) per Ni(II) and Mn(II) are shown in Figure 2 and Figure 3, respectively. The μ_{eff} values 3.07 and 5.46 from each complex at room temperature indicate that the two metal ions are in the high spin state, *i.e.* S=1 for Ni(II) and S=5/2 for Mn(II), respectively. Slight increase of μ_{eff} in **1** with decreasing temperature, with the maximum at ca. 15 K, suggests operation of weak ferromagnetic coupling between the two Ni(II) ions. On the other hand, continuous decrease of μ_{eff} in **2** with decreasing temperature evidently indicates antiferromagnetic coupling between the two Mn(II) ions. Their magnetic beghavior was confirmed by the best-fitting technique between observed and theoretical magnetic data. In each complex, because of large separation and no existence of bridging ligand between the two dinuclear units, magnetic interaction between the units can be neglected. Thus, their magnetic data were analyzed with Van Vleck equations based on isotropic Heisenberg model ($\mathscr{H} = -2JS_1 \bullet S_2$; $S_1 = S_2 = 1$ for **1** and $S_1 = S_2 = 5/2$ for **2**), to give the best-fitting parameters g = 2.13, J = +3.1 cm^{-1}, $N\alpha$ = 200 x 10^{-6} cm^3 mol^{-1}, and θ = -3.5 K for **1**,[13] and g = 2.00, J = -4.6 cm^{-1}, and $N\alpha$ = 0 cm^3 mol^{-1} for **2**.

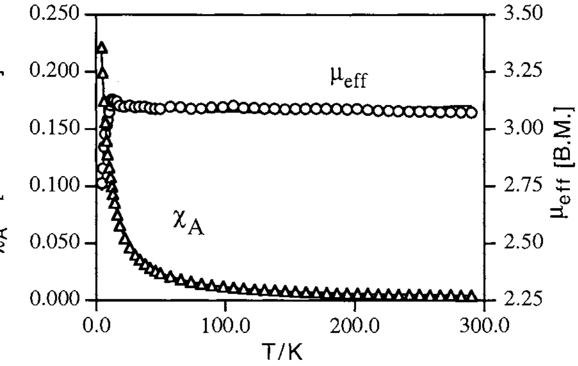


Figure 2. Temperature dependences of χ_A (△) and μ_{eff} (○) of **1**. Solid curves are calculated for g = 2.13, J = +3.1 cm^{-1}, $N\alpha$ = 200 x 10^{-6} $cm^3 mol^{-1}$, and θ= -3.5 K.

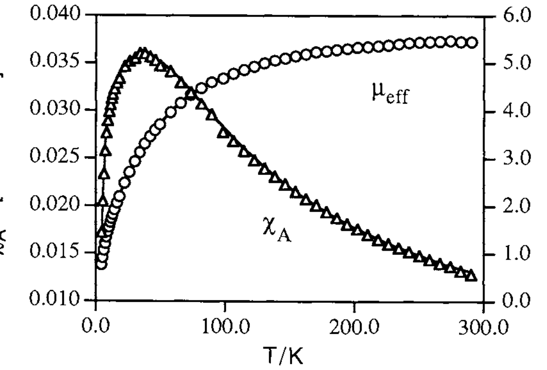


Figure 3. Temperature dependences of χ_A (△) and μ_{eff} (○) of **2**. Solid curves are calculated for g = 2.00, J = -4.6 cm^{-1}, and $N\alpha$ = 0 cm^3 mol^{-1}.

This work was supoported in part by a Grant-in-Aid for Scientific Research (No. 08404046) and Grant-in-Aid for Scientific Research on Priority Areas (No. 10149242 "Metal-assembles Complexes") from the Ministry of Education, Science, Sports and Culture, Japan.

References and Notes

1 A. J. Eawards, B. F. Hoskins, E. H. Kachab, A. Markiewicz, K. S. Murray, and R. Robson, *Inorg. Chem.*, **31**, 3585(1992); M. J. Grannas, B. F. Hoskins, and R. Robson, *Inorg. Chem.*, **33**, 1071(1994); P. E. Kruger and V. McKee, *Chem., Commun.*, **1997**, 1341; S. Mohanta, K. K. Nanda, R. Werner, W. Haase, A. K. Mukhejee, S. K. Dutta, and K. Nag, *Inorg. Chem.*, **36**, 4656(1997).

2 G. Dismukes, *Photochem. Photobiol.*, **42**, 187(1986); G. Renger, *Angew. Chem., Int. Ed. Engl.*, 1987, **26**, 643.

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

4 K. Motoda, H. Sakiyama, N. Matsumoto, H. Ōkawa, and D. Fenton, *J. Chem. Soc. Dalton Trans.*, **1995**, 3419.

5 To a solution of 10.06 g (0.016 mol) of H_2L and 11.46 g (0.068 mol) of $NaHCO_3$ dissolved in 150 cm^3 of methanol was added 150 cm^3 of a methanol solution containing 11.186 g (0.068 mol) of 2-(chloromethyl)pyridine monohydrocloride. The reaction mixture was refluxed with stirring under Ar atmosphere for 17 h. The mixture was pored into 100 cm^3 of cold water, and then extracted with $CHCl_3$ (100 cm^3 x 3). The combined organic layer was dried with anhydrous Na_2SO_4, and then evaporated to dryness. To the red sticky oil as the residue a small quantity of aceton was added, giving a off-white powder. The powder was washed with cold methanol and then recrystalized from ethanol. Yield: 5.0 g (32%) : ^{1}H NMR (CD_3CN) : δ 8.49 (d, 4H), 7.61 (d, 4H), 7.47 (d, 4H), 7.12 (m, 4H), 6.91 (s, 4H), 3.84 (s, 8H), 3.77 (s, 8H), 3.62-3.48 (m, 24H), 2.77 (t, 8H), 2.21 (s, 6H).

6 Found: C, 45.86; H, 5.11; N, 6.43; Ni, 13.55%. Anal. Calcd for $C_{66}H_{92}O_{27}N_8Cl_2Ni_4$: C, 45.69; H, 5.34; N, 6.46; Ni, 13.53%.

7 Found: C, 46.44; H, 5.17; N, 6.61; Mn, 12.60%. Anal. Calcd for $C_{66}H_{92}O_{27}N_8Cl_2Mn_4$: C, 46.07; H, 5.39; N, 6.51; Mn, 12.77%.

8 Found: C, 45.03; H, 5.08; N, 6.32; Zn, 14.45%. Anal. Calcd for $C_{66}H_{92}O_{27}N_8Cl_2Zn_4$: C, 44.99; H, 5.34; N, 6.26; Zn, 14.84%.

9 **1**: ν_{as} = 1606 cm^{-1}, ν_s =1431 cm^{-1}. **2**: ν_{as} = 1597 cm^{-1}, ν_s = 1435 cm^{-1}. **3**: ν_{as} = 1605 cm^{-1}, ν_s = 1435 cm^{-1}.

10 K. Nakamoto, "Infrared and Raman Spectra of Inorganic and Coordination Compounds, 3rd ed, Wiley, New York(1978), p.227.

11 W. J. Geary, *Coord. Chem. Rev.*, 7, 81(1971).

12 A single crystal used for X-ray analysis was obtained by recrystalization of **1** from acetonitrile. Crystal data of **1'**: $C_{70}H_{92}O_{24}N_{10}Cl_2Ni_4$; FW = 1762.02; Enraf-Nonius CAD4-Express; triclinic, space group $P\bar{1}$ (# 2), Z = 1; a = 12.568(1) Å, b = 12.842(1) Å, c = 15.486(2) Å; α = 97.47(1)°, β = 107.964(1)°, γ = 116.96(1)°, V = 2009.0(5) Å^3, D_{calcd} = 1.457 g/cm^3; μ = 11.39 cm^{-1} (Mo-Kα, λ =0.71073 Å); $2\theta_{max}$ = 52.6°. 8128 reflections and 4453 observed ($I > 3.00\sigma(I)$), and 483 parameters. R = 0.067, Rw =0.088. The structure was solved by a direct method and refined by full-matrix least-squares method using MolEN program package.

13 The Weiss constant θ was introduced as the correction term to account for a secondary effect such as zero-field splitting of S_{Ni} = 1 or very weak antiferromagnetic interaction between the dimer pair. T. Koga, H. Furutachi, T. Nakamura, N. Fukita, M. Ohba, K. Takahashi, and H. Ōkawa, *Inorg. Chem.*, **37**, 989(1998).