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Template Synthesis and Structure of a Dilead(II) Complex of a Macrocycle with N_8O_2 Donor Set

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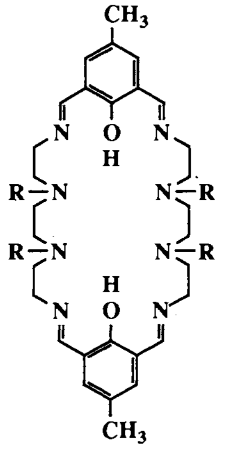
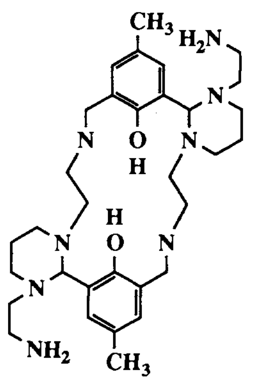
A new tetranucleating macrocycle (H_2L) comprised of 2,6-diformyl-4-methylphenol and 1,8-diamino-3,6-dimethyl-3,6-diazaoctane in the 2:2 ratio was obtained as a lead(II) complex of the formula $Pb_2(H_2L)(dmf)_4(ClO_4)_4$, whose crystal structure was determined by X-ray method.

The design of elaborate tetranucleating ligands has received significant recent attention with the hope to mimic the active site structure and function of the water oxidation center (WOC) of photosystem II in green plants.1) We previously reported the template synthesis of tetranuclear copper(II) complexes of the macrocycle **1a** (R=H),2) the 2:2 condensation product of 2,6-diformyl-4-methylphenol and 1,8-diamino-3,6-diazaoctane (trien). In order to synthesize tetramanganese complexes of **1a** as an active site model of WOC it was desired to prepare precursor complexes of a labile metal ion such as lead(II). In spite of many efforts, however, we are unsuccessful in obtaining lead complexes of **1a** by similar template reaction. In the related study using 1,9-diamino-3,7-diazanonane in place of trien, it was found that an unusual condensation occurs between the two secondary amino groups of the



1a :R=H
1a :R=CH_3



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tetramine and a carbonyl group of 2,6-diformyl-4-methylphenol to form a hexahydropyrimidine ring, providing the very rare macrocycle **2**.3) In order to avoid the unusual condensation it is advisable to use a tetramine alkylated at the secondary amino nitrogens. In this study template synthesis of the macrocycle **1b** ($R=CH_3$) was attempted using 1,8-diamino-3,6-dimethyl-3,6-diazaoctane instead of trien. Here we report the synthesis and structure of a dilead(II) complex of **1b** (abbreviated as H_2L hereafter).

To a stirred methanol solution (10 cm^3) of 2,6-diformyl-4-methylphenol (164 mg, 1 mmol) and lead(II) perchlorate trihydrate (460 mg, 1 mmol) was dropwise added a methanol solution (5 cm^3) of 1,8-diamino-3,6-dimethyl-3,6-diazaoctane (174 mg, 1 mmol), and the resulted yellow mixture was gently refluxed for 30 minutes and allowed to stand at ambient temperature to form yellow microcrystals4) (Yield 400 mg). They were dissolved in a minimum amount of N,N-dimethylformamide (dmf) and the dmf solution was diffused with 2-propanol to give $Pb_2(H_2L)(dmf)_4(ClO_4)_4$ as well-grown yellow prisms. Anal. Found: C, 32.42; H, 4.72; N, 9.80%. Calcd for $C_{46}H_{80}Cl_4N_{12}O_{22}Pb_2$: C, 32.32; H, 4.72; N, 9.83%.

The structure of the complex was determined by single crystal X-ray method.5) The crystal consists of the centrosymmetric complex cation $[Pb_2(H_2L)(dmf)_4(ClO_4)_2]^{2+}$ and two perchlorate ions. The ORTEP view of the complex cation is shown in Fig. 1, together with the numbering scheme. The selected bond distances and angles are given in Table 1.6)

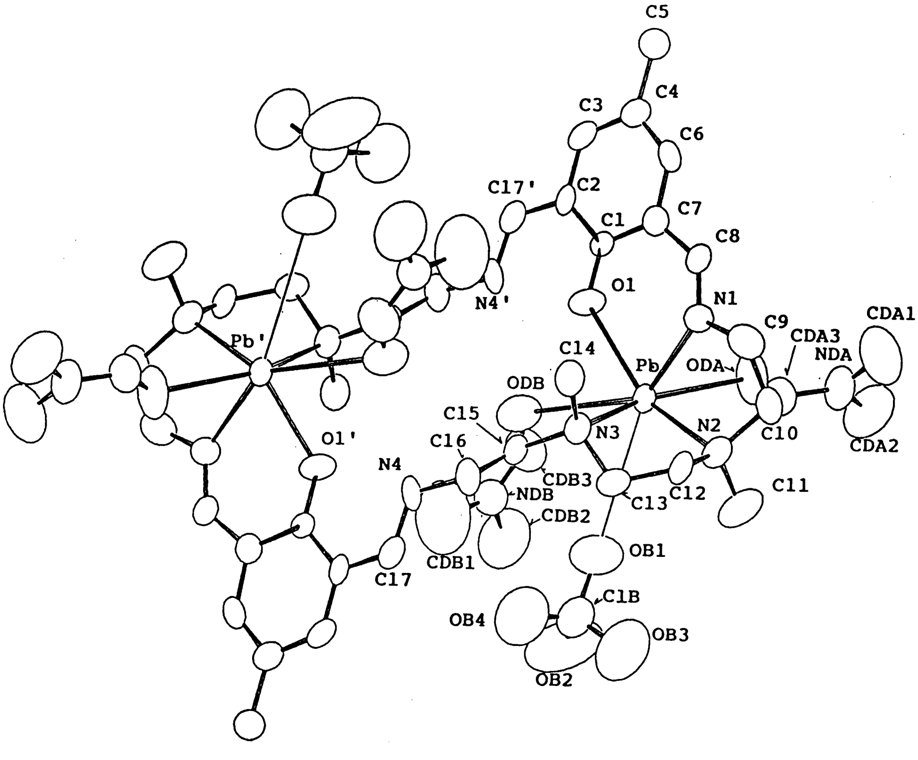

Fig. 1. The ORTEP view of $[Pb_2(H_2L)(dmf)_4(ClO_4)_2]^{2+}$.

Table 1. Selected Bond Distances and Angles

Bond distances/Å		Bond angles/deg			
Pb—O1	2.39(1)	O1—Pb—N1	75.0(4)	O1—Pb—N2	141.3(4)
Pb—N1	2.42(1)	O1—Pb—N3	93.6(4)	O1—Pb—ODA	102.1(4)
Pb—N2	2.59(1)	O1—Pb—ODB	64.8(3)	N1—Pb—N2	69.8(4)
Pb—N3	2.61(1)	N1—Pb—N3	88.9(5)	N1—Pb—ODA	75.4(5)
Pb—ODA	2.61(2)	N1—Pb—ODB	139.4(4)	N2—Pb—N3	70.7(4)
Pb—ODB	3.16(1)	N2—Pb—ODA	84.3(5)	N2—Pb—ODB	145.1(4)
Pb—OB1	3.52(2)	N3—Pb—ODA	153.9(4)	N3—Pb—ODB	88.3(4)
Pb ... Pb'	8.098(2)	ODA—Pb—ODB	117.2(5)		

The X-ray structure analysis has revealed that the ligand involved in the complex is indeed the 2:2 condensation product of the constituents, 2,6-diformyl-4-methylphenol and 1,8-diamino-3,6-dimethyl-3,6-diazaoctane, and contains two Pb(II) ions. Each Pb(II) ion is bonded to the phenolic oxygen O1, imino nitrogen N1, and amino nitrogens N2 and N3. The imino nitrogens N4 and N4' are free from the coordination to the Pb(II) ions. The Pb-O1 bond distance (2.39(1) Å) is significantly short and suggests that the phenolic oxygen coordinates to the Pb(II) ion in the deprotonated form.[7-9] It is likely that the protons of H_2L is attached to the imino nitrogen N4 (N4') and hydrogen bonded to the adjacent phenolic oxygen O1' (O1). The O1-C1-C2-C17'-N4' entry forms a good coplane; the deviations of the atoms from the least-squares plane being less than 0.01 Å. The Pb-N1 bond distance (2.42(1) Å) is also short compared with the Pb-N2 and Pb-N3 bond distances (2.51(9) and 2.61(1) Å, respectively). The open face of the Pb coordination sphere is occupied by two dmf oxygens (ODA and ODB), with normal Pb-ODA bond length (2.61(2) Å) but elongated Pb-ODB length (3.16(1) Å). Further, a perchlorate oxygen (OB1) interacts with the Pb(II) ion but the Pb-OB1 separation (3.52(2) Å) is too large to be taken as coordination bond. Thus, the surrounding about each Pb(II) ion is of six-coordination markedly distorted from regular octahedron. The separation between two Pb(II) ions is 8.098(2) Å. Two perchlorate ions are captured in the crystal lattice.

Our preliminary studies have confirmed that this dilead(II) complex acts as a good precursor for tetranuclear complexes of transition metal ions.[10] Studies on those tetranuclear complexes of H_2L and its homologs are under way in our laboratory.

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4) Analytical results agree with $Pb_2(H_2L)(H_2O)_2(ClO_4)_4$. Found: C, 27.85; H, 3.99; N, 8.29%. Calcd for $C_{34}H_{56}Cl_4N_8O_{20}Pb_2$: C, 28.10; H, 3.89; N, 7.71%.
5) Crystal data: formula=$C_{46}H_{80}Cl_4N_{12}O_{22}Pb_2$, F.W.=1709.42, triclinic, space group $P\bar{1}$, a=11.957(2) Å, b=12.344(3) Å, c=11.363(2) Å, α=97.90(2)°, β=100.27(2)°, γ=82.70(2)°, V=1625.7(6) Å^3, Z=1, D_c=1.747 cm^{-1}, μ(Mo-Kα)=54.5 cm^{-1}, R=0.0516, R_W=0.0594. 2991 reflections were measured in the range $2.5° \leq 2\theta \leq 40°$ and 2542 with $F>3\sigma(F)$ were assumed to be observed. Intensity data were collected on a Rigaku AFC-5 automated four-cycle diffractometer using graphite-monochromated Mo-Kα radiation. The structure was solved by heavy-atom method and refined by the block-diagonal least-squares method using the UNICS-III program system. Corrections for Lorentz and polarization factors and empirical absorption effects were made.
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