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Template Synthesis and Structure of a Dinuclear Lead(II) Complex of Novel Macrocycle Derived from 2,6-Diformyl-4-methylphenol and 1,9-Diamino-3,7-diazanonane

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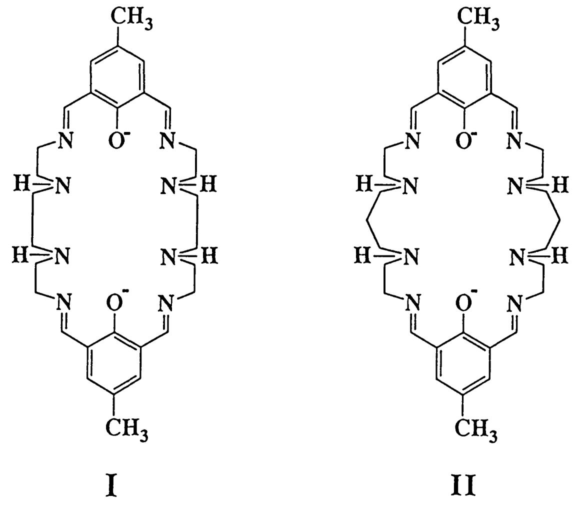
Synopsis. The reaction of 2,6-diformyl-4-methylphenol and 1,9-diamino-3,7-diazanonane in methanol in the presence of lead(II) ion forms a dinuclear lead(II) complex of a very rare macrocycle containing hexahydropyrimidine rings. The structure of the complex is determined by single crystal X-ray method.

The design of new elaborate tetranucleating ligands is becoming the subject of recent interest to mimic the oxygen evolving center of photosystem II in green plants where a tetranuclear manganese cluster plays an essential role to oxidize water to dioxygen.[1] For the purpose we recently reported the template synthesis of a macrocycle **I** (see Fig. 1), the 2 : 2 condensation product of 2,6-diformyl-4-methylphenol and 1,8-diamino-3,6-diazaoctane (trien), as a tetranuclear copper(II) complex.[2] In spite of many efforts, however, we were unsuccessful in synthesizing the corresponding tetracopper(II) complex of the larger homolog **II** by analogous template reactions. Our attempts to synthesize tetranuclear manganese complexes of **I** and **II** were also all in vain.

One of promising ways for the synthesis of tetranuclear transition metal complexes of **I** and **II** is the use of proper precursor complexes of labile metal ions such as lead(II). Thus, we attempted to synthesize lead(II) complexes of **I** and **II** by template reactions. The isolated products from these reactions, however, showed two IR vibrations characteristic of primary amine group in the region 3350—3200 cm^{-1}, suggesting that the cyclization is incomplete or unusual condensation occurs when lead(II) ion is adopted as the template ion. In this study a lead(II) complex of the 2 : 2 condensation product (abbreviated as H_2L) between 2,6-diformyl-4-methylphenol and 1,9-diamino-3,7-diazanonane was obtained as large single crystals. We herein report the crystal structure of the lead(II) complex.



I II

Fig. 1. Chemical structures of tetranucleating macrocycles.

Experimental

Materials. 2,6-Diformyl-4-methylphenol was obtained by the modified Duff reaction.[3] 1,9-Diamino-3,7-diazanonane was synthesized according to the method of Anderegg.[4]

Preparation of Complex. A mixture of lead(II) perchlorate trihydrate (920 mg, 2 mmol) and 2,6-diformyl-4-methylphenol (328 mg, 2 mmol) in absolute methanol (40 cm^3) was refluxed with stirring for 20 min to form a clear yellow solution. This solution was dropwise added to a stirred solutiin of 1,9-diamino-3,7-diazanonane (320 mg, 2 mmol) in methanol (20 cm^3) and the mixture was refluxed for two hours to give yellow microcrystals. They were separated by filtration, washed with absolute methanol, and dried over P_2O_5 in a vacuum desiccator. The yield was 1.17 g. The crude product was dissolved in *N,N*-dimethylformamide (DMF) and the solution was layered with absolute ether. After one week well-grown single crystals were obtained.

Anal. Found: C, 32.49; H, 4.89; N, 10.60%. Calcd for $Pb_2(H_2L)(ClO_4)_4(DMF)_6$ ($C_{50}H_{90}Cl_4N_{14}O_{24}Pb_2$): C, 32.86; H, 4.96; N, 10.73%.

Crystal Structural Analysis. A crystal of approximate dimensions of 0.4×0.2×0.1 mm^3 was used for the structural analysis. Intensities and lattice parameters were obtained on a Rigaku Denki AFC-5 automated four-circle diffractometer with graphite-monochromatized Mo *Kα* radiation (λ= 0.71069 Å) at 20±1 °C. Three standard reflections were mon-

Table 1. Crystal Data for $Pb_2(H_2L)(ClO_4)_4(DMF)_6$

Formula	$C_{50}H_{90}Cl_4N_{14}O_{24}Pb_2$
F.W.	1827.56
Cryst. syst.	Monoclinic
Space group	$P2_1/n$
a/Å	19.295(3)
b/Å	11.552(2)
c/Å	16.762(3)
β/deg	107.90(2)
V/Å^3	3555(1)
Z	2
D_x/g cm^{-1}	1.707
μ(Mo $K\alpha$)/cm^{-1}	14.3
R/%	5.92
R_w/%	8.07

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itored every 100 reflections and showed no systematic decrease in the intensity. Corrections for absorption effects were made by Furnas method.[5] For the intensity data collections the ω–2θ scan mode was used at a scan rate of $2^\circ\,\mathrm{min}^{-1}$ in the range $2.5^\circ<2\theta<50^\circ$. The scan width was $(1.00+0.5\tan\theta)^\circ$. The octant measured was $(+h, +k, \pm l)$. 3336 independent reflections with $|F_o|>3\sigma(|F_o|)$ were used for the analysis. Crystal data are summarized in Table 1.

The structure was solved by the standard heavy-atom method and refined by the block-diagonal least-squares method, where the function minimized is $\Sigma w(|F_o|-|F_c|)^2$ and equal weight (w=1) was adopted for all reflections. The contributions for hydrogen atoms bound to carbons were introduced in the calculated positions. These hydrogen atoms were included in the structure factor calculation but not refined. The atomic scattering factors were taken from Ref. 6. All computations were performed on a FACOM M 780 computer at the Computer Center of Kyusyu University using UNICS III program system.[7] The final atomic coordinates are given in Table 2. Tables of observed and calculated structure factors, listing of atomic positional and anisotropic thermal parameters, and full lists of bond lengths and angles with their estimated standard deviations have been deposited as Document No. 8990 at the Office of the Editor of Bull. Chem. Soc. Jpn.

Table 2. Final Atomic Coordinates for Non-Hydrogen Atoms ($\times10^4$) of $Pb_2(H_2L)(ClO_4)_4(DMF)_6$

Atom	x	y	z	B_{eq}
Pb	211.7(5)	1828.3(6)	1658.2(5)	3.0
O	595(8)	224(10)	1086(9)	3.9
N1	1101(9)	2755(12)	612(9)	3.0
N2	−194(9)	1920(16)	−832(10)	4.4
N3	1549(8)	2203(12)	2023(8)	2.6
N4	803(9)	775(15)	2938(10)	4.0
C1	1175(10)	6(13)	882(10)	2.2
C2	1281(12)	−1137(16)	617(11)	3.4
C3	786(11)	−2047(16)	611(12)	4.2
C4	1913(12)	−1421(17)	367(11)	3.7
C5	2424(12)	−587(17)	392(12)	3.8
C6	3092(13)	−825(23)	116(15)	5.6
C7	2322(11)	523(18)	678(12)	3.5
C8	1736(10)	836(16)	926(11)	3.1
C9	1697(10)	2082(15)	1211(10)	2.8
C10	1060(12)	2588(17)	−301(12)	3.7
C11	303(13)	2867(14)	−860(14)	4.4
C12	1252(13)	4010(16)	824(12)	4.0
C13	1233(12)	4197(18)	1706(13)	4.2
C14	1722(12)	3404(17)	2315(12)	4.2
C15	1946(11)	1329(16)	2671(11)	3.2
C16	1560(12)	1207(18)	3332(12)	4.1
Cl1	−1485(4)	4244(5)	1118(4)	5.4
O1	−2035(11)	4198(17)	339(12)	8.6
O2	−1586(14)	3302(20)	1603(14)	10.7
O3	−1547(15)	5293(16)	1529(13)	9.9
O4	−814(11)	4154(19)	987(13)	8.7
Cl2	3949(3)	2567(5)	1834(4)	4.8
O5	4648(8)	3106(17)	2142(10)	6.6
O6	3882(13)	1675(20)	2313(14)	11.0
O7	3439(11)	3370(18)	1761(22)	14.2
O8	3869(15)	2162(24)	1013(14)	12.2
OD1	313(8)	3177(15)	3020(10)	5.5
ND1	−318(11)	4443(17)	3558(12)	5.3
CD1	−644(23)	3545(30)	3926(21)	10.6
CD2	−574(16)	5600(24)	3587(19)	7.1
CD3	112(14)	4173(21)	3122(15)	5.6
OD2	−742(8)	42(14)	1612(9)	5.1
ND2	−1731(10)	−243(20)	2029(11)	5.9
CD4	−1731(22)	−1494(33)	1985(21)	11.2
CD5	−2295(16)	294(42)	2296(20)	11.5
CD6	−1248(13)	409(25)	1835(14)	5.7
OD3	−4729(10)	5768(15)	1183(11)	6.4
ND3	−4011(11)	4647(19)	673(12)	5.8
CD7	−3806(17)	3466(22)	533(18)	7.3
CD8	−3687(16)	5596(25)	350(18)	7.1
CD9	−4501(14)	4832(22)	1066(15)	5.4

Results and Discussion

The ORTEP view of the essential part of the complex is shown in Fig. 2 together with the numbering system. The selected bond distances and angles are given in Table 3.

The crystal is comprised of a very rare macrocycle in the neutral form (H_2L), two Pb(II) ions, four perchlorate ions, and six DMF molecules. There is an inversion center at the center of the complex molecule. The macrocycle H_2L is formed by the 2:2 condensation between 2,6-diformyl-4-methylphenol and 1,9-diamino-3,7-diazanonane as follows: The tetramine condenses through a primary amino group with a formyl group of one 2,6-diformyl-4-methylphenol to form C=N linkage and through two secondary amino groups with a formyl group of another 2,6-diformyl-4-methylphenol to form six-membered hexahydropyrimidine ring. One of the primary amino groups of the tetramine remains intact. The chemical structure of the macrocycle is shown in Fig. 2.

Each Pb(II) ion is coordinated by a phenolic oxygen, two nitrogens (N1 and N3) of a hexahydropyrimidine ring, and an intact primary amino nitrogen (N4). The azomethine nitrogen N2 is free from the coordination to the Pb(II) ion. The separation between the two Pb ions is 6.828(2) Å.

The Pb–O (phenolic oxygen) bond distance (2.31(1) Å) is considerably short, suggesting that the phenolic oxygen coordinates to the Pb in the deprotonated form. It is likely that the protons of H_2L are attached to the imino nitrogens, though this can not be proved from our X-ray structure analysis. The hexahydropyrimidine ring assumes usual chair form so as to allow the coordination of both nitrogen atoms (N1 and N3) to the Pb(II)

Table 3. Selected Bond Distances (Å) and Angles (deg) for $Pb_2(H_2L)(ClO_4)_4(DMF)_6$

Bond distance/Å					
Pb–Pb	6.828(2)	Pb–O	2.31(1)	Pb–N1	3.00(2)
Pb–N3	2.50(2)	Pb–N4	2.42(2)	Pb–O4	3.32(2)
Pb–OD1	2.72(2)	Pb–OD2	2.75(2)		

Bond angles/deg			
O–Pb–N1	74.4(5)	O–Pb–N3	78.6(5)
O–Pb–N4	80.9(5)	O–Pb–O4	137.9(5)
O–Pb–OD1	149.1(4)	O–Pb–OD2	71.5(5)
N1–Pb–N3	49.4(4)	N1–Pb–N4	119.9(5)
N1–Pb–O4	84.4(5)	N1–Pb–OD1	112.3(5)
N1–Pb–OD2	138.5(4)	N3–Pb–N4	72.6(5)
N3–Pb–O4	113.9(5)	N3–Pb–OD1	83.9(5)
N3–Pb–OD2	140.2(5)	N4–Pb–O4	140.8(6)
N4–Pb–OD1	69.7(5)	N4–Pb–OD2	77.1(5)
O4–Pb–OD1	72.7(5)	O4–Pb–OD2	105.9(5)
OD1–Pb–OD2	109.1(5)		

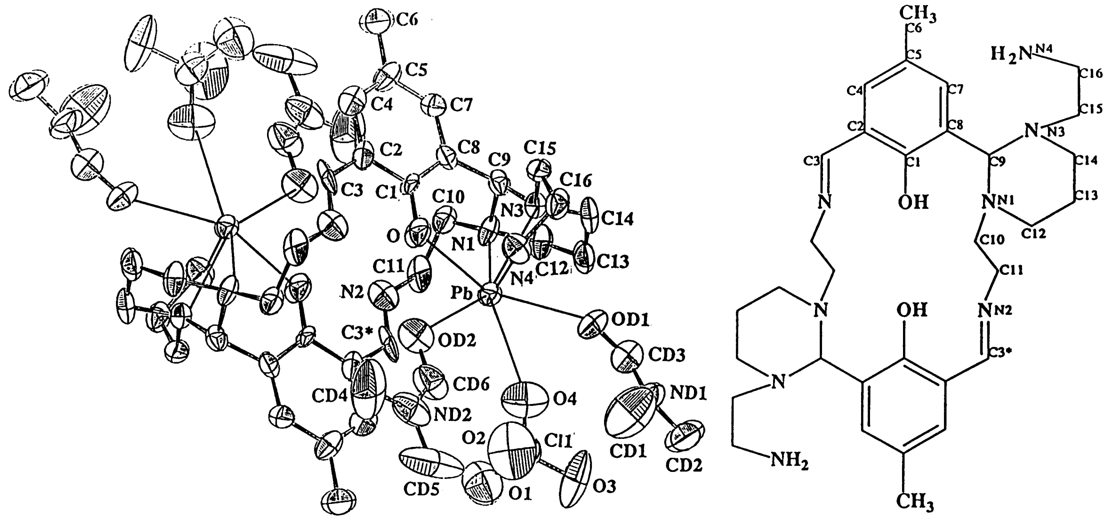

Fig. 2. ORTEP view of the essential part of the complex (left) and the chemical structure of the macrocyclic ligand H_2L (right).

ion. The Pb–N3 and Pb–N4 bond distances are 2.50(2) and 2.42(2) Å, respectively, which are common for Pb(II)–N bonding. The Pb–N1 bond distance is elongated (3.00(2) Å) probably because of a steric reason.

Each Pb(II) ion is further coordinated by two DMF oxygens (Pb–OD1 2.72(2); Pb–OD2 2.75(2) Å) and very weakly by a perchlorate oxygen (Pb–O4 3.32(2) Å). Thus, the geometry about each Pb(II) ion is of distorted seven-coordination. Two perchlorate ions and two DMF molecules are non-coordinating and captured in the crystal lattice.

Similar condensations between dicarbonyl compounds and polyamines to afford macrocycles containing five-membered imidazolidine ring have been reported.[8–10] Related condensations between dicarbonyl compounds and 1,3-diamino-2-hydroxypropane to afford macrocycles containing oxazolidine ring are also known.[11] In the 2:2 condensation between 2,6-diformyl-4-chlorophenol and 1-(2-pyridyl)-2,5,8-triazaoctane in the presence of Ba^{2+} as a template ion,[8] an imidazolidine-containing macrocycle has been isolated as a mononuclear Ba(II) complex. Similarly, the 2:2 condensation of 2,6-diacetylpyridine and 1,5-diamino-3-azapentane in the presence of Ba^{2+} forms an imidazolidine-containing macrocycle as a mononuclear Ba(II) complex.[9] In both complexes the five-membered imidazolidine ring functions as a unidentate ligand through one of the imidazolidine nitrogens. This is in contrast to the present complex where six-membered hexahydropyrimidine ring functions as a bidentate ligand through its two nitrogen atoms.

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