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# Template Synthesis and Crystal Structure of a Dilead(II) Complex of a Macrocycle with $N_4O_2$ Donor Set

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(Received June 6, 1990)

**Synopsis.** A dilead(II) complex of a binucleating macrocycle formed by the condensation of two molecules of 2,6-diformyl-4-methylphenol and two molecules of 1,3-diaminopropane has been obtained by template reaction. The crystal structure of this complex was analyzed by single-crystal X-ray method.

Binucleating macrocycles comprised of two molecules of 2,6-diformyl-4-methylphenol and two similar and dissimilar alkanediamines (Fig. 1, abbreviated as $(R^{m,n})^{2-}$) have been synthesized by "direct"[1] or "stepwise"[2] template reaction, and those and related macrocycles have been extensively used for the studies on homo- and hetero-binuclear complexes and mixed-valence complexes.[3–7] In general the success in template synthesis of macrocycles depends upon the choice of the template metal ion.[8,9] For the template synthesis of the $(R^{m,n})^{2-}$ macrocycles, first low transition metal ions were generally used as template metal ions. Recently, Mandal et al.[10] have reported the template synthesis of the macrocyclic complex $[Pb_2(R^{3,3})](NO_3)_2\cdot 4H_2O$ using lead(II) as the template metal ion. However, the crystal structure of this complex is not reported yet. In this study we have synthesized the perchlorate salt $[Pb_2(L)](ClO_4)_2$ and analyzed its crystal structure by single crystal X-ray method.

## Experimental

**Preparation.** To a suspension of 2,6-diformyl-4-methylphenol (0.5 g) in acetonitrile (20 cm$^3$) were added a solution of NaOH (0.07 g) in a minimum water and a solution of lead(II) perchlorate trihydrate (1.4 g) in acetonitrile (40 cm$^3$) and the mixture was stirred for 30 minutes to give a yellow solution. Then 1,3-diaminopropane (0.23 g) was added and the mixture was refluxed for one hour to give yellow microcrystals. They were collected, washed with acetonitrile and then with ether, and dried in air. The yield was 64%.

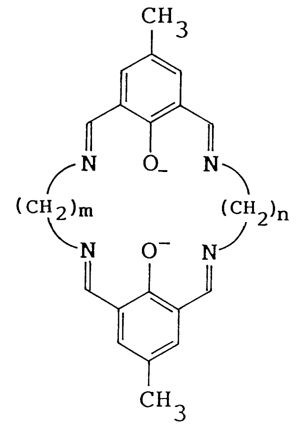

Fig. 1. Chemical structure of macrocycles $(R^{m,n})^{2-}$.

Found: C, 28.87; H, 2.67; N, 5.80%. Calcd for $Pb_2C_{24}H_{26}N_4O_{10}Cl_2\cdot 1/2MeCN$: C, 28.97; H, 2.67; N, 6.08%.

**Crystal Structure Determination.** Single crystals of $[Pb_2(R^{3,3})](ClO_4)_2$ were grown by slow crystallization from acetonitrile and a crystal with approximate dimensions 0.2×0.3×0.3 mm was used for the X-ray diffraction study. Reflection data were measured on a Rigaku Denki AFC-5 automated four-circle diffractometer, using graphite monochromatized Mo $K\alpha$ radiation ($\lambda$=0.71073 Å) at 20±1 °C. Lattice parameters and their estimated standard deviations were obtained from a least-squares fit to 25 $2\theta$ values in the range $15° < 2\theta < 30°$.

**Crystal Data:** $C_{24}H_{26}Cl_2N_4O_{10}Pb_2$, F.W.=1015.78, monoclinic, $P2_1/n$, $a$=10.792(2), $b$=15.557(2), $c$=9.035(2) Å, $\beta$=110.98(1)°, $V$=1416.3(4) Å$^3$, $Z$=2, $D_c$=2.382 g cm$^{-1}$, $F(000)$=952, $\mu$(Mo $K\alpha$)=9.8 cm$^{-1}$. For the intensity data collection, the $\theta$–$2\theta$ scan mode was used at a scan rate of 6° min$^{-1}$. Three standard reflections were monitored every 100 reflections and their intensities showed a good stability. 2541 independent reflections with $|F_o| > 3\sigma(|F_o|)$ were used for the structure determination. The intensity data were corrected for Lorentz-polarization effects but not for absorption.

The data was reduced by using UNICS III program system[11] of the Computer Center of Kyushu University. The structure was solved by the heavy-atom method and refined by the block-diagonal least-squares method. Atomic scattering factors were taken from Ref. 12. Hydrogen atoms were included in their calculated positions and held fixed. Final $R$ and $R_w$ values are 7.17 and 8.29%, respectively.

Table 1. Positional Parameters of Non-Hydrogen Atoms

| Atom | $x/a$ | $y/b$ | $z/c$ | $B_{eq}/Å^2$ |
|---|---|---|---|---|
| Pb | 0.0277(1) | 0.1249(1) | 0.0397(1) | 1.97 |
| O1 | −0.046(1) | 0.015(1) | −0.149(2) | 2.3 |
| N1 | 0.138(2) | 0.149(1) | −0.156(2) | 2.8 |
| N2 | 0.256(2) | 0.110(1) | 0.211(2) | 3.0 |
| C1 | 0.365(2) | 0.163(2) | 0.185(3) | 3.6 |
| C2 | 0.372(2) | 0.155(2) | 0.022(3) | 3.5 |
| C3 | 0.259(2) | 0.198(1) | −0.107(3) | 3.4 |
| C4 | 0.083(2) | 0.134(1) | −0.304(2) | 2.6 |
| C5 | −0.040(2) | 0.087(1) | −0.383(2) | 2.3 |
| C6 | −0.097(2) | 0.097(1) | −0.546(2) | 2.7 |
| C7 | −0.216(2) | 0.060(1) | −0.640(2) | 2.7 |
| C8 | −0.273(3) | 0.075(2) | −0.818(3) | 3.9 |
| C9 | −0.277(2) | 0.008(1) | −0.565(2) | 2.8 |
| C10 | −0.222(2) | −0.009(1) | −0.404(3) | 2.5 |
| C11 | −0.100(2) | 0.029(1) | −0.307(2) | 2.4 |
| C12 | −0.304(2) | −0.065(1) | −0.338(2) | 2.6 |
| CL | −0.3873(6) | 0.1748(3) | −0.2388(6) | 3.1 |
| O2 | −0.455(3) | 0.098(1) | −0.216(3) | 8.0 |
| O3 | −0.246(2) | 0.169(2) | −0.158(3) | 7.5 |
| O4 | −0.409(2) | 0.189(1) | −0.399(2) | 5.2 |
| O5 | −0.437(3) | 0.245(1) | −0.174(3) | 8.1 |

Positional parameters of non-hydrogen atoms are given in Table 1. The observed and calculated structure factors, atomic positional and anisotropic thermal parameters, and complete lists of bond distances and angles with their estimated standard deviations have been deposited as Document No. 8945 at Office of the Editor of Bull. Chem. Soc. Jpn.

## Results and Discussion

An ORTEP view of the complex is given in Fig. 2 together with the atom numbering system. An edge-on view is shown in Fig. 3. Selected bond distances and angles are given in Table 2.

The result clearly demonstrates that the ligand involved is indeed the macrocycle, $(R^{3,3})^{2-}$, formed by the 2:2 condensation of 2,6-diformyl-4-methylphenol and 1,3-diaminopropane. The crystal is composed of $(R^{3,3})^{2+}$, two lead(II) ions, and two perchlorate ions and there is inversion center at the center of a molecule. Two lead(II) ions are bound at the $N_2O_2$ coordination sites, sharing the bridging phenolic oxygens. The Pb-O1 and Pb-O1′ (−*x*, −*y*, −*z*) bond distances are 2.35(1) and 2.36(1) Å, respectively, which are common for Pb-O(phenolic) bond.[13] The Pb-N1 and Pb-N2 bond distances (2.48(2) and 2.41(2) Å, respectively) are also common for Pb-N(imine) bond.[13,14] A perchlorate anion bridges two neighboring macrocyclic molecules. One of perchlorate oxygen atoms coordinates to Pb ion of the macrocyclic molecule and two of them coordinate to Pb ion of the neighboring macrocyclic molecule. As shown in Fig. 2, a perchlorate oxygen O3 coordinates to Pb with the bond distance of 2.93(2) Å and the neighboring oxygen atoms O4″ and O5″ (*x*+1/2, *y*+1/2, *z*+1/2) coordinates to Pb with 2.98(2) and 3.18(2) Å, respectively. Thus, the geometry around each metal can be regarded as seven coordination. In accord with the bridging mode of the perchlorate ion the vibration near 1100 cm$^{-1}$ splits into three (1130, 1090, 1060 cm$^{-1}$).

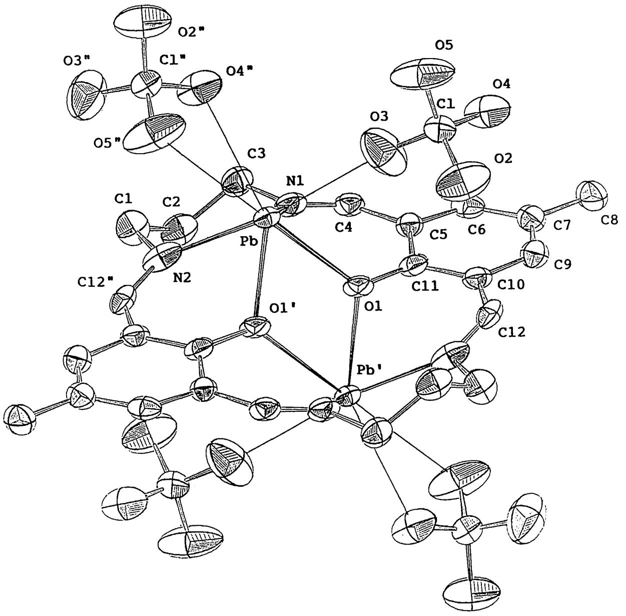

Fig. 2. An ORTEP view of the complex molecule and the neighboring perchlorate anion with the atom numbering system.

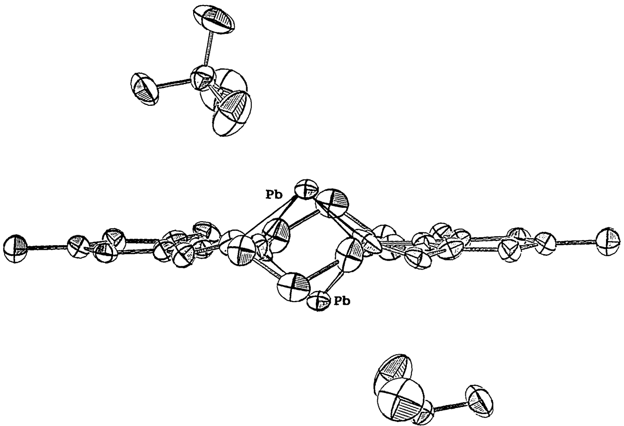

Fig. 3. An edge-on view of the macrocyclic complex.

Some least-squares planes with the atom deviations are given in Table 3. The macrocyclic ligand moiety forms a close coplane except for the central carbon atoms in the two trimethylene chains (C2 and C2′ (−*x*, −*y*, −*z*)) (see Fig. 3). The six-membered chelate ring formed by Pb, N2, C1, C2, C3, and N1 adopts the chair

Table 2. Relevant Bond Distances and Angles

| | |
|---|---|
| Bond distances (Å) | |
| Pb-O1 | 2.36(1) |
| Pb-O1′ | 2.37(1) |
| Pb-N1 | 2.48(2) |
| Pb-N2 | 2.42(2) |
| Pb-O3 | 2.93(2) |
| Pb-O4″ | 2.98(2) |
| Pb-O5″ | 3.18(2) |
| Bond angles (deg) | |
| O1 -Pb-O1′ | 66.2(4) |
| O1 -Pb-N1 | 73.2(5) |
| O1 -Pb-N2 | 113.5(5) |
| O1 -Pb-O3 | 73.8(6) |
| O1 -Pb-O4″ | 147.1(5) |
| O1 -Pb-O5″ | 164.3(7) |
| O1′-Pb-N1 | 116.7(5) |
| O1′-Pb-N2 | 74.1(5) |
| O1′-Pb-O3 | 112.1(6) |
| O1′-Pb-O4″ | 146.3(4) |
| O1′-Pb-O5″ | 105.7(5) |
| N1 -Pb-N2 | 80.6(6) |
| N1 -Pb-O3 | 99.8(7) |
| N1 -Pb-O4″ | 81.5(6) |
| N1 -Pb-O5″ | 122.1(7) |
| N2 -Pb-O3 | 172.4(6) |
| N2 -Pb-O4″ | 82.0(5) |
| N2 -Pb-O5″ | 75.1(7) |
| O3 -Pb-O4″ | 90.5(6) |
| O3 -Pb-O5″ | 98.6(7) |
| O4″-Pb-O5″ | 44.0(6) |

Key to symmetry operations: prim (−*X*, −*Y*, −*Z*); double prim (*X*+1/2, −*Y*+1/2, *Z*+1/2).

Table 3. Some Least-Squares Planes with the Atom Deviations

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Plane 1: Coordination plane N1, N2, O1, O1′ (′; $-x$, $-y$, $-z$)
$0.70474x - 0.69473y - 0.14562z = -0.00003$
The atom deviations from the plane in Å: N1, −0.01; N2, 0.01; O1, 0.01; O1′, −0.01; Pb, −1.28; C2, 1.07.

Plane 2: Macrocyclic ligand O1, O1′, N1, N1′, N2, N2′, C1–C12, C1′–C12′
$0.62547x - 0.76279y - 0.16416z = 0.00000$
Pb, −1.42; C2, 0.59; the others, less than −0.30.

Plane 3: Saturated six-membered chelate ring N1, N2, C1, C3
$-0.54702x + 0.81449y + 0.19330z = 0.57579$
N1, −0.03; N2, 0.03; C1, −0.03; C3, 0.04; Pb, 0.98; C2, −0.73.

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The planes are described by the four coefficients of the expression: $Ax+By+Cz=D$. ($x$, $y$, $z$ in Å unit along the orthogonal axes.

form, (Pb and C2 are derived by 0.98 and −0.73 Å, respectively, from the least-squares plane of N1, N2, C1, C2 atoms). Because of long Pb–N and Pb–O bond distances, the lead(II) ion cannot reside in the $N_2O_2$ coordination cavity but are deviated by 1.28 Å from the least-squares plane of the $N_2O_2$ to the opposite direction to each other.

The present result reveals that lead(II) ion can function as a template metal ion to afford the binucleating macrocycle $(R^{3,3})^{2-}$ in spite of the mismatch between the size of the $N_2O_2$ coordinating cavity and the radius of the metal ion.

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