Crystal Structure of a Dinuclear 1,2-Bis(diphenylphosphinooxide)ethane-bridged (6,8,15,17-Tetramethyldibenzo[*b,i*][1,4,8,11]-tetraazacyclotetradecinato)zinc(II) Complex

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A dinuclear 1,2-bis(diphenylphosphinooxide)ethane-bridged (6,8,15,17-tetra-methyldibenzo[*b,i*][1,4,8,11]tetraazacyclotetradecinato)zinc(II) complex was synthesized and its crystal structure was determined by a single-crystal X-ray diffractometry. The crystal system is monoclinic with the space group of $P2_1/n$ (#14) and $Z = 2$. The unit cell dimensions are $a = 15.456(3)\text{\AA}$, $b = 9.993(2)\text{\AA}$ and $c = 21.691(2)\text{\AA}$ with $\beta = 103.23(1)^\circ$, $V = 3261(1)\text{\AA}^3$. Each zinc(II) ion is coordinated through four nitrogen atoms of the macrocyclic ligand and one oxygen atom of 1,2-bis(diphenylphosphinooxide)ethane to form a five-coordinated dinuclear complex of square-pyramidal geometry.

(Received May 1, 2003; Accepted June 30, 2003; Published on Web October 15, 2003)

The chemistry of macrocyclic ligand (for example porphyrin) complexes includes a vast area of research ranging over many areas of chemistry and biochemistry. 5,14-Dihydro-6,8,15,17-tetramethyldibenzo[*b,i*][1,4,8,11]tetraazacyclotetradecine, abbreviated as H₂tmtaa, is also a macrocyclic ligand. It is related to the porphyrin but has a smaller N₄ coordination cavity "hole size" and typically possesses a non-planar, saddle-shaped conformation. The similarity of the H₂tmtaa to the porphyrin means that this synthetic macrocycle is of bioinorganic relevance, while its distinctive individual characteristics make it an interesting ligand in its own right. It is tunable, easily prepared and readily introduced. It provides a reliable and a generally robust framework that continues to allow new main group and transition metal chemistry to flourish. We synthesized and characterized five-coordinated mononuclear tmtaa zinc(II) complexes several years ago^{1,2} and reported several diamine-bridged dinuclear tmtaa zinc(II) complexes containing Zn-N bonds recently.³ Here, we further report the synthesis and crystal structure of a 1,2-bis(diphenylphosphinooxide)ethane-bridged dinuclear tmtaa zinc(II) complex containing Zn-O bonds.

Zn(tmtaa) (0.408 g, 1.0 mmol)¹ and P(C₆H₅)₂(CH₂)₂(C₆H₅)₂P

(0.199 g, 0.5 mmol) were dissolved in benzene (15 ml). After being refluxed for 5 h, the solution was filtered. Then the solvent was reduced to half and acetonitrile (5 ml) was further added. Finally, chunky red crystals of the title complex, Zn(tmtaa)[μ-OP(C₆H₅)₂(CH₂)₂(C₆H₅)₂PO]Zn(tmtaa) (Fig. 1), containing two molecules of acetonitrile were obtained in a yield of 68% after the solution was kept at 5°C for 48 h. *Anal.* Found: H, 5.72; C, 67.14; N, 10.38. Calc. for C₇₄H₇₄N₁₀P₂Zn₂O₂: H, 5.62; C, 66.92; N, 10.55%. The oxidation state of phosphorus in the starting reagent,

Table 1 Crystal and experimental data

Formula: C ₇₀ H ₆₈ N ₈ O ₂ P ₂ Zn ₂ ·2CH ₃ CN
Formula weight = 1328.17
Temperature: 293 K
Crystal size: 0.40 × 0.20 × 0.10 mm
Crystal color: red
Crystal description: plate
Crystal system: monoclinic
Space group: $P2_1/n$ (#14) $Z = 2$
$a = 15.456(3)\text{\AA}$
$b = 9.993(2)\text{\AA}$ $\beta = 103.23(1)^\circ$
$c = 21.691(2)\text{\AA}$
$V = 3261(1)\text{\AA}^3$
$D_{\text{calc}} = 1.352\text{ g cm}^{-3}$
Radiation: 0.71069 Å (Mo K _α)
$\mu(\text{Mo K}\alpha) = 8.40\text{ cm}^{-1}$
Monochromator: graphite
No. of reflections used: 7865
No. of parameters: 406
$2\theta_{\text{max}} = 56.0^\circ$
$R = 0.048$
Goodness of fit = 1.02
$(\Delta/\sigma)_{\text{max}} = 0.001$
$(\Delta\rho)_{\text{max}} = 0.88\text{ e}\text{\AA}^{-3}$
$(\Delta\rho)_{\text{min}} = -0.44\text{ e}\text{\AA}^{-3}$
Measurement: Rigaku AFC7R
Program system: teXsan
Structure determination: direct methods (SIR92)
Refinement: full-matrix least-squares

Fig. 1 Chemical structure of the title complex.

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Fig. 2 ORTEP drawing of the title complex. The thermal ellipsoids are drawn at the 30% probability level. The H atoms have been omitted for clarity. Symmetry code: $[(*)-X, -Y, -Z + 2]$.

$P(C_6H_5)_2(CH_2)_2(C_6H_5)_2P$, is +III. However, it was oxidized to +V oxidation state and two oxygen atoms were introduced between two $Zn(tmtaa)$ molecules and one bridged ligand during subsequent isolation and purification procedures.

X-ray diffraction data were collected at room temperature on a Rigaku AFC7R diffractometer with graphite monochromated $Mo-K\alpha$ radiation ($\lambda = 0.71069 \text{ \AA}$) and a rotating anode generator. The structure was solved by direct methods⁴ and expanded using Fourier techniques.⁵ The non-hydrogen atoms were refined anisotropically. Hydrogen atoms were included but not refined. Crystal data and details associated with data collection are summarized in Table 1. Figure 2 shows the ORTEP view of the title complex without solvents. The final positional parameters are given in Table 2.

The title complex has a crystallographic center of symmetry in its crystal structure. Only half of the formula unit is independent. The whole structure reveals a dinuclear complex bridged with a 1,2-bis(diphenylphosphino)ethane group. The planes of two phenyl groups connecting with the same phosphorus atom are approximately orthogonal. The dihedral angle is 103.3° . Each zinc(II) ion is coordinated through four nitrogen atoms of $tmtaa$ and one oxygen atom of 1,2-bis(diphenylphosphino)ethane to form a five-coordinated dinuclear complex of square-pyramidal geometry. The mean $Zn-N$ bond distance is $2.035 \text{ \AA}$. This is slightly different from those of mononuclear five-coordinated $tmtaa$ zinc(II) complexes ($2.050 \text{ \AA}$ in $Zn(tmtaa)N(C_2H_5)_3$ ¹ and $2.024 \text{ \AA}$ in $Zn(tmtaa)OPPh_3$ ²) and other dinuclear five-coordinated $tmtaa$ zinc(II) complexes ($2.207 \text{ \AA}$ in $Zn(tmtaa)(\mu-N,N,N',N'$ -tetramethylethylenediamine)- $(tmtaa)Zn$ and $2.177 \text{ \AA}$ in $Zn(tmtaa)(\mu-N,N'$ -dimethylethylenediamine)- $(tmtaa)Zn$). The zinc atom is displaced from the N_4 plane toward the benzenoid face of the saddle-shaped $tmtaa$ ligand, as is commonly observed in other mononuclear and dinuclear $tmtaa$ zinc(II) complexes. The displacement is $0.468 \text{ \AA}$, which is shorter than that of mononuclear and dinuclear $tmtaa$ zinc(II) complexes.¹⁻³ This assumes that the $Zn-N$ coordination ability in this complex is a little stronger than in other complexes.

Acknowledgements

We are grateful to the Center for Instrumental Analysis, Kyushu

Table 2 Positional and equivalent isotropic displacement parameters along with their estimated standard deviations

Atom	x	y	z	$B_{eq}(\text{\AA}^2)$
Zn(1)	0.29265(3)	0.11853(5)	0.99928(2)	2.47(1)
P(1)	0.07771(8)	0.0349(1)	0.92816(6)	2.78(3)
O(1)	0.1573(2)	0.0923(3)	0.9702(2)	3.49(8)
N(1)	0.3491(2)	-0.0027(3)	0.9450(2)	2.43(8)
N(2)	0.3196(3)	-0.0107(4)	1.0739(2)	2.75(8)
N(3)	0.2988(2)	0.2510(4)	1.0714(2)	2.60(8)
N(4)	0.3248(2)	0.2601(4)	0.9402(2)	2.78(9)
C(1)	0.4666(3)	-0.1632(5)	0.9301(2)	3.7(1)
C(2)	0.4042(3)	-0.1029(4)	0.9679(2)	2.84(10)
C(3)	0.4137(3)	-0.1524(4)	1.0291(2)	3.1(1)
C(4)	0.3792(3)	-0.1076(5)	1.0801(2)	2.91(10)
C(5)	0.4209(4)	-0.1679(6)	1.1441(3)	4.6(1)
C(6)	0.2851(3)	0.0418(5)	1.1228(2)	2.9(1)
C(7)	0.2505(3)	-0.0321(6)	1.1654(2)	3.7(1)
C(8)	0.2109(4)	0.0277(6)	1.2092(2)	4.4(1)
C(9)	0.2052(4)	0.1645(7)	1.2097(2)	4.4(1)
C(10)	0.2328(3)	0.2427(5)	1.1663(2)	3.5(1)
C(11)	0.2749(3)	0.1828(5)	1.1223(2)	2.9(1)
C(12)	0.3640(4)	0.4494(6)	1.1350(3)	4.5(1)
C(13)	0.3362(3)	0.3713(5)	1.0737(3)	2.97(9)
C(14)	0.3556(3)	0.4313(5)	1.0198(2)	3.4(1)
C(15)	0.3544(3)	0.3793(5)	0.9589(2)	2.94(9)
C(16)	0.3979(4)	0.4702(5)	0.9182(3)	4.3(1)
C(17)	0.3277(3)	0.1979(5)	0.8826(2)	2.8(1)
C(18)	0.3112(3)	0.2607(5)	0.8231(2)	3.7(1)
C(19)	0.3110(4)	0.1901(7)	0.7690(3)	4.5(1)
C(20)	0.3218(4)	0.0533(7)	0.7717(2)	4.4(1)
C(21)	0.3352(3)	-0.0122(5)	0.8285(2)	3.6(1)
C(22)	0.3405(3)	0.0552(5)	0.8849(2)	2.72(10)
C(23)	0.0431(3)	0.1276(5)	0.8556(2)	3.2(1)
C(24)	0.0929(3)	0.1159(7)	0.8106(2)	4.8(1)
C(25)	0.0717(4)	0.1946(8)	0.7563(3)	6.1(2)
C(26)	0.0019(4)	0.2808(7)	0.7465(3)	5.5(2)
C(27)	-0.0474(4)	0.2943(6)	0.7908(3)	5.3(2)
C(28)	-0.0277(3)	0.2154(5)	0.8450(2)	3.8(1)
C(29)	0.0935(3)	-0.1359(5)	0.9078(2)	2.88(10)
C(30)	0.0308(4)	-0.1999(6)	0.8609(3)	4.7(1)
C(31)	0.0420(5)	-0.3333(7)	0.8480(3)	6.6(2)
C(32)	0.1131(5)	-0.4040(6)	0.8807(3)	5.8(2)
C(33)	0.1746(5)	-0.3405(6)	0.9267(3)	5.7(2)
C(34)	0.1649(4)	-0.2082(5)	0.9402(3)	4.0(1)
C(35)	-0.0146(3)	0.0349(5)	0.9674(2)	3.3(1)

$$B_{eq} = (8/3)\pi^2(U_{11}(aa^*)^2 + U_{22}(bb^*)^2 + U_{33}(cc^*)^2 + 2U_{12}aa^*bb^*\cos\gamma + 2U_{13}aa^*bb^*\cos\beta + 2U_{13}aa^*bb^*\cos\alpha).$$

Institute of Technology, Japan for elemental analyses and X-ray structure determination.

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