$[Os_{10}C(CO)_{23}(NO)]^-$.[8] Given the site of NO^+ substitution, it is quite possible that NO^+ initially coordinates at the open face, as in the case of metallic electrophiles, followed by CO loss. It is clear that the site of attack is *not* a metal–metal bond involving the capping $Re(CO)_3$ moiety, as in the case of $Os_{10}C(CO)_{24}^{2-}$.[8] However, we cannot at this stage eliminate the alternative pathway of initial electron transfer followed by coordination of neutral NO.

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Note Added in Proof. Chemical oxidation of $[Re_7C(CO)_{21}]^{3-}$ with $[Cp_2Fe]^+$ (1 equiv) followed by NO addition also gives $[Re_7C(CO)_{20}(NO)]^{2-}$.

Contribution from the Department of Medicinal Chemistry,
Hiroshima University School of Medicine, Kasumi,
Minami-ku, Hiroshima 734, Japan, and Coordination
Chemistry Laboratories and Division of Applied
Molecular Science, Institute for Molecular Science,
Okazaki National Research Institutes, Okazaki 444, Japan

A Trigonal-Bipyramidal Zinc(II) Complex of a Phenol-Pendant Macrocyclic Triamine

Eiichi Kimura,*[†,‡] Tohru Koike,[†] and Koshiro Toriumi[§]

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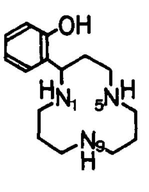
Structurally well-defined five-coordinate, trigonal-bipyramidal Zn(II) complexes are scarce,[1] despite the intense synthetic efforts to mimic the active sites in Zn(II)-containing enzymes (e.g. carboxypeptidase A[2,3] or carbonic anhydrase (CA)[2,4]). The Zn(II) in CA is ligated by three imidazoles and a water molecule. This coordination number 4 is considered to expand to 5 in a transient manner or by anion inhibitor binding.[5–7] In a mechanism for CA, the observed pK_a value of ca. 7 is assigned to the zinc-bound water, and its conjugate base appears to attack closely positioned carbon dioxide to convert it into bicarbonate ion.[4,8] It was postulated[6,7] that the incoming anions (to five-coordinate) enhance the basicity of ZnOH in CA to affect its nucleophilicity.

Herein we report the X-ray crystal structure of a Zn(II) complex **2** with a recently developed phenol-pendant macrocyclic triamine [2-(2-hydroxyphenyl)-1,5,9-triazacyclododecane, **1**[9]] that



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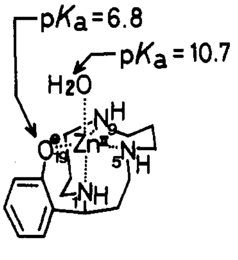

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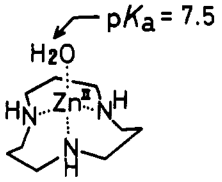

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is distinctly five-coordinate and trigonal bipyramidal with an additional apical H_2O coordination. The ligand was originally designed for an ideal tetrahedral N_3O^- coordinate environment, and its complexations with Cu^{2+}, Ni^{2+}, and Zn^{2+} in aqueous solution were reported.[9]

The corresponding 12-membered macrocyclic triamine (without the phenol pendant) was earlier reported to form a four-coordinate (possibly tetrahedral) Zn(II) complex with an additional aquo ligand **3**, whose ionization (to ZnOH) constant pK_a is 7.5.[10] Thus, the phenolate-pendant coordination in **2** offers the first model for an associative anion interaction.

Table I. Summary of Crystal Data, Intensity Collection, and Refinements

formula	$C_{15}H_{24}N_3OZnClO_4{\cdot}H_2O$
fw	445.2
cryst system	monoclinic
space group	$P2_1/a$
cell dimens	
a, b, c, Å	16.673 (2), 13.952 (2), 8.286 (1)
β, deg	91.73 (1)
V, Å^3	1926.5 (5)
Z	4
density calcd, g cm^{-3}	1.536
cryst color	colorless
cryst dimens, mm^3	0.36 × 0.11 × 0.11
radiation	Mo Kα (graphite monochromated)
μ, mm^{-1}	1.488
2θ range, deg	2–55
index range	$+h,+k,\pm l$
scan width, deg	1.3 + 0.5 tan θ
refinement	block-diagonal least-squares method
no. of measd reflcns	4920
no. of indp reflcns with $\lvert F_o\rvert \geq 3\sigma(F_o)$	2239
final R	0.044
final R_w	0.056

Table II. Fractional Coordinates (×10^4) and Equivalent Isotropic Temperature Factors (Å^2) for **2**(ClO_4)

atom	x	y	z	B_{eq}[a]
Zn	1070.9 (4)	1289.2 (4)	5495.9 (7)	3.0
N(1)	1132 (3)	2778 (3)	6106 (6)	3.8
C(2)	1103 (4)	3357 (1)	4641 (7)	4.1
C(3)	1876 (4)	3170 (4)	3724 (7)	4.3
C(4)	2041 (4)	2171 (5)	3088 (7)	4.5
N(5)	2125 (3)	1394 (3)	4345 (6)	4.1
C(6)	2829 (3)	1466 (5)	5465 (8)	4.9
C(7)	2764 (4)	867 (5)	6987 (8)	5.1
C(8)	2187 (4)	1209 (4)	8266 (7)	4.6
N(9)	1321 (3)	1001 (3)	7884 (6)	4.3
C(10)	759 (4)	1460 (5)	8973 (7)	5.0
C(11)	744 (4)	2556 (5)	8899 (8)	5.4
C(12)	499 (4)	2990 (5)	7288 (7)	4.8
C(13)	338 (3)	3212 (4)	3578 (7)	3.9
C(14)	−64 (3)	2321 (4)	3351 (6)	3.2
C(15)	−706 (3)	2308 (4)	2250 (7)	4.3
C(16)	−964 (4)	3107 (5)	1411 (7)	4.9
C(17)	−576 (4)	3961 (5)	1687 (8)	5.8
C(18)	58 (4)	4008 (4)	2761 (8)	4.9
O(19)	146 (2)	1504 (2)	4085 (4)	3.7
O(H_2O)	979 (2)	−282 (3)	5112 (5)	4.2
Cl	3004 (1)	4109 (1)	−1436 (2)	5.0
O(1Cl)	2809 (4)	3981 (4)	153 (6)	9.8
O(2Cl)	3600 (4)	4793 (4)	−1562 (7)	10.0
O(3Cl)	3314 (5)	3257 (5)	−2060 (8)	12.8
O(4Cl)	2362 (4)	4412 (7)	−2384 (9)	14.5

[a] $B_{eq} = {}^4/_3\sum_i\sum_j\beta_{ij}{\cdot}a_i{\cdot}a_j$.

Experimental Section

All materials were obtained commercially and were used without further purification. The experimental procedure for the ligand synthesis

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[†] Hiroshima University School of Medicine.

[‡] Coordination Chemistry Laboratories, Institute for Molecular Science.

[§] Division of Applied Molecular Science, Institute for Molecular Science.

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Table III. Bond Distances (Å)

Zn–N(1)	2.139 (5)	Zn–N(5)	2.029 (5)
Zn–N(9)	2.050 (5)	Zn–O(19)	1.930 (4)
Zn–O(H_2O)	2.219 (4)	N(1)–C(2)	1.458 (7)
N(1)–C(12)	1.490 (8)	N(5)–C(4)	1.507 (8)
N(5)–C(6)	1.478 (7)	N(9)–C(8)	1.498 (8)
N(9)–C(10)	1.468 (8)	C(2)–C(3)	1.537 (9)
C(3)–C(4)	1.519 (9)	C(6)–C(7)	1.520 (9)
C(7)–C(8)	1.529 (9)	C(10)–C(11)	1.531 (10)
C(11)–C(12)	1.511 (9)	C(2)–C(13)	1.541 (8)
C(13)–C(14)	1.422 (8)	C(14)–C(15)	1.386 (7)
C(15)–C(16)	1.376 (9)	C(16)–C(17)	1.372 (9)
C(17)–C(18)	1.362 (9)	C(13)–C(18)	1.376 (8)
O(19)–C(14)	1.335 (6)	Cl–O(1Cl)	1.378 (6)
Cl–O(2Cl)	1.383 (7)	Cl–O(3Cl)	1.401 (7)
Cl–O(4Cl)	1.376 (8)		

Table IV. Bond Angles (deg)

N(1)–Zn–N(5)	90.3 (2)	N(1)–Zn–N(9)	87.4 (2)
N(1)–Zn–O(19)	91.4 (2)	N(1)–Zn–O(H_2O)	174.4 (2)
N(5)–Zn–N(9)	108.3 (2)	N(5)–Zn–O(19)	113.0 (2)
N(9)–Zn–O(19)	138.7 (2)	O(19)–Zn–O(20)	90.9 (1)
N(5)–Zn–O(20)	93.5 (2)	N(9)–Zn–O(20)	87.5 (2)
Zn–O(19)–C(14)	127.0 (3)	N(1)–C(2)–C(3)	108.1 (5)
N(1)–C(12)–C(11)	108.9 (5)	C(2)–C(3)–C(4)	119.4 (5)
C(2)–N(1)–C(12)	115.5 (5)	C(3)–C(4)–C(5)	115.7 (5)
C(4)–N(5)–C(6)	116.1 (5)	N(5)–C(6)–C(7)	114.1 (5)
C(6)–C(7)–C(8)	117.7 (5)	C(7)–C(8)–N(9)	114.6 (5)
C(8)–N(9)–C(10)	114.5 (5)	N(9)–C(10)–C(11)	114.9 (5)
C(10)–C(11)–C(12)	116.1 (5)	C(2)–C(13)–C(14)	124.7 (5)
C(2)–C(13)–C(18)	116.0 (5)	C(13)–C(14)–C(15)	116.8 (5)
C(14)–C(15)–C(16)	123.1 (6)	C(15)–C(16)–C(17)	118.7 (6)
C(16)–C(17)–C(18)	120.3 (6)	C(17)–C(18)–C(13)	121.9 (6)
O(19)–C(14)–C(15)	118.4 (5)	O(19)–C(14)–C(13)	124.8 (5)

and the pH-metric titration method was described previously in detail.[9]

Synthesis of Zn(phenolate-pendant-[12]aneN$_3$)(H_2O)ClO$_4$ (2(ClO$_4$)). Phenol-pendant-[12]aneN$_3$ (0.26 g, 0.10 mmol) and $Zn(ClO_4)_2 \cdot 6H_2O$ (0.37 g, 1.0 mmol; Soekawa Chemical Co.) were dissolved in 10 mL of aqueous 95% MeOH solution containing 1 equiv of NaOH (40 mg) at 50 °C. The resulting colorless solution was filtered, and the filtrate was allowed to stand for 1 day at room temperature. The colorless crystals of **2** (as a monoperchlolate salt) were obtained in ca. 70% yield (0.31 g). IR (KBr): 3400 (w), 3280 (s), 2900 (w), 1595 (s), 1560 (s), 1478 (s), 1445 (s), 1370 (m), 1300 (s), 1280 (s), 1260 (s), 1100 (w, ClO_4^-), 1000 (s), 980 (s), 880 (w), 860 (s), 760 (s), 665 (s) cm^{-1}.

Crystallography. Intensity data were collected at room temperature on a Rigaku AFC-5 four-circle diffractometer. The cell parameters and details for data collection and structure refinement are listed in Table I. The structure was solved by the heavy-atom method and refined by a block-diagonal least-squares technique with anisotropic thermal parameters for non-hydrogen atoms and isotropic for hydrogens. A weighting scheme $1/w = (\sigma_{count})^2 + (0.03|F_o|)^2$ was employed. The final R and R_w factors are 0.044 and 0.056, respectively. Atomic scattering factors and anomalous scattering corrections are taken from ref 11. All the calculations were carried out on a HITAC M-200H computer with a universal program UNICS-III.[12] Atomic coordinates, bond lengths, and bond angles are listed in Tables II–IV, respectively.

Results and Discussion

The molecular structure of **2**(ClO$_4$) is shown in Figure 1. This is also the first report on the metal complexes of **1**[9] studied by X-ray crystal structure analysis. In complex **2**, Zn(II) is surrounded trigonal bipyramidally by three N atoms of the macrocyclic ligand, the O(19) atom of the phenolate-pendant moiety of the ligand, and a water molecule. The Zn atom is located in the basal plane defined by the N(5), N(9), and O(19) atoms. The apical angle N(1)–Zn–O(H_2O) is almost linear at 174.4 (2)°, and the total of the equatorial angles of 113.0 (2)° (O(19)–Zn–N(5)), 108.3 (2)° (N(5)–Zn–N(9)), and 138.7 (2)° (N(9)–Zn–O(19)) is *just* 360°. The apical Zn–OH$_2$ (2.219 (4) Å) and Zn–N(1) (2.139 (5) Å) bonds are significantly longer than the average distance (2.003 Å) of the three basal bond distances. It is concluded that the strong electrostatic interaction of Zn(II)···O$^-$ (phenolate) and the instrinsic property of Zn to adopt five-coordination first fix the phenolate oxygen O(19) at an equatorial position of the trigonal bipyramid. Then the two macrocyclic nitrogens, N(5) and N(9), occupy the remaining equatorial positions as observed, with the last nitrogen, N(1), occupying an elongated apical site. The other apical H_2O–Zn(II) bond length is longer.

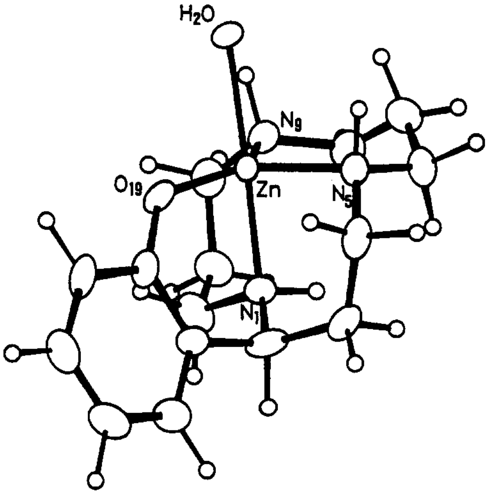

Figure 1. Perspective view of **2**. The perchlorate is omitted for clarity.

Previously, we determined the formation constant $K_{ZnH_{-1}L}$ (= $[ZnH_{-1}L]a_{H^+}/[Zn^{2+}][L]$; $ZnH_{-1}L$ is **2**) to be $10^{-0.42}$ at 25 °C and $I = 0.1$ (NaClO$_4$).[9] The deprotonation of the pendant phenol group (pK_a = 6.8) is promoted by its proximity to Zn(II), causing it to become the fourth donor, which renders the basicity of Zn^{II}OH in **2** higher (pK = 10.7), as now established by the pH-metric titration. In the pendant-free [12]aneN$_3$ complex **3**, the fourth donor H_2O is possibly more firmly bound, on the basis of its lower pK value of 7.5.[10] Undoubtedly, only one OH$^-$ anion donor is sufficient to cause the charge distribution of the Zn^{2+} ion in the 12-membered macrocyclic N$_3$ complexes.

In a conceptualization of anion inhibition of CA,[5-7] the competitive anion coordination (e.g. SCN$^-$) is thought to spread the charge density of Zn^{2+} ion. Then it may block the ionization of Zn^{II}OH$_2$ to Zn^{II}OH, the latter being a more powerful nucleophilic form. The present trigonal-bipyramidal Zn(II) complex **2** may offer a simple model of the anion additive effect around the Zn^{2+} ion in CA.

Registry No. **2**(ClO$_4$), 116302-03-5.

Supplementary Material Available: Listings of anisotropic thermal parameters of non-hydrogen atoms and fractional coordinates and isotropic thermal parameters of hydrogen atoms (2 pages); a table of calculated and observed structure factors (6 pages). Ordering information is given on any current masthead page.

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