Crystal Structures and Spectroscopic Properties of Zinc(II) Ternary Complexes of Vitamin L, H′ and Their Isomer *m*-Aminobenzoic Acid with Bipyridine

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The crystal structures of the three Zn(II) complexes, [Zn(bpy)(*o*-AB)$_2$] (1) (bpy=2,2′-bipyridine, *o*-AB=*o*-aminobenzoic acid=Vitamin L), [Zn(bpy)(*m*-AB)Cl]$_2$ (2) (*m*-AB=*m*-aminobenzoic acid), [Zn(bpy)(*p*-AB)Cl]·*p*-AB·H$_2$O (3) (*p*-AB=*p*-aminobenzoic acid=Vitamin H′), have been determined and the basic coordination geometries and architectures organized by hydrogen-bonds and π–π interactions also characterized. The substitute amine group at *ortho*-, *meta*-, and *para*-position of AB plays an important role to produce completely different coordination motif of these complexes, further, in all complexes, aromatic amines are not coordinated to Zn(II) atom. While two different types of coordination modes of the carboxylate O atoms are present in these complexes: one mode consists of the usual Zn–O bond lengths (2.009(2)—2.251(2) Å) in complex 1, 2 and 3; another consists of a very long Zn–O bond lengths (2.422(2) Å) in complex 1. Each of the complexes has the characteristic UV absorption bands around 250—310 nm region, and the intense fluorescence band at near 325 nm.

Key words zinc(II) ternary complexes; X-ray crystal analysis; *m*-aminobenzoic acid; Vitamin L; Vitamin H′; 2,2′-bipyridine

Zn(II) is an essential trace element in animals and human beings. It plays an important role in the maintenance of their lives with less toxic than the other elements.[1,2] Zinc was successfully used in the treatment of acodermatitis enteropathica, Wilson's disease, gastrointestinal disorders, infertility and other diseases.[3] Zinc complexes with some small molecules such as amino acids, picolinic acid, vitamins and allixin (isolated from garlic) are found to have high *in vitro* insulinomimetric activity and *in vivo* anti-diabetic activity.[4—7] Recent report described the action mechanism of Zn complexes, *i.e.*, Zn(maltolate)$_2$, Zn(threoninate)$_2$ and Zn(picolinate)$_2$, which promote the glucose uptake into the adipocytes by affecting at least three sites in the adipocytes.[8] Bontchev[9] discussed the complexation of bioligands with biometals and its potential application in medicine. He mentioned zinc complex as a new effective drug for treatment of pulmonary diseases of different type: chronic respiratory insufficiency, dust-detd, lung fibrosis (pneumoconiosis) and pneumonia in cases of immunocompromised patients.

Zinc is also present in the zinc-based domain (termed zinc fingers) in a wide variety of proteins involved in gene regulation.[10] Zinc finger domains of the Cys$_2$His$_2$ type identified in protein transcription factor IIIA[11] appear to represent the most abundant DNA binding motif in eukaryotic transcription factors.[12] Thus, array of zinc fingers are well suited for combinatorial recognition of DNA sequences.[13—18]

In the His$_2$Cys$_2$-type zinc finger, zinc atom has a tetrahedral coordination geometry and is coordinated by two N atoms of His and two S atoms of Cys residues, and this coordination appears to be responsible for the specific structure and function of the zinc fingure proteins.[19,20]

Moreover, the Zn···Zn separation in the dinuclear or trinuclear zinc complexes are of current interest, because the zinc separation is ranging from 3.2—3.9 Å in di- or tri-nuclear zinc-enzymes[21,22] such as phospholipase C,[23] nuclease P1,[24] *E. coli* alkaline phosphatase[25,26] or *E. coli* DNA polymerase I.[27,28] The coordination geometry and the nature of the bridging system by carboxylate ligand in di- or trinuclear zinc complexes would be of value to synthesize as models for the catalytic centers in the hydrolytic enzymes.[21,22]

Our study stems from the value of the zinc complexes containing carboxylate ligands. By far many Zn carboxylate complexes have been reported,[29—36] but rare is related about the aminobenzoic acid (AB). In the viewpoint of constructing functional compounds, we prepared several Zn(II) complexes involving some natural products such as *o*-aminobenzoic acid, Vitamin L (*o*-AB) and its isomers *m*-aminobenzoic acid (*m*-AB) and *p*-aminobenzoic acid, Vitamin H′ (*p*-AB). *o*-AB, Vitamin L, constitutes an important group of antiflammatory agent and as an aromatic nucleus, it gained prominence after the discovery of mefenamic acid (*N*-(2,3-xylyl) anthranilic acid) and meclofenamate (2-(2,6-dichloro-3-methylphenylamino) benozoate).[37] One of its isomer *m*-AB, is also an important substance with biological activity and was found to inhibit the carcinogenic effect of *N*-2-fluorenyl acetamide which induced to liver tumor of animals.[38] Another isomer, *p*-AB, Vitamin H′, is well known for its potent natural antimutagen[39] besides its usage as a good factor for several microorganisms.

Besides the bioactive properties of all these ligands, on the other hands, all the molecules above mentioned have many potential binding sites around the aromatic ring. The diversity coordination modes of these isomers with the key substitutes located at different positions are mainly investigated in this paper. With an effort on designing new coordination compounds containing multifunctional ligands and investigating their characteristics, we also apply heterocycle N ligands such as 2,2′-bipyridine (bpy) in the system. Successfully we have obtained three zinc complexes described as [Zn(*o*-AB)$_2$(bpy)] (**1**), [Zn(*m*-AB)(bpy)Cl]$_2$ (**2**), [Zn(*p*-AB)(bpy)Cl]·*p*-AB·H$_2$O (**3**), and characterized their structures. The fascinating structures of these compounds provide important additional information about the coordination sphere and coordinated ligands at the metal binding site,

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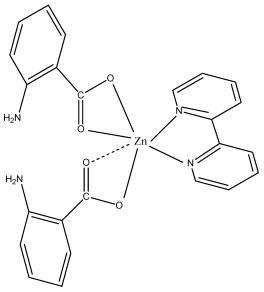
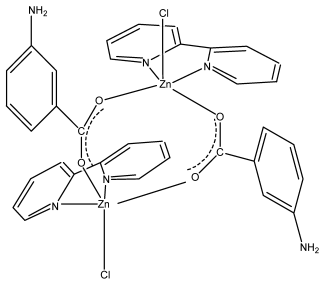
[Zn(bpy)(o-AB)$_2$] (1)



[Zn(bpy)(m-AB)Cl]$_2$ (2)



[Zn(p-AB)(bpy)Cl]·p-AB·H$_2$O (3)

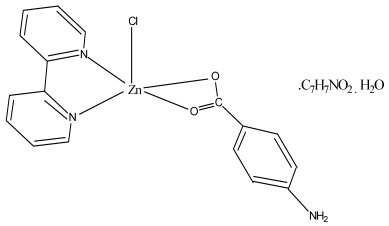


Fig. 1. Chemical Structures of Three Complexes **1**—**3**

which may be used as a basis for modeling of metal complexes of natural simple molecules. In this study, the UV and fluorescence properties of the complexes have also been featured.

Experimental

Materials Analytical grade of 2,2′-bipyridyl (bpy), *o*-aminobenzoic acid (*o*-AB), *m*-aminobenzoic acid (*m*-AB), *p*-aminobenzoic acid (*p*-AB) and $ZnCl_2$ were obtained from Wako Pure Chemicals, Industries Ltd. (Osaka, Japan). UV and fluorescence measurements were performed with a Shimadzu UV-190 spectrophotometer and a Hitachi 850 spectrofluorometer, respectively. All spectroscopic measurements were performed at room temperature. Element analysis was done by using YANACO CHN Coder MT-3.

Preparation of the Single Crystals of Complexes All single crystals of the complexes were prepared at 1 : 1 : 1 mole ratio of the metal, bpy and the other ligands. The typical synthesis is described below:

[Zn(bpy)(*o*-AB)$_2$] (**1**): (Di-2-aminobenzenecarboxylato-κ^2O,O')(2,2′-bipyridine-κ^2N,N')zinc(II): Five milligrams (0.04 mmol) *o*-AB was dissolved in 5 ml water and was mixed with the methanol solution of 6 mg (0.04 mmol) bpy. Then 5 mg (0.04 mmol) $ZnCl_2$ solution was added drop wise to such mixture and reacted for no less than 30 min. The solution was placed at the room temperature and kept for slow evaporation. Two week later yellow prismatic crystals suitable for X-ray diffraction studies were obtained from mother liquor.

Anal. Calcd for [Zn(bpy)(*o*-AB)$_2$]: C: 51.939, H: 3.590, N: 10.691. Found: C: 51.720, H: 3.399, N: 10.431.

[Zn(bpy)(*m*-AB)Cl]$_2$ (**2**): Di[chloro(3-aminobenzenecarboxylato-κ^2O,O')(2,2′-pyridine-κ^2N,N')zinc(II)]: Five milligrams (0.04 mmol) *m*-AB was dissolved in 80 v/v% methanol–water and was mixed with the 80 v/v% methanol–water solution of 6 mg (0.04 mmol) bpy. Then 5 mg (0.04 mmol) $ZnCl_2$ methanol solution was added drop wise to such mixture and reacted for no less than 30 min. The solution was placed at the room temperature and kept for slow evaporation. One week later yellow prismatic crystals suitable for X-ray diffraction studies were obtained from mother liquor.

Anal. Calcd for [Zn(bpy)(*m*-AB)Cl]$_2$: C: 52.575, H: 4.228, N: 10.221. Found: C: 52.702, H: 4.402, N: 10.025.

[Zn(bpy)(*p*-AB)Cl]·*p*-AB·H$_2$O (**3**): Chloro(4-aminobenzenecarboxylato-κ^2O,O')(2,2′-bipyridine-κ^2N,N')zinc(II)-4-aminobenzenecarboxylic acid–water (1 : 1 : 1): Five milligrams (0.04 mmol) *p*-AB was dissolved in 5 ml water and was mixed with the methanol solution of 6 mg (0.04 mmol) bpy. Then 5 mg (0.04 mmol) $ZnCl_2$ solution was added drop wise to such mixture and reacted for no less than 30 min. The solution was placed at the room temperature and kept for slow evaporation. One week later yellow prismatic crystals suitable for X-ray diffraction studies were obtained from mother liquor.

Anal. Calcd for [Zn(bpy)(*p*-AB)Cl]: C: 58.369, H: 4.082, N: 11.347. Found: C: 58.368, H: 4.225, N: 11.356.

X-Ray Crystal Analysis The X-ray measurements were made on a Rigaku RAXIS RAPID diffractometer with a graphite monochromatised Mo$K\alpha$ radiation (λ=0.71069 Å) using ω scan mode. A summary of the crystallographic data and structure refinements is given in Table 1. The data were corrected for Lorentz and polarization effects. The structure was solved by direct methods[40] using the Crystal Structure[41] software package. The refinement was performed using SHELXL-97.[42] All H atoms except the disordered H52 and H53 atoms of water molecule were located from difference Fourier maps and treated as riding, with C–H distance of 0.93, phenol O–H distance of 0.82 and U_{iso}(H) values equal to 1.2 U_{eq}(C) and U_{iso}(water H) values equal to 1.5 U_{eq}(C) (U_{eq} is the equivalent isotropic displacement parameter for the pivot atom). The positional parameters of the disordered water H atoms were calculated on the basis of the positions of the other H atoms and treated as riding.

The function of $\Sigma w(F_o^2-F_c^2)^2$ was minimized by using the weight scheme of $w=1/[\sigma^2(F_o^2)+(aP)^2+bP]$, where $P=(F_o^2+2F_c^2)/3$. Final R [$=\Sigma(|F_o|-|F_c|)/\Sigma|F_o|$], R$w$ [$=(\Sigma w(|F_o|-|F_c|)^2/\Sigma w|F_o|^2)^{1/2}$] and S (goodness of fit) [$=(\Sigma w(|F_o|-|F_c|)^2/(M-N)^{1/2}$], where M=no. of reflections and N=no. of variables used for the refinement] are given in Table 1. Anisotropic displacement coefficients were refined for all non-hydrogen atoms. Selected bond distances and angles are listed in Tables 2—4, respectively.

The final anisotropic displacement coefficients, anisotropic temperature factors, bond lengths, bond angles, torsion angles of non-H atoms, and the atomic coordinates of H atoms have been deposited in the Cambridge Crystallographic Data Centre, Cambridge University Chemical Laboratory, Cambridge CB21EW, U.K. (CCDC 256323 for complex **1**, CCDC 258369 for complex **2**, CCDC 261632 for complex **3**)

Result and Discussion

Crystal Structure In complex **1**, Zn(II) is located in a very distorted octahedron coordination with five strong bonds to two N atoms from bpy and three carboxylate O atoms from two *o*-AB molecules; the sixth weaker Zn-coordination is to one carboxylate O22 atom with much longer Zn–O distance of 2.422(2) Å (as shown its ORTEP view in Fig. 2 with broken line indicating weaker interaction). The O11, O12, O21, N1 atoms occupy the 'basal' plane with the maximum deviation of Zn atom of 0.171(1) Å from the plane, while O22 and N2 atoms occupy the 'apical' positions with the angle of O22–Zn1–N2 being 154.30(8)°. This coordination geometry around Zn atom remarkably resembles to the structure of (2,2′-bipyridyl-κ^2N,N') bis (salicylato-κ^2O,O')zinc(II), in which the Zn atom lies 0.168(1) Å out of the plane.[43] The other detailed bond and angle data are summarized in Table 2.

The two pyridine rings including N1 and N2 atoms are almost coplanar with the interplanar angle of 1.3(1)°. The torsion angles C12/C11/C17/O11: −177.2(3)° and C12/C11/C17/O12: 3.4(5)° indicate the carboxylate group O11–C17–O12 is nearly coplanar with its aromatic ring, as well as the other

Table 1. Crystal Data and Structure Refinement for Compounds **1**—**3**

	1	**2**	**3**
Formula	$C_{24}H_{20}N_4O_4Zn$	$C_{34}H_{28}Cl_2N_6O_4Zn_2$	$C_{17}H_{14}Cl_1N_3O_2Zn\cdot C_7H_7NO_2\cdot H_2O$
Formula weight	493.83	786.30	548.3
Crystal System	Triclinic	Monoclinic	Monoclinic
Space group	P-1	C2/c	P21/n
a (Å)	7.846(7)	19.46(2)	11.680(7)
b (Å)	9.946(7)	9.603(7)	12.03(1)
c (Å)	14.06(1)	17.53(1)	17.53(1)
α (°)	97.79(3)	90.00	90.00
β (°)	93.77(4)	93.78(3)	98.54(3)
γ (°)	100.57(3)	90.00	90.00
V (Å^3)	1064.0(14)	3269(5)	2436(3)
Z	2	4	4
D_{calc} (g/cm^{-3})	1.535	1.598	1.495
T (K)	296.1	296.1	296.1
F(000)	508	1600	1128
Crystal size (mm)	0.10×0.10×0.10	0.30×0.30×0.15	0.35×0.30×0.20
Absorption coefficient (mm^{-1})	1.195	1.680	1.161
Reflection measured/unique	10613/4840	15981/3728	19603/5546
Observed reflections	2603	3193	4387
R($F^2>2\sigma(F^2)$)	0.0330	0.0430	0.0290
wR(F^2)	0.0940	0.1420	0.0890
Goodness of fit	0.900	1.132	1.095
No. of variables	299	218	327

Table 2. Bond Distances (Å) and Angles (°) for [Zn(bpy)(o-AB)$_2$] (**1**)

Bond distances			
Zn1–O11	2.051(2)	Zn1–N2	2.110(2)
Zn1–O12	2.251(2)	O11–C17	1.264(3)
Zn1–O21	2.010(2)	O12–C17	1.257(3)
Zn1–O22	2.422(2)	O21–C27	1.269(3)
Zn1–N1	2.108(2)	O22–C27	1.248(3)
Bond angles			
O11–Zn1–O21	144.86(8)	O21–Zn1–O12	103.64(7)
O11–Zn1–N1	95.71(8)	O11–Zn1–O12	60.64(7)
O11–Zn1–N2	111.32(9)	O21–Zn1–O22	58.03(7)
O11–Zn1–O22	94.15(8)	O12–Zn1–O22	105.78(8)
O21–Zn1–N2	99.18(9)	N2–Zn1–O22	154.30(8)
O21–Zn1–N1	107.86(9)	N1–Zn1–O12	147.63(9)
N1–Zn1–N2	77.63(8)	N1–Zn1–O22	97.15(8)
N2–Zn1–O12	90.27(8)		

Table 3. Bond Distances (Å) and Angles (°) for [Zn(bpy)(m-AB)Cl]$_2$ (**2**)

Bond distances			
Zn1–O11	2.009(2)	Zn1–Cl1	2.278(1)
Zn1–O12$^{a)}$	2.121(2)	O11–C17	1.258(4)
Zn1–N1	2.101(3)	O12–C17	1.253(4)
Zn1–N2	2.173(3)		
Bond angles			
O11–Zn1–Cl1	108.96(7)	O11–Zn1–N1	140.91(9)
O12$^{a)}$–Zn1–Cl1	100.56(7)	O11–Zn1–N2	87.5(1)
Cl1–Zn1–N1	108.88(7)	O12$^{a)}$–Zn1–N1	91.72(9)
Cl1–Zn1–N2	100.56(8)	O12$^{a)}$–Zn1–N2	158.2(1)
O11–Zn1–O12$^{a)}$	90.78(8)	N1–Zn1–N2	76.3(1)

Symmetry code: a) $1-x, y, 3/2-z$.

Table 4. Bond Distances (Å) and Angles (°) for [Zn(bpy)(p-AB)Cl]·p-AB·H$_2$O (**3**)

Bond distances			
Zn1–O1	2.221(1)	O1–C17	1.252(2)
Zn1–O2	2.099(1)	O2–C17	1.286(2)
Zn1–N1	2.057(2)	O3–C27	1.331(2)
Zn1–Cl1	2.2249(19)	O4–C27	1.226(2)
Zn1–N2	2.093(1)		
Bond angles			
Cl1–Zn1–O1	107.34(4)	O1–Zn1–O2	60.69(5)
Cl1–Zn1–O2	117.35(3)	O1–Zn1–N1	89.24(5)
Cl1–Zn1–N1	115.85(4)	O1–Zn1–N2	141.72(5)
Cl1–Zn1–N2	110.58(4)	N1–Zn1–O2	124.40(5)
N1–Zn61–N2	79.11(5)	N2–Zn1–O2	96.43(5)

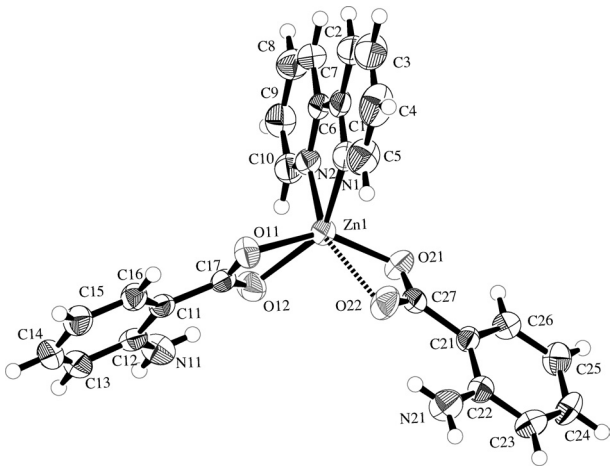


Fig. 2. ORTEPII Drawing of Complex **1**, Showing 50% Probability Displacement Ellipsoids

A weak Zn–O interaction is indicated by dashed line.

carboxylate group O21–C27–O22 in another coordinated o-AB molecule. The ligand molecules around the central Zn(II) atom exhibit wide steric dispersion as characterized by the following dihedral angles between the ligand planes: the dihedral angle between C11/C12/C13/C14/C15/C16 plane and bpy plane is 68.61(9)°, between C21/C22/C23/C24/C25/C26 plane and bpy plane is 73.23(9)° and between two o-AB molecules is 89.53(9)°. In the packing of [Zn(bpy)(o-AB)$_2$] shown in Fig. 3, a typical π–π interaction occurs between the related bpy molecules with the interplane distance of

3.546(4) Å along a axis and another set of π–π interaction is observed between the C11/C12/C13/C14/C15/C16 plane to the adjacent one with the symmetry code of $(1-x, 1-y, -z)$ with the interplane distance of 3.491(4) Å. To accommodate this kind of packing, the shape of the [Zn(bpy)(*o*-AB)$_2$] unit should allow an efficient interlocking stacks between neighboring molecules (as shown in Fig. 3). However no packing effect exists in C21/C22/C23/C24/C25/C26 planes, and they lie just perpendicularly to C11/C12/C13/C14/C15/C16 planes and participate the intra- and inter-molecular H-bond network with the N21 atom as a donor. As a result, one-dimensional zig-zag sheet is formed along *b* axis through independent *o*-AB ligands and intermolecular H-bonding between the complexes. Similar one-dimensional zig-zag chain is also observed in the zinc complex with 4,4′-bipyridine and 4-hydroxybenzoic acid in which the zig-zag chain is formed through two independent 4,4′bpy ligands alternatively linking five-coordinated Zn(II) centers.[36] The overall structure is stabilized and extended to three dimensions by the significant H-bond network (Table 5) which is mainly provided by the uncoordinated amine N atoms, together with two kinds of strong π–π interactions mentioned above.

The structure of complex **2** (Fig. 4) is made up of a centrosymmetric dinuclear [Zn(bpy)(*m*-AB)Cl]$_2$ unit, in which two Zn(II) atoms are linked by two *m*-AB molecules. Each metal center is linked to two pyridine N atoms, two carboxylate O atoms from two *m*-AB molecules and one chloride anion. The structural index τ is defined by $\tau=(\beta-\alpha)/60°$ (where α and β are the two largest angles around the central metal atom).[44,45] The τ value represents the relative amount of trigonality of the five-coordination geometry as $\tau=0$ for a square pyramid and $\tau=1$ for a trigonal bipyramid. In complex **2**, the calculated value of τ is 0.288, therefore, the coordination geometry around Zn(II) center seems to be classified as a square pyramid rather than a trigonal bipyramid. Further, as shown in Fig. 4, in Zn1 moiety, N1, N2 atoms from bpy, and O11 and O12 $(1-x, +y, 3/2-z)$ atoms from the two bidentate *m*-AB molecules clearly form the equatorial square plane, and Cl1 atom occupies the axial position. The deviations of N1, N2, O11 and O12 $(1-x, +y, 3/2-z)$ atoms from the mean plane through these atoms are 0.1397(13) Å, 0.1980(18) Å, 0.0955(1) Å and 0.1040(10) Å, respectively. The maximum deviation of Zn1 atom from the mean plane is 0.5444(10) Å. These also indicate that the five-coordination geometry around each Zn center is classified as a distorted square-pyramidal with ZnN_2O_2Cl core.

The Zn···Zn separation in the dinuclear complex **2** is 3.9170(5) Å, and this value matches the value of 3.94 Å for that in the active site of alkaline phosphatase,[25] and 3.9 Å in DNA polymerase.[27,28] Thus, the coordination mode of **2**

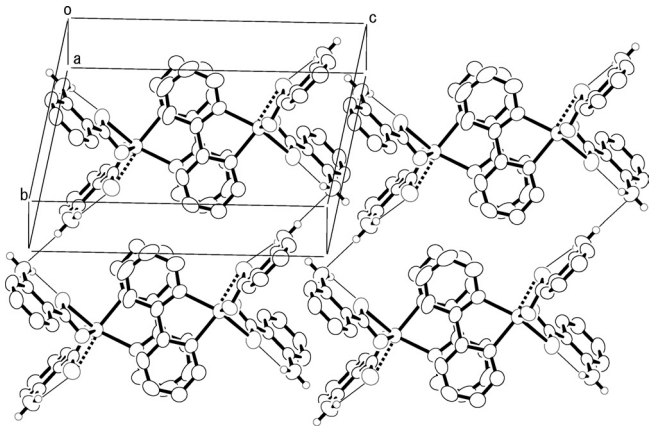


Fig. 3. A View of Packing Pattern in Complex **1,** Including H-Bond Networks Indicated by Thin Lines

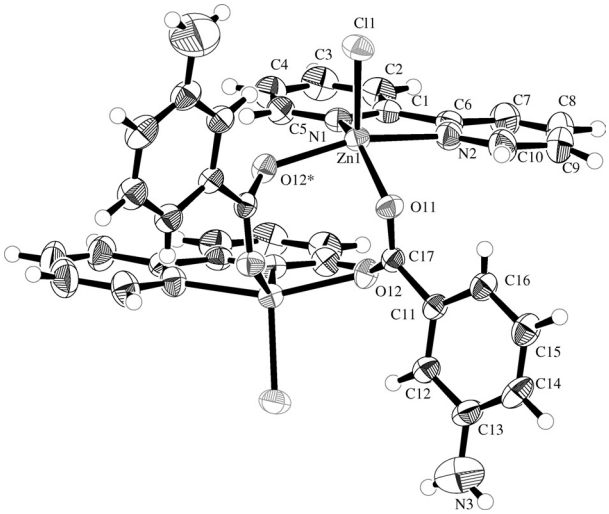


Fig. 4. ORTEPII Drawing of Complex **2**, Showing 50% Probability Displacement Ellipsoids

Symmetry code of *: $1-x, y, 3/2-z$.

Table 5. Hydrogen Bond Data for Compounds **1**—**3**

Donor (D–H)	Acceptor (A)	Sym. code of A	D···A (Å)	H···A (Å)	D–H···A (°)
Compound **1**					
N11	O12	$+x, +y, +z$	2.679(3)	2.06	130
N21	O22	$+x, +y, +z$	2.734(4)	2.10	129
N21	N11	$+x, 1+y, +z$	3.256(4)	2.40	173
Compound **2**					
N3	O12	$1/2-x, -1/2+y, 3/2-z$	3.465(7)	2.69	151
Compound **3**					
N11	Cl1	$-1/2+x, 1/2-y, 1/2+z$	3.609(2)	2.81	156
N11	Cl1	$3/2-x, -1/2+y, 5/2-z$	3.489(2)	2.81	136
N21	O4	$3/2-x, 1/2+y, 3/2-z$	3.040(2)	2.32	141
O3	O2	$2-x, -y, 2-z$	2.668(3)	1.87	165
O5	O4	x, y, z	2.943(3)	2.35	118
O5	O5	$2-x, -y, 1-z$	2.946(2)	2.34	119
O5	N11	$x, y, -1+z$	3.466(4)	2.98	111

bridged by two *O*,*O*′-bidentate carboxylate groups may be useful as a good model for producing Zn···Zn separation in the active site of thses enzymes. This value can also be compared to the corresponding value in the other Zn dimer complex: 3.0533(4) Å in $[Zn_2(C_7H_5O_2)_4(C_{20}H_{21}NO_4)_2]$[46]; 3.275 (2) Å in $[Zn_2(bpy)_2(MeCO_2)_3]^+$[47]; 3.54 Å in $[Zn_2(O_2C\text{-}CH_3)_3]^+$[48]; 3.569(1) Å in $[Zn(pht)(Im)(H_2O)]_2$ (pht is *o*-phthalic acid and Im is imidazole).[29]

As shown in Fig. 4, the carboxylate group in each *m*-AB ligand bridges neighboring Zn(II) atom to form a diametric complex in a *syn–anti* configuration.[31] The two carboxylate groups and two Zn(II) atoms form an eight-membered cyclic ring like a crown shape in one dimer unit, and it is largely twisted by the different coordination force of the atoms around Zn center. The contact distance of Zn1–O12 is 2.937(2) Å which is too weak so that we described the coordination number of Zn as five without including it. This coordination mode of carboxylate is different from complex **1**. In **1**, both O atoms of one carboxylate group are bonded to one Zn(II) center, although one Zn–O interaction is much weaker than another. While in **2**, each Zn(II) sphere is completed by two carboxylate O atoms from two different *m*-AB molecules.

Each dimer unit is stabilized by the π–π interaction between two N1 pyridine rings. The interplane distance between them is about 3.392(3) Å, while no stacking effect exists between N2 pyridine rings for they are separated far from each other by the eight-membered cyclic ring. In **2**, only one *m*-AB molecule is bonded around the Zn center and Cl anion is involved in the coordination to neutralize the complex. This coordination motif is largely different from complex **1**.

The amine group is still uncoordinated in **2** as that in **1**, and it acts as a donor to form the intermolecular hydrogen bond N3–H31···O12 ($1/2-x$, $-1/2+y$, $3/2-z$). This weak H-bond with the N1–O12 distance of 3.465(7) Å connects the neighboring dimer molecules along a axis (Fig. 5). Moreover, bpy planes belonging to the adjacent dimer seem to parallel to each other (related symmetry code being $1-x$, $1-y$, $1-z$) and a strong π–π interaction along c axis exists between them with the interplane distance of 3.435(6) Å. Therefore the whole structure is stabilized in two dimensional directions by the intra-dimer and inter-dimer π–π interactions, as well as the intermolecular H-bond network.

Complex **3** crystallizes as a mononuclear with the ZnN_2O_2Cl coordination core (Fig. 6). Zn(II) is bonded to two N atoms from bpy, two carboxylate O atoms from one *p*-AB molecule and one chloride anion. In this case, the value of τ is 0.292 Å for Zn(II) center, this value resembles to that for the complex **2** (τ=0.288). Thus coordination geometry of complex **3** is best described as a distorted square pyramid, in which O1, O2, N1 and N2 atoms define the square plane with the Zn deviated from that plane by 0.8232(7) Å. The coordination is completed by a slightly shorter Zn–Cl1 bond as compared to complex **2** and Zn–N1 bond. The value of Zn–Cl1 (2.220(4) Å) is shorter than that in **2**, where the Cl atom is located at the vertex of the pyramid with the Zn1–Cl1 distance of 2.278(1) Å. The corresponding values reported in the literature are listed below: 2.221(3) Å in [Zn(pic-H)(pic)Cl](pic is picolinate anion)[49]; 2.207—2.218 Å in $[ZnCl_2(4\text{-}CN\text{-}py)_2]$(py is pyridine and CN is cyano)[50]; 2.206(3) Å—2.216(3) Å in $[ZnCl_2(4\text{-}ac\text{-}py)_2]$(ac is acetyl)[50]; 2.222(1) Å—2.229(2) Å in $[ZnCl_2(C_5H_4N_4)_2]$[51]; 2.241(1) Å—2.244(1) Å in $[ZnCl_2(C_9H_7N)_2]$.[52]

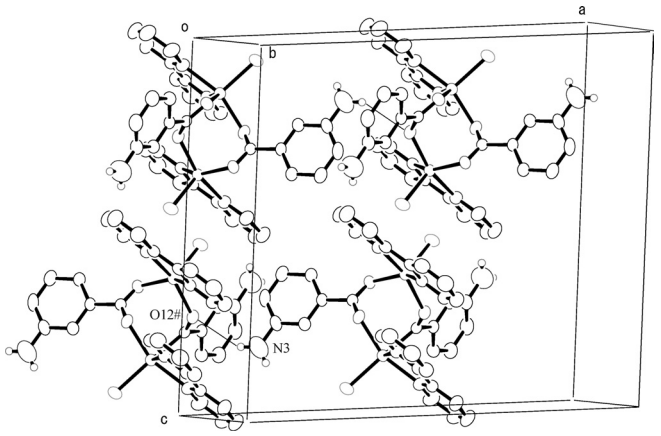


Fig. 5. A View of Packing Pattern in Complex **2**, Including H-Bond Networks Indicated by Thin Lines

Symmetry code of #: $1/2-x$, $-1/2+y$, $3/2-z$.

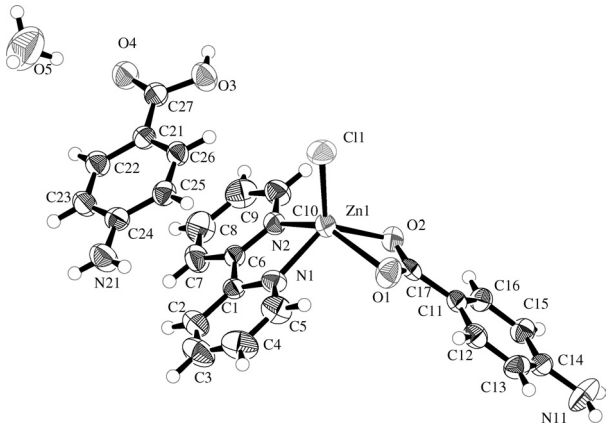


Fig. 6. ORTEPII Drawing of Complex **3**, Showing 50% Probability Displacement Ellipsoids

Around the ZnN_2O_2Cl moiety, there is one free *p*-AB molecule and one water molecule coexisting in the unit. Also one type of π–π interaction between the free *p*-AB benzene plane and the N2 pyridine plane of the coordinated bpy molecule is present. The shortest atom–atom separation is 3.469(4) Å between the atom C26 and C6. *p*-AB ligand here acts as a bidentate donor, together with the bidentate bpy, so Zn coordination sphere is saturated and has no tendency to form dimer as in **2**. The dihedral angle of two pyridine rings of bpy is 1.0(2)°, indicating the bpy molecule is essentially planar. The arrangement of C11/C12/C13/C14/C15/C16 plane nearly perpendicular to bpy is also very benefit for the steric interlocking, leading to the overlapping of the bpy molecules in a related symmetry center. The π–π interactions with the interplane distance of 3.569(3) Å between the related bpy molecules, together with the π–π interactions between bpy N2 rings and the free *p*-AB molecules mentioned above along c axis are shown in Fig. 7.

The molecules are also linked by the intermolecular N–H···Cl and O–H···O type hydrogen bonds. In the first of these types, H-bonds are formed between the H111 atom of the uncoordinated *para*-amine group and Cl1 ($3/2-x$,

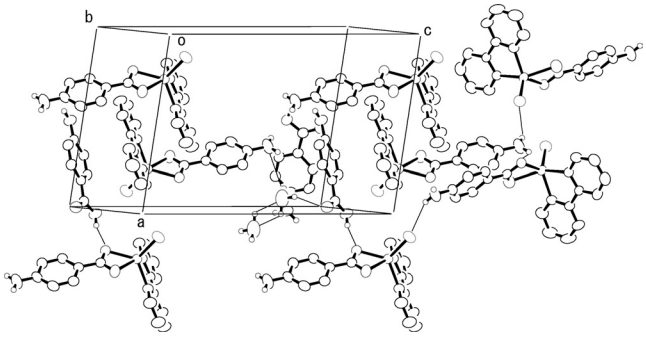


Fig. 7. A View of Packing Pattern in Complex **3**, Including H-Bond Networks Indicated by Thin Lines

$-1/2+y$, $-1/2-z$) atom, and between the H112 atom and Cl1 ($1/2+x$, $1/2-y$, $-1/2+z$) atom. This type of H-bond connects the molecules to form chain along *a* and *c* axis. The second type of H-bond is between the free *p*-AB molecules and the coordinated *p*-AB molecules with O3–H31···O2 ($1-x$, $-y$, $-z$) along a direction. The free water molecule is also involved in the H-bond network, in which the H52 and H53 atoms are disordered. While through the O5–H52···O4 along b direction, the overall H-bond networks are completed three dimensionally.

All of these structures indicate that the substitute on the different position plays an important role in the coordination stereochemistry. It is noticed that the amine groups located in the *ortho*-, *meta*-, and *para*-position produce completely different coordination motif, although the complexes were synthesized in almost the same conditions. From the above mentioned packing view, it may be considered as followings: In complex **1**, the intramolecular H-bonds N11–H112···O12 and N21–H212···O22 make the carboxylate group fixed at the corresponding positions, producing the intrinsically smaller steric hindrance and around each Zn(II) sphere, every two *o*-AB molecules can accommodate with each other very well from perpendicular direction. In **2**, the presence of *meso*-amino group leads to the relatively free carboxylate group which is largely deviated from benzene plane by the torsion angle C12–C11–C17–O11 being 158.6(3)° and C12–C11–C17–O12 being −24.8(4)° and is facile to form a dimer motif. Between the dimers, a typical π–π interaction is present and it may be the barrier for the second *m*-AB molecule to be bonded to zinc instead of a relatively small Cl anion; In complex **3**, for the *para*-substituted amino group, *p*-AB molecule is extending in a long linear size, so the final Cl anion bonded to zinc instead of another *p*-AB is a consequence to avoid the crowded stacking.

In all complexes, aromatic amines are not involved in the bonding to Zn(II) atom. The fact that AB molecule in each complex is not N,O-bidentate ligand testifies that the amino N atom is not an active donor to zinc atom in the presence of some stronger heterocyclic N ligand such as bpy. The electron density of amine may be somewhat dispersed by the conjugation effect with the carboxylate group on the phenyl ring, which makes the amine group exhibiting chemically inert. Another example of uncoordinated amine group is observed in [(η^3-TpPh) Zn (anthranilate)] (TpPh=hydrotris (3-phenylpyrazol-1-yi) borate.[53] The bond distances between zinc and bpy N atoms are unremarkable at 2.038(6) Å to 2.173(3) Å, which are within the acceptable range of the corresponding values of analogues Zn complexes.[33,35,47,54,55] However, those between zinc and carboxylate O atoms are relatively longer such as Zn1–O22 in complex **1**. In **1**, the carboxylate groups of the ligand molecules are fully deprotonated, as well as that in complex **3**. While in complex **2**, the carboxylate group is ionized with the electron delocalization indicated by the two C–O bond distances are very near (O11–C17: 1.258(4) Å, O12–C17: 1.253(4) Å), corresponding to the Zn1–O11 distance only slightly shorter than Zn1–O12 ($1-x$, $+y$, $3/2-z$). In conclusion, two different types of coordination modes of the carboxylate O atoms were present in these complexes: one mode consists of the usual Zn–O bond lengths (2.009(2) Å—2.251(2) Å) in complex **1**, **2** and **3**; another consists of a very long Zn–O bond length (2.422(2) Å) in complex **1**. In addition, carboxylate group doesn't act as a bridge role to form polymer structure as often observed in the carboxylato metal complexes such as some of the transition metal or Ag complexes.[29,32,56—61] The possible reason may be the use of bpy as blocking ligand prevents such polymerization by saturating the Zn(II) centers, resulting in the formation of mononuclear ZnN_2O_4 core in **1**, dimer $(ZnN_2O_2Cl)_2$ core in **2** and mononuclear ZnN_2O_2Cl core in **3**.

Spectroscopic Properties The UV absorption spectra and the fluorescence spectra of the complexes **1**—**3** in methanol solution are shown in Figs. 8, 9. As shown in Fig. 8a, all of the three complexes show strong maximum absorption in 250—310 nm region. The free bpy and free AB also exhibit moderate transitions in the UV region as shown in Fig. 8b. Especially, a relatively moderate strong absorption peak is observed for *p*-AB near 280 nm. The strong transition band at 280 nm in free bpy is assigned as S_3 ($\pi\pi^*$, $^1B_1$) polarized along long-axis, when the N atoms are cis conformation.[62]

As the result of complex formation, the strong band at 280 nm as well as the other moderate and weak bands at near 290 and 303 nm in the free bpy remarkably changed in their intensity with a little red-shift of the absorption bands. Complexes **1** and **2** have the similar spectral shapes, both of which exhibit two sharp absorption peaks at near 304 and 293 nm. Moreover, the higher absorption intensity of complex **2** than complex **1** can be explained by the ratio of *m*-AB to bpy being 2 : 2 in the dimer, while in **1** the ratio of *o*-AB to bpy being 2 : 1. The maximum absorption peak of complex **3** appears around 280 nm, a little shorter wavelength as compared to **1** and **2**, and it displays the highest and broadest absorption peak reflected by the broad band of *p*-AB.

The fluorescence spectra for three complexes were measured upon the excitation at 300 nm. All of them have the similar shape and the intense fluorescence peaks appear at near 325 nm. The fluorescence peak at near 325 nm may be attributed to bpy, since the weak fluorescence peak of free bpa is measured at near 325 nm in the same conditions as shown in Fig. 9. The fluorescence intensity of the each complex is highly increased as compared with their free ligands. It may be explained by the fact that the planar five-chelate ring was formed when bpy coordinated to Zn with N donors, which increases the rigidity of the whole complex molecule with the conjugated planar chelate structure. It is noticed that two peaks are observed in complex **1**, one of which appears

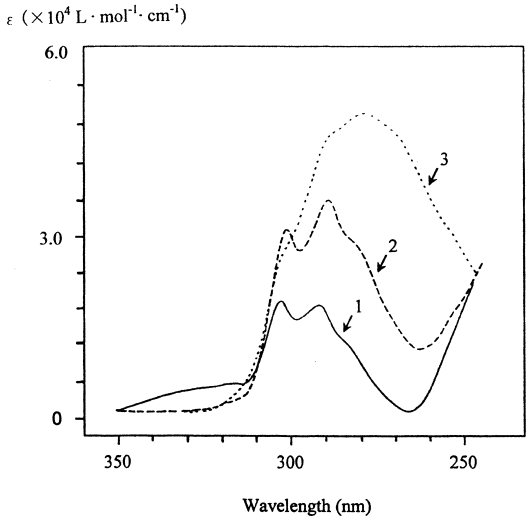


Fig. 8a. UV Spectra of Complexes **1**—**3** in Methanol Solution

The concentrations of each complex is 1.7×10^{-5} M.

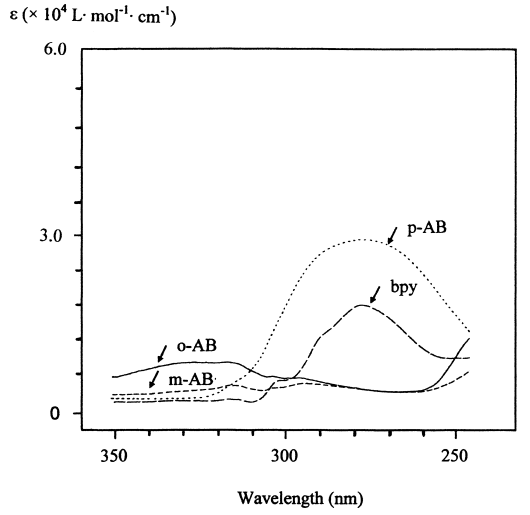


Fig. 8b. UV Spectra of Free Ligands in Methanol Solution

The concentration of each ligand is 1.7×10^{-5} M.

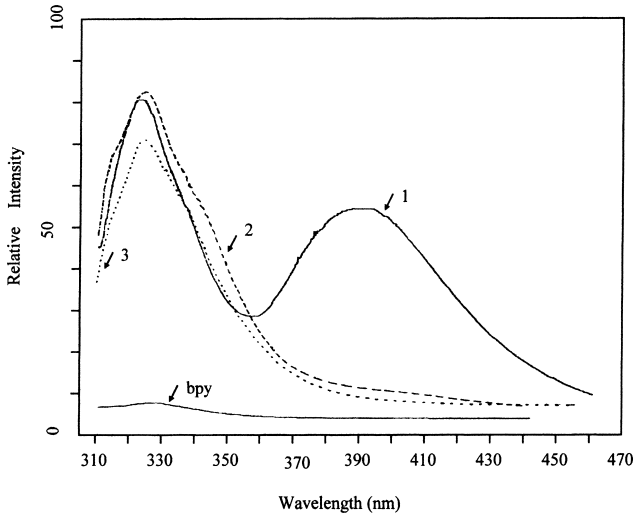


Fig. 9. Fluorescence Spectra of Complexes **1**—**3** and Free bpy in the Methanol Solution

The concentration of each complex is 3.4×10^{-5} M. The excitation wavelength was 300 nm.

at 396 nm. This maximum emission can be attributed to the *o*-AB, because *o*-, *m*- and *p*-AB have the fluorescence peaks around 396, 415 and 345 nm, respectively (data are not shown here). While in **2** and **3**, no fluorescence of *m*-AB or *p*-AB was observed. This fact may be explained by the crystal structures of complexes **2** and **3**, in which the well-known fluorescence quencher, Cl anion is coordinated to the metal center. The coordinated Cl atom might quench the fluorescence caused from *m*- and *p*-AB in complexes **2** and **3**, although it is not yet clear why it did not quench the fluorescence at near 325 nm. At the present, the biological function of complexes **1**, **2** and **3** are not yet clear. In the following functional study of these complexes, however, the spectroscopic properties may be available as a suitable indicator reflecting the interaction with biological or chemical substances such as proteins, nucleic acids or other ligands in solution.

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