

Studies on Zinc(II) Perchlorate Complex with Tripod Ligand Tris(*N*-methylbenzimidazol-2-ylmethyl)Amine and Salicylate

Huilu Wu, Kaitong Wang, Xingcai Huang, Ruirui Yun, Tao Sun, Ke Li, and Xuyang Fan

School of Chemical and Biological Engineering, Lanzhou Jiaotong University, Lanzhou, China

A novel five-coordinate zinc(II) complex with the tripod ligand tris(*N*-methylbenzimidazol-2-ylmethyl)amine (Mentb) and salicylate, with the composition [Zn(Mentb)(salicylate)](ClO₄) · 1.5DMF, was synthesized and characterized by means of elemental analyses, electrical conductivities, thermal analyses, i.r., u.v. and ¹Hn.m.r. spectra. The crystal structure of the complex has been determined by a single-crystal X-ray diffraction method, and shows that the Zn^{II} atom is bonded to a tris(*N*-methylbenzimidazol-2ylmethyl)amine (Mentb) ligand and a salicylate molecule through four N atoms and one O atom, giving a distorted trigonalbipyramidal coordination geometry [τ (Zn) = 0.78], with approximate *C*₃ molecular symmetry.

Keywords Crystal structure, synthesis and characterization, tris(*N*-methylbenzimidazol-2-ylmethyl)amine, zinc(II) complex

INTRODUCTION

Imidazole is a typical heterocyclic ligand with nitrogen as the donor atom. It is also a component of biologically important molecules.^[1] Because of this, the coordination chemistry of related ligands has been the subject of numerous investigations.^[1] Amongst them, the coordinating behavior of chelating benzimidazolic ligands has been studied by several research groups, some of them with an interest in mimicking biological activities.^[2–4] Benzimidazoles exhibit a wide variety of pharmacological activities like fungicides or anti-

helminthics amongst others.^[5] Tripodal ligands have long been used in both coordination and organometallic chemistry,^[6–7] typically polypyrazolylborate and tris(2-pyridyl) tripodal ligands. However, their potential use in supramolecular chemistry for the construction of various cagelike or boxlike complexes has not been fully realized until quite recently.^[8–10] In particular, the use of C_3 -symmetric tripodal ligands in crystal engineering has been reviewed.^[11] The tetradentate tripodal ligand, tris(Nmethylbenzimidazol-2-ylmethyl)amine (Mentb) (Figure 1), is similar to the imidazole in terms of its mode of coordination.^[12] Since the three arms of this type of ligand can each rotate freely around an N(apical)-C bond, multicomponent complexes or coordination polymeric networks may be expected to form the assembly of this ligand by metal ions of low coordination number.^[13–17] In this paper, we have prepared and investigated the properties and crystal structure of the zinc(II) complex with Mentb and salicylate as an exogenous ligand. The zinc(II) in the complex adopts a distorted trigonal-bipyramidal coordination geometry with the N₄O ligand donor set.

EXPERIMENTAL

Materials and Physical Measurements

All chemicals were reagent grade and were used without further purification. C, H and N elemental analysis were determined using a Carlo Erba 1106 elemental analyzer. Metal contents were determined by EDTA titration. Thermal studies of the complex was made in the 25–800°C range using a ZRY-2P thermal analyser with a heating rate of 10°C min⁻¹. The IR spectra were recorded in the 4000–400 cm⁻¹ region with a Nicolet FI-IR AVATAR 360 spectrometer using KBr pellets. Electronic spectra were taken on a TU-Visible spectrophotometer. Electrolytic conductance measurements were made with a DDS-11A type conductivity bridge using a 10^{-3} mol L⁻¹ solution in DMF at room temperature. ¹H NMR spectra were recorded on a Bruker AM200A NMR spectrometer with TMS as internal standard and d⁶-DMSO as solvent.

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Address correspondence to Dr. Hui-Lu Wu School of Chemical and Biological Engineering, 88 West Anning Rd., Lanzhou Gansu, Lanzhou 730070, China. E-mail: wuhuilu@163.com



FIG. 1. Structure of Mentb.

Preparation of Tris(N-methylbenzimidazol-2-ylmethyl) amine (Mentb) and the Zinc Complex

Tris(*N*-methylbenzimidazol-2-ylmethyl)amine (Mentb). This compound was synthesized by the literature method.^[12] Yield: 4.6 g (51%); m.p.: 215–217°C (m.p.: 215°C in the literature ^[12]). The infrared spectra and ¹H NMR spectra of the Mentb were consistent with the literature.^[12]

[Zn(Mentb)(salicylate)](ClO₄)·1.5DMF. To a stirred solution of tris(N-methylbenzimidazol-2-ylmethyl)amine (0.0899 g, 0.2 mmol) in hot MeOH (10 mL) was added Zu(ClO₄)₂·6H₂O (0.0745 g, 0.2 mmol), followed by a solution of Na(salicylate) (0.0320 g, 0.2 mmol) in MeOH (5 mL). A colorless crystalline product formed rapidly. The precipitate was filtered off, washed with MeOH and absolute Et₂O, and dried in vacuo. The dried precipitate was dissolved in DMF to a colorless solution that was allowed to evaporate at room temperature. colorless crystals suitable for X-ray diffraction studies were obtained after two weeks. Yield, 0.085 g (49%). (found: C, 53.74; H, 5.01; N, 13.66; Zn, 7.24. Calcd. for C_{38.5}H_{42.5}ClZnN_{8.5}O_{8.50} (MW 861.16): C, 53.70; H, 4.97; N, 13.83; Zn, 7.59%). $\Lambda_{\rm M}$ (DMF, 297 K): 64.7 S cm² mol⁻¹.

X-ray Structure Determination of [Zn(Mentb)(salicylate)] (ClO₄) · 1.5DMF

All data were mounted using a Rigaku R-axis Spider diffractometer with the graphite-monochromated MoK α radiation $(\lambda = 0.071073 \text{ nm})$ at 153 (2) K. Data reduction and cell refinement were performed using Rapid Auto programs.^[18] The absorption corrections were carried out by the multi-scan. The structure was solved by direct methods (Bruker Shelxtl) using all unique data.^[19] All H atoms associated with the cation were visible in difference Fourier maps but were placed geometrically with C-H distances ranging from 0.95 to 0.99 Å and O-H = 0.82 Å. They were allowed to ride during subsequent refinement with $U_{iso}(H) = 1.2$ or 1.5 $U_{eq}(C/O)$. The DMF molecule on the general position is refined in two coplanar orientation, each with 50% site occupancy. The DMF molecule lying on the twofold rotation axis is modelled as one molecule with 50% site occupancy, with bond distancees tightly restained (C40-O9 = 1.200 (5), C40-N9 = 1.320 (5), N9-C37/C38 = 1.420(5) Å) and the whole molecule restrained to be plainar. The

TABLE 1Crystal data and structure refinement for[Zn(Mentb)(salicylate)] (ClO₄) · 1.5DMF

Formula	C _{38.5} H _{42.5} ClZnN _{8.5} O _{8.50}
Molecular weight (g mol^{-1})	861.13
Crystal system	monclinic
Space group	C2/c
Unit cell dimensions	
<i>a</i> (Å)	27.7110 (7)
b (Å)	11.4499 (3)
<i>c</i> (Å)	25.1395 (6)
β (°)	102.829 (1)
Vol (Å ³)	7777.3 (3)
Z	8
T (K)	153 (2)
D (calculated) $(g \cdot cm^{-3})$	1.471
Absorption coefficient (mm^{-1})	0.77
F(000)	3584
Crystal size (mm)	$0.78 \times 0.59 \times 0.52$
θ range for data collection (°)	3.02 to 27.48
Index ranges	$-35 \le h \le 34, -14 \le k \le$
	$14, -32 \le 1 \le 32$
Refinement method	Full-matrix least-squares on F ²
Data/restraints/parameters	$\frac{8893[R(int) = 0.0242]}{8/600}$
Goodness-of-fit on F ²	1.002
Finial R1 and wR2 $[I > 2\sigma(I)]$	0.0363, 0.1060 ^a
R1 and wR2 indices (all data)	0.0425, 0.1113

^aw = $1/[\sigma^2 F_0^2 + (0.0680P)^2 + 9.5996P]$, where P = $(F_0^2 + 2F_c^2)/3$.

atoms of this molecule are refined with isotropic displacement parameters. The largest peak in the residual electron density is associated with the perchlorate anion. The crystal data and experimental parameters relevant to the structure determination are listed in Table 1 and the final positional and thermal parameters are available as supplementary material.

RESULTS AND DISCUSSION

The zinc complex is soluble in DMF and DMSO, but insoluble in water and organic solvents, such as methanol, ethanol, benzene, petroleum ether, trichloromethane etc. The elemental analyses show that the composition is [Zn(Mentb)(salicylate)] (ClO₄)·1.5DMF. A comparison of molar conductance value, shows the 1:1 electrolytes of the complex in DMF with those previously reported in the literature.^[20]

Thermogravimetric analysis (TGA) curve of the zinc(II) complex shows that the initial mass loss within the 163–167°C range is attributed to elimination of the DMF molecules. Differential thermal analysis (DTA) curve indicates that the process appears an endothermic peak. The decomposition of the



FIG. 2. The [Zn(Mentb)(salicylate)]⁺ cation with displacement ellipsoids drawn at the 50% probability level. H atoms are omitted.

complex starts at 242°C and is completed at ca 575°C, yielding ZnO as the final product.

Crystal Structure of [Zn(Mentb)(salicylate)] (ClO₄)·1.5DMF

The molecular structure and crystal packing of the zinc(II) complex are shown in Figures 2 and 3; selected bond distances and angles are shown in Table 2. The asymetric unit

consists of a discrete [Zn(Mentb)(salicylate)] cation, a perchlorate anion, 1.5 molecules of DMF molecules. One dimethylformamide molecule lies on a general position and is disordered over two coplanar orientations with equal occupancy. A second dimethylformamide molecule is disordered about a twofold rotation axis. The Zn^{II} atom is five-coordinate with a ZnN₄O chromophore. The Mentb ligand acts as a tetradentate N-donor, and an O atom of carboxylate groups of the salicylate complete the



FIG. 3. Packing diagram. H atoms are omitted for clarity.

 TABLE 2

 Selected bond distances (Å) and bond angles (°)

Bond distances			
Zn-O(1)	1.9970 (16)	Zn-N(5)	2.0521 (17)
Zn-N(1)	2.0780 (16)	Zn-N(7)	2.4361 (18)
Zn-N(3)	2.0463 (18)	$Zn \cdot \cdot \cdot O(2)$	3.135 (2)
Bond angles			
O(1)-Zn- $N(1)$	92.78 (7)	N(1)-Zn-N(7)	73.14 (6)
O(1)-Zn- $N(3)$	113.72 (7)	N(3)-Zn-N(7)	74.68 (7)
O(1)-Zn-N(5)	110.70 (7)	N(5)-Zn-N(7)	74.91 (6)
N(1)-Zn- $N(3)$	112.91 (7)	C(28)–O(1)–Zn	123.95 (14)
N(3)-Zn-N(5)	110.35 (7)	O(1)-C(28)-O(2)	123.6 (2)
N(5)-Zn-N(1)	115.42 (6)	O(1)-C(28)-C(29)	117.67 (19)
O(1)-Zn-N(7)	165.80 (6)	O(2)-C(28)-C(29)	118.76 (19)

 TABLE 3

 Selected hydrogen bonding distances (Å) and angles (°)

D–H···A	D–H	D···A	$H{\cdots}A$	∠ D–H···A
O3–H3···O2	0.84	2.556 (3)	1.82	146

coordination. The coordination geometry of the Zn^{II} atom is best described as distorted trigonal-bipyramid ($\tau = 0.84$), with approximate molecular symmetry C_3 . The parameter τ is defined as $(\beta - \alpha)/60$ [where $\beta = N(7)-Zn-O(1)$, $\alpha = N(1)-Zn-N(5)$] and its value varies from 0 (in regular square-based pyramidal) to 1 (in regular trigonal bipyramidal).^[21] The coordination geometry around the Zn^{II} atoms appears to relieve the steric crowding. The equatorial plane is occupied by three N atoms of three benzimidazolyl groups, while the Zn^{II} atom protrudes towards O(1) and is 0.560(2) Å from the plane of atoms N(1)/N(3)/N(5). The axial positions are occupied by N(7) and O(1), with Zn-N(7) 2.4361(18) Å, Zn-O(1) 1.9966(14) Å and N(7)-Zn-O(1) is 165.79(6)°. The three benzimidazole ring arms of the Mentb ligand form a cone-shaped cavity. The angles N(3)–Zn–N(1), N(5)-Zn-N(1) and N(5)-Zn-N(3) are 112.96(6), 115.33(6) and 110.38(6)°, respectively. The N(7)-Zn-N(1) 73.13(6), N(7)-Zn-N(3) 74.72(6) and N(7)-Zn-N(5), 74.86(6)° angles, which are all ca 16° less than the ideal 90° , are imposed by the geometry of the Mentb ligand. The distance between Zn^{II} and O(2) is 3.135(2) Å, so O(2) is not coordinated. The angles and distance in the Mentb and salicylate are within the normal ranges. Weak supramolecular $\pi \cdots \pi$, OH–O hydrogen-bonding interactions play important roles in the crystal packing modes in the complex (Figure 3). The selected hydrogen bonds are listed in Table 3.

TABLE 4		
I.r. spectral data for the Zn complex and their relative assignments (cm^{-1})

Compound ^a	$v_{as}COO$	ν _s COO	$\Delta \nu$	v Ar–O	ν C=N	ν C=N–C=C	$\nu \text{ ClO}_4^-$
NaL	1523 s	1374 s	149	1228 m	_		_
Mentb			—	_	1515 m	1475 s	_
Zn complex	1594 s	1367 s	227	1245 m	1499 m	1458 s	1085 bs

 $^{a}L =$ salicylate; b = broad; s = strong; m = mediun.





	δ Ha ₁	δHa_2	δHb	δCH_2	δCH_3	δОН
Compound	(m)	(m)	(m)	(s)	(s)	(bs)
Mentb Zn complex	7.66 8.13	7.24 7.72	7.22 7.36	4.22 4.71	3.45 3.93	9.23

 $^{a}m =$ multiple, s = singlet, bs = broad singlet.

I.r. and Electronic Spectra

The i.r. spectra data for the zinc complex along with their relative assignments are given in Table 4. In the free ligand Mentb, a strong band is found at $ca 1475 \text{ cm}^{-1}$ together along with a weak band at 1515 cm^{-1} . By analogy with the assigned bands of imidazole, the former can be attributed to ν (C=N-Cd=C), while the latter can be attributed to ν (C=N).^[12,22-23] They shift to the higher frequency ca 16–17 cm^{-1} in the complex, which implies direct coordination of all four imine nitrogen atoms to zinc(II). This is the preferred nitrogen atom for coordination as found for other metal complexes with benzimidazoles.^[24] Information regarding the possible bonding modes of the perchlorate may also be obtained from the i.r. spectra. The strong, fairly broad absorption band at 1085 cm⁻¹ indicate that the ionic perchlorate groups (T_d) are present.^[25] Since the carboxylate group can coordinate to the metal ion in a bidentate or a monodentate fashion, the ' Δ criterion', which is based on the difference between the ν_{as} (O–C–O) and ν_{s} (O–C–O) values, compared to the corresponding value in sodium carboxylate, is currently employed to determine the coordinating mode of the carboxylate group.^[26,27] The data in Table 4 suggests that the carboxylate group of salicylate in the complex behaves as a monodentate ligand. This conclusion is confirmed by the result of the crystal structure analysis.

A DMSO solution of Mentb ligand and the copper complex show, as expected, identical u.v. spectra. The u.v. bands of Mentb (290 nm) is only marginally blue shifted (12 nm) in complex, which show clear evidence of C–N coordination to zinc. The absorption band is assigned to $\pi \rightarrow \pi^*$ (imidazole).

¹H-N.M.R. Spectra

The ¹H-N.M.R. spectra of the free ligand Mentb and zinc(II) complex were recorded for d^6 -DMSO solutions and the chemical shift data are given in Table 5. The ligand Mentb exhibits three groups of aromatic proton resonances (δ 7.66, δ 7.24 and δ 7.22). In the zinc(II) complex the three groups of the aromatic proton resonances are observed on shifted downfield slightly, with $\Delta \delta Ha_2 > \Delta \delta Ha_1 > \Delta \delta Hb$. The order is believed to be due to the decrease of the shielding effect on aromatic protons in the order $Ha_2 > Ha_1 > Hb$. In addition, because only one set of benzimidazole proton resonances appears in the spectrum, it is assumed that all three benzimidazole groups are involved in coordination to the same metal ion in solutions. The methylene proton resonance occurs as a singlet, indicating equivalent methylene protons, but is shifted slightly downfield (0.5 ppm) with respect to the free ligand. The slight shift of the methylene protons signal suggests coordination of the apical nitrogen also.^[28] The proton signals of the methyl groups of in the complex are apparently shifted downfield (0.4 ppm) as compared with free Mentb ligand. Proton signals at 9.23 ppm. due to phenolic OH in the complex, appeared suggesting that the phenolic oxygen atoms are not involved in coordination.

SUPPORTING INFORMATION AVAILABLE

Crystallographic data (excluding structure factors) for the structure in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication CCDC 669530 Copies of the data can be obtained, free of charge, on application to the CCDC, 12 Union Road, Cambridge CB2 1EZ, UK.

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