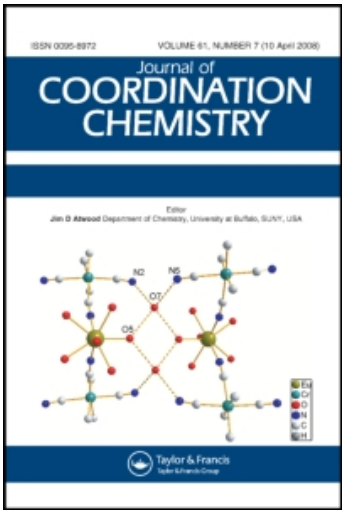

Journal of Coordination Chemistry
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713455674

Synthesis and characterization of a zinc(II) complex of 1,3-bis(1-benzylbenzimidazol-2-yl)-2-oxopropane

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First published on: 15 October 2009

To cite this Article Wu, Hui-Lu , Yun, Rui-Rui , Wang, Kai-Tong , Li, Ke , Huang, Xing-Cai , Sun, Tao and Wang, Yao-Yu(2010) 'Synthesis and characterization of a zinc(II) complex of 1,3-bis(1-benzylbenzimidazol-2-yl)-2-oxopropane', Journal of Coordination Chemistry, 63: 2, 243 — 249, First published on: 15 October 2009 (iFirst)
To link to this Article: DOI: 10.1080/00958970903342125
URL: http://dx.doi.org/10.1080/00958970903342125

Journal of Coordination Chemistry
Vol. 63, No. 2, 20 January 2010, 243–249

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Synthesis and characterization of a zinc(II) complex of 1,3-bis(1-benzylbenzimidazol-2-yl)-2-oxopropane

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(*Received 2 June 2009; in final form 24 July 2009*)

A ligand 1,3-bis(1-benzylbenzimidazol-2-yl)-2-oxopropane (Bobb) and the zinc(II) complex, $[Zn(Bobb)_2](picrate)_2 \cdot 2DMF$, were synthesized and characterized by elemental analyses, electrical conductivities, IR, and UV. The crystal structures of the ligand and the zinc complex have been determined by single crystal X-ray diffraction. The ligand displays a V-shaped configuration and the Zn(II) cation is six-coordinate by four nitrogens and two oxygens from Bobb. The N_4O_2 donor set is a distorted octahedron.

Keywords: Synthesis; Characterization; Crystal structures; Zinc(II) complex

1. Introduction

Benzimidazole derivatives and their metal complexes have been extensively investigated [1–3]. Benzimidazole is a typical heterocyclic ligand with nitrogen donor and a component of biologically important molecules [4]. Interaction of transition metal complexes with nucleic acids has gained prominence [5, 6] because of their relevance in the development of new reagents for biotechnology and medicine. The benzimidazole core is of wide interest because of its diverse biological activities, and it is well known in medicinal chemistry [7]. Bis-1*H*-benzimidazoles are strong coordinating agents forming stable complexes with various transition metals. If the ring substituents change or if there is deviation in the bridging section, the electron distribution and coordination ability are affected [8–10].

In previous papers we investigated the coordinating ability of the polyfunctional benzimidazole ligand tris(*N*-methylbenzimidazol-2-ylmethyl)amine (Mentb) with copper(II) [11]. To continue our interest in the V-shaped ligand, in this article we

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Journal of Coordination Chemistry
ISSN 0095-8972 print/ISSN 1029-0389 online
DOI: 10.1080/00958970903342125

describe the synthesis, crystal structures, IR, and UV-Vis spectra of the ligand Bobb and $[Zn(Bobb)_2](picrate)_2 \cdot 2DMF$.

2. Experimental

2.1. *Materials and physical measurements*

All chemicals were of reagent grade and used without purification. C, H, and N contents were determined using a Carlo Erba 1106 elemental analyzer. IR spectra were recorded on a Nicolet FT-VERTEX 70 spectrometer using KBr pellets. Electronic spectra were taken on a LabTech UV BlueStar plus spectrophotometer. Conductance measurements were made with a DDS-11A conductivity bridge using a 10^{-3} mol L^{-1} solution in DMF at room temperature.

2.2. *Preparation of 1,3-bis(1-benzylbenzimidazol-2-yl)-2-oxopropane (Bobb) and the zinc complex*

1,3-Bis(benzimidazol-2-yl)-2-oxopropane was synthesized following the literature [12]. 5.56 g (20 mmol) 1,3-bis(benzimidazol-2-yl)-2-oxopropane with 1.56 g (40 mmol) potassium in 150 mL tetrahydrofuran was followed by adding 5.06 g (40 mmol) benzyl bromide. The resulting solution was concentrated and recrystallized from methanol giving white block crystals. Yield: 9 g (74%); m.p.: 177–178°C. Anal. Calcd for $C_{30}H_{26}N_4O$ (%): C, 78.58; H, 5.71; N, 12.22. Found (%): C, 78.51; H, 5.73; N, 12.24. Selected IR data (KBr ν/cm^{-1}), 1078 (ν_{C-O-C}), 1496 ($\nu_{C=N}$), 1463 ($\nu_{C=N-C=C}$).

$[Zn(Bobb)_2](picrate)_2 \cdot 2DMF$. To a stirred solution of Bobb (183.2 mg, 0.4 mmol) in hot MeOH (10 mL) was added zinc(II) picrate (104.32 mg, 0.2 mmol) in MeOH (5 mL). A yellow crystalline product which formed rapidly was filtered off, washed with MeOH and absolute Et_2O, and dried *in vacuo*. The dried precipitate was dissolved in DMF resulting in a yellow solution that was allowed to evaporate at room temperature. Yellow crystals suitable for X-ray diffraction studies were obtained after 2 weeks. Yield: 191 mg (66%). Anal. Calcd for $C_{78}H_{70}ZnN_{16}O_{18}$ (MW 1584.89) (%): C, 59.11; H, 4.45; N, 14.14. Found (%): C, 59.20; H, 4.41; N, 14.18. Λ_M (DMF, 297 K): 112.75 S cm^2 mol^{-1}. Selected IR data (KBr ν/cm^{-1}), 1066 (ν_{C-O-C}), 1481 ($\nu_{C=N}$), 1454 ($\nu_{C=N-C=C}$).

2.3. *X-ray structure determinations of Bobb and $[Zn(Bobb)_2](picrate)_2 \cdot 2DMF$*

A suitable single crystal was mounted on a glass fiber and intensity data were collected on a Rigaku R-axis Spider diffractometer with graphite-monochromated Mo-Kα radiation ($\lambda = 0.71073$ Å) at 153 K. Data reduction and cell refinement were performed using Rapid Auto programs [13]. Absorption corrections were carried out by the empirical method. The structure was solved by direct methods and refined by full-matrix least-squares against F^2 using SHELXTL [14]. All hydrogens were found in difference electron maps and subsequently refined in a riding-model approximation with C–H distances ranging from 0.95 to 0.99 Å, $U_{iso}(H) = 1.2U_{eq}(C)$. A summary of parameters for the data collections and refinements is given in table 1.

Table 1. Crystallographic data and data collection parameters for Bobb and $[Zn(Bobb)_2](picrate)_2 \cdot 2DMF$.

Complex	Bobb	$[Zn(Bobb)_2](picrate)_2 \cdot 2DMF$
Empirical formula	$C_{30}H_{26}N_4O$	$C_{78}H_{70}ZnN_{16}O_{18}$
Formula weight	458.55	1584.89
Crystal system	Triclinic	Monoclinic
Space group	*P-1*	*P2(1)/c*
Unit cell dimensions (Å, °)		
a	8.5477(3)°	13.3235(2)°
b	11.8976(5)°	18.1630(3)°
c	12.3961(5)°	30.0144(5)°
A	101.3000(1)	90
B	92.3940(1)	97.2670(1)
γ	107.7650(1)	90
Volume ($Å^3$), *Z*	1170.28(8), 2	7205.0(2), 4
Calculated density ($g\,cm^{-3}$)	1.301	1.461
F(000)	484	3296
Crystal size (mm^3)	$0.58 \times 0.52 \times 0.19$	$0.33 \times 0.25 \times 0.14$
θ range for data collection (°)	3.03–27.48	3.04–27.48
Limiting indices	$-11 \le h \le 10$; $-15 \le k \le 15$; $-16 \le l \le 16$	$-17 \le h \le 17$; $-23 \le k \le 22$; $-38 \le l \le 38$
Reflections collected	11531	65605
Independent reflections	5275 [R(int) = 0.0127]	16426 [R(int) = 0.0385]
Refinement method	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2
Data/restraints/parameters	5275/0/317	16426/0/1019
Goodness-of-fit on F^2	1.091	1.151
Final R indices [$I > 2\sigma(I)$]	$R_1 = 0.0382$, $wR_2 = 0.1113$	$R_1 = 0.0407$, $wR_2 = 0.1013$
R indices (all data)	$R_1 = 0.0460$, $wR_2 = 0.1264$	$R_1 = 0.0666$, $wR_2 = 0.1293$
Largest differences peak and hole ($e\,Å^{-3}$)	0.496 and −0.338	0.542 and −0.858

3. Results and discussions

The ligand and zinc complex are soluble in DMF and methanol but insoluble in other organic solvents. Elemental analyses show that the composition is $[Zn(Bobb)_2](picrate)_2 \cdot 2DMF$. Molar conductance shows a ratio of 1 : 2 electrolyte for the complex in DMF consistent with those previously reported in the literature [15].

3.1. *Description of crystal structure*

The selected bond lengths and angles of Bobb (**1**) and $[Zn(Bobb)_2](picrate)_2 \cdot 2DMF$ (**2**) are in table 2.

The ORTEP structure of ligand with atom-numbering is shown in figure 1. The C–O–C angle, 110.65(9)°, slightly deviates from tetrahedral and the dihedral angles between the benzimidazole ring system and phenyl ring in each of the benzyl-benzimidazole moieties are 76.79(12) and 86.10(11) Å, indicating that it is asymmetric.

As shown in figure 2, the zinc(II) is six-coordinate with four imino nitrogens and two oxygens of the two ligands Bobb. The average Zn–N and Zn–O bond distances are 2.1058 and 2.355 Å, respectively, longer than those reported for Zn(II) coordination complexes. Examples are $[Zn(FeCO_2)_2(prbbm)]_2 \cdot 2CH_3OH \cdot 2H_2O$ (prbbm = 1,1′-(1,3-propanediyl)bis-1H-benzimidazole) [16] and $[Zn_4(o\text{-bda})_4(p\text{-pbim})_4]_n$

Table 2. Selected atomic distances (Å) and bond angles (°) for **1** and **2**.

1			
Bond distances			
O–C(8)	1.4211(14)	O–C(9)	1.4350(14)
Bond angles			
C(8)–O–C(9)	110.65(9)	C(7)–N(1)–C(1)	104.47(10)
C(7)–N(2)–C(6)	106.33(9)	C(7)–N(2)–C(24)	128.47(10)
C(10)–N(4)–C(11)	106.39(10)	N(2)–C(24)–C(25)	114.13(10)
C(10)–N(3)–C(16)	104.83(10)	C(11)–N(4)–C(17)	126.55(10)
2			
Bond distances			
Zn–N(1)	2.0974(18)	Zn–N(5)	2.1164(16)
Zn–N(3)	2.0988(17)	Zn–O(2)	2.3533(14)
Zn–N(7)	2.1106(16)	Zn–O(1)	2.3567(14)
Bond angles			
N(1)–Zn–N(3)	136.28(6)	N(3)–Zn–O(2)	119.08(6)
N(1)–Zn–N(7)	100.17(6)	N(7)–Zn–O(2)	70.51(5)
N(3)–Zn–N(7)	105.03(7)	N(5)–Zn–O(2)	68.58(5)
N(1)–Zn–N(5)	93.77(6)	N(1)–Zn–O(1)	70.02(6)
N(3)–Zn–N(5)	90.27(7)	N(3)–Zn–O(1)	69.62(6)
N(7)–Zn–N(5)	138.74(6)	N(7)–Zn–O(1)	103.72(6)
N(1)–Zn–O(2)	102.74(6)	O(2)–Zn–O(1)	170.22(5)

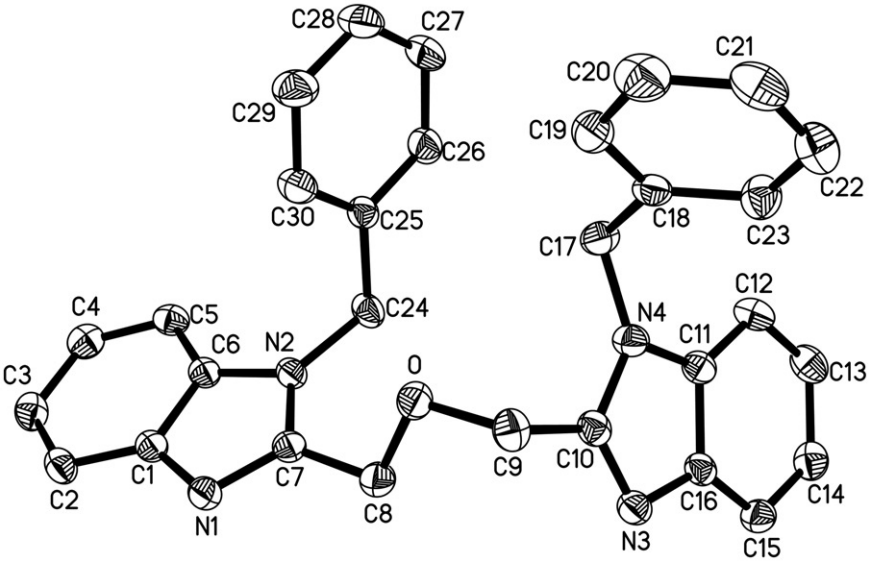

Figure 1. The structure of Bobb.

(o-bda^{2-} = o-phenylenediacetic acid dianion, p-pbim = 4-pyridylbenzimidazole) [17]. The angles N(1)–Zn–O(1), N(3)–Zn–O(1), N(5)–Zn–O(2), and N(7)–Zn–O(2) are 70.02(6)°, 69.62(6)°, 68.58(5)°, and 70.51(5)°, respectively, which are imposed by the geometry of the Bobb ligand. Bobb is tridentate and the Zn(II) can be described as a distorted octahedron [18]. The coordination geometry around Zn(II) appears to relieve steric crowding. The coordination cations are stabilized by weak $\pi\cdots\pi$ stacking with

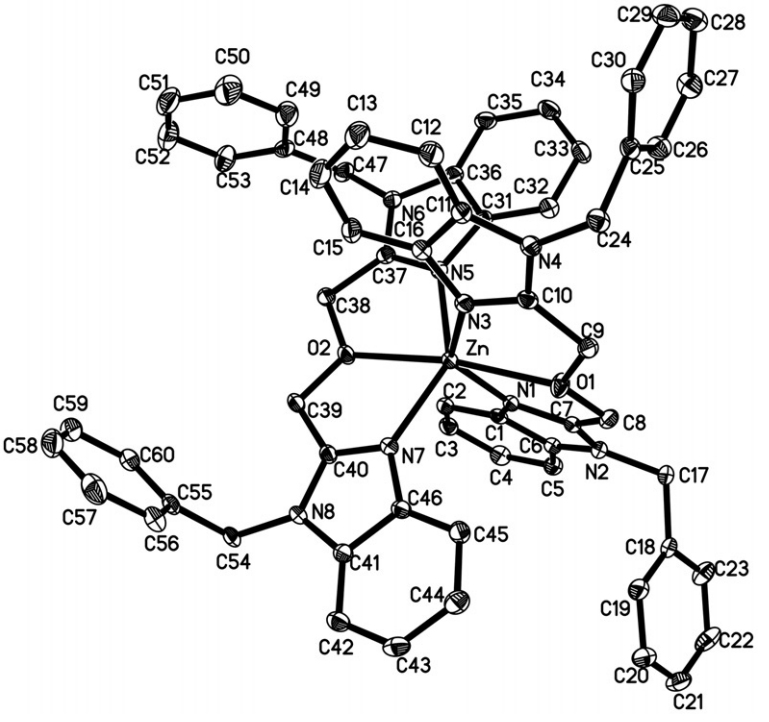

Figure 2. The cation of the zinc(II) complex showing displacement ellipsoids at the 30% probability level. Hydrogen atoms have been omitted for clarity.

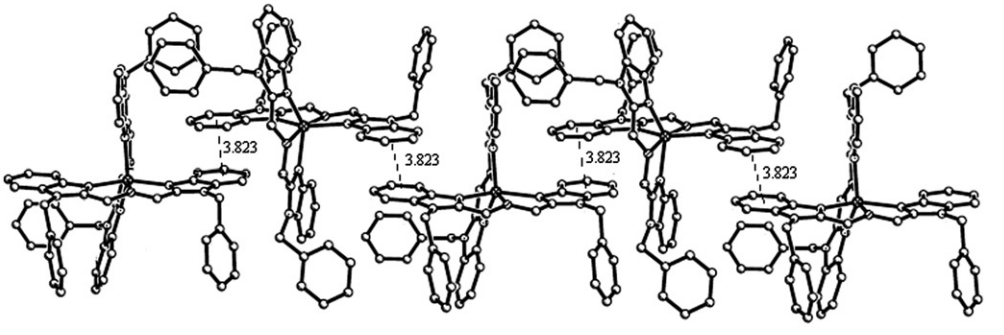

Figure 3. View of the 1-D cation chain $\{[Zn(Bobb)_2]^{2+}\}_n$ of the complex linked via $\pi\cdots\pi$ stacking interaction.

the centroid distances 3.823(1) Å (figure 3). Each picrate anion and DMF form acceptor hydrogen bonds with the neighboring $[Zn(Bobb)_2]^{2+}$ cations.

3.2. *IR spectra*

IR spectra of the complex show that the strong $\nu_{C=N}$ in free Bobb at 1496 cm^{-1} shifts to 1481 cm^{-1}. The red shift indicates that the imino nitrogens of the ligands are

coordinated to zinc(II). These are the preferred nitrogens for coordination, as found in other metal complexes with benzimidazoles [19]. The ν_{C-O-C} (1078 cm^{-1}) in the ligand also showed bathochromic shift to 1066 cm^{-1} in the complex, suggesting that ethereal oxygens of Bobb are involved in bonding [20]. The bands at 707, 1163, 1365, and 747 cm^{-1} indicate that ionic picrate and benzimidazole rings are present.

UV absorption spectra of the ligand and zinc complex show bands at 277 and 280 nm, respectively. The red shift reveals that the ligand is coordinated, agreeing with X-ray diffraction.

4. Concluding remarks

We have synthesized Bobb and its zinc complex. Bobb is tridentate and the Zn(II) is distorted octahedral. The zinc complex exhibits infinite 1-D trapeziform architectures with weak $\pi \cdots \pi$ stacking interactions between the benzimidazole rings.

Supplementary material

Crystallographic data (excluding structure factors) for the structure in this article have been deposited with the Cambridge Crystallographic Data Center as supplementary publication CCDC 721400 and 721078. Copies of the data can be obtained, free of charge, on application to the CCDC, 12 Union Road, Cambridge CB2 1EZ, UK.

Acknowledgements

We thank the financially support and grant from "Qing Lan" Talent Engineering Funds and Student's Science and Technology Innovation Funds (grant no. DXS2008-041) by Lanzhou Jiaotong University. The grant from the "Long Yuan Qing Nian" of Gansu Provinces is also acknowledged.

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