

Synthesis and Crystal Structure of (*o*-Diaminobenzene)₂Zn(OAc)₂¹

L. Mei^{a,*}, J. Li^a, Z. S. Ming^b, L. Q. Rong^b, and L. X. Liang^a

^a Hefei University of Technology, Hefei 230009, P.R. China

^b University of Science and Technology of China, Hefei 230009, P.R. China

*e-mail: luomei@pku.edu.cn; luomeihuahua@sohu.com

Received February 20, 2009

Abstract—The treatment of *o*-diaminobenzene with Zn(OAc)₂ · 2H₂O in alcohol results in the formation of mononuclear bis(*o*-diaminobenzene)diacetate Zinc, Zn[C₈H₁₁N₂O₂]₂. Its structure was determined by X-ray diffraction analysis. The complex is also characterized by elemental analysis, ¹H NMR and IR. The crystal is monoclinic space group C2, parameters: *a* = 16.297(5), *b* = 4.775(3), *c* = 11.664(5) Å, β = 97.646(5)°, λ = 1.54184 Å, *V* = 899.6(7) Å³, *Z* = 2, ρ_c = 1.476 g/cm³, *M_r* = 399.75, *F*(000) = 416.0, *R*₁ = 0.0594, *wR*₂ = 0.1439 for 995 observed reflections with *I* > 2σ(*I*).

DOI: 10.1134/S107032840912001X

INTRODUCTION

The Zn–N complexes have been reported by many literatures [1–6], because they occupied an important position in catalytic processes. For example, as the catalysts they have showed high activities in the organic reaction and polymerization [7, 8]. Inspired by their work, we first synthesized the novel Zn–N complex with the simple one-pot method. The crystal structure was obtained in the process of recrystallization and characterized by elemental analysis, ¹H NMR and IR.

EXPERIMENTAL

The ¹H NMR spectra were obtained using a Bruker AM-300 spectrometer. Infrared spectra were recorded on a Mattson Galaxy Series Spectrum-100 spectrometer. Elemental analysis was performed on a VARIO ELIII elemental analyzer. And crystal structure was determined by Gemini S Ultra diffractometer.

Synthesis of bis(2-aminopyridine) zinc complex (I). *o*-Diaminobenzene (0.3244 g, 3 mmol) was added to an ethanolic solution (30 ml) of Zn(OAc)₂ · 2H₂O (0.6575 g, 3 mmol) in dry ethanol 100-ml Schlenk flask under free-water and free-oxygen conditions. The reaction mixture was stirred vigorously while refluxing for 24 h and then filtered. The solution was slowly cooled to room temperature, and a silver-gray solid slowly separated out. Recrystallizing the silver-gray solid with dichloromethane, colorless block crystals, which were

suitable for X-ray single crystal analysis, were obtained. The yield of I was 37% (0.24 g).

For Zn[C₈H₁₁N₂O₂]₂

anal. calcd, %: C, 48.07; H, 5.55; N, 14.02.

Found, %: C, 48.20; H, 5.636; N, 14.13.

¹H NMR (300 MHz, CDCl₃; 27°C; δ, ppm): 6.46–7.09 (s, 8H), 2.30–3.57 (s, 8H), 1.78–2.16 (s, 6H). IR spectrum (KBr pellet; ν, cm⁻¹): 3412, 3348, 3266, 3232, 3130, 3045, 2925, 2796, 2720, 2507, 1912, 1872, 1750, 1663, 1625, 1571, 1507, 1401, 1337, 1305, 1222, 1111, 1020, 935, 858, 741, 681, 655, 529, 481, 440.

X-ray structure determination. A colorless block monoclinic crystal of compound I approximating to 0.28 × 0.26 × 0.20 mm was selected for the data collection on a Gemini S Ultra diffractometer with graphite monochromated MoK_α radiation (λ = 1.54184 Å). Reflections were collected in a range of 3.82° < θ < 62.79° by using “multi-scan” techniques at 295 K, C₁₆H₂₂N₄O₄Zn, *M* = 399.75, γ = 90°, *V* = monoclinic, space group C₂, *a* = 16.297(5), *b* = 4.775(3), *c* = 11.664(5) Å, β = 97.646(5)°, *V* = 899.6(7) Å³, *Z* = 2, ρ_{calcd} = 1.47 g/cm³, the final *R* factor was *R*₁ = 0.0594, 995 for reflections with *I*₀ > 2σ(*I*₀), *Rw* = 0.1439 for all data, largest peak and hole was 0.82 and -0.58 e Å⁻³, respectively. H atoms on N(1) atom were fixed geometrically and constrained to ride on it parent atom, with N–H = 0.90 Å, and with *U*_{iso}(H) = 1.2*U*_{eq}(N). H atoms on N(2) atom were located in difference Fourier maps and refined isotropically, with restraints of N–H = 0.90(4). The remaining H atoms were positioned geometrically with C–H = 0.93 and 0.96 Å, for aromatic and methyl H atoms and constrained to ride on their parent atoms, with *U*_{iso}(H) =

¹ The article is published in the original.

Table 1. Selected bond distances and bond angles for complex I

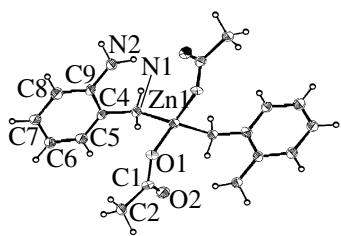
Bond	<i>d</i> , Å	Angle	ω , deg
Zn(1)–O(1)	1.9619	O(1)Zn(1)O(1)	99.70
Zn(1)–N(1)	2.0522	O(1)Zn(1)N(1)	101.55
O(1)–C(1)	1.3153	N(1)Zn(1)N(1)	106.44
O(2)–C(1)	1.2084	C(1)O(1)Zn(1)	111.71
N(1)–C(4)	1.4487	C(4)N(1)Zn(1)	115.33
N(2)–C(9)	1.3723	O(2)C(1)O(1)	121.12
		O(2)C(1)C(2)	122.23
		O(1)C(1)C(2)	116.64

$xU_{eq}(C)$, where $x = 1.2$ for aromatic H and $x = 1.5$ for methyl H atoms. The structure was solved by full-matrix least squares on F^2 using the SHELXTL program [9–11]. Selected bond distances and bond angles are listed in Table 1.

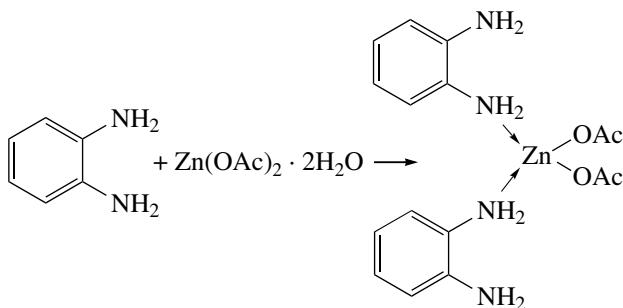
The atomic coordinates and other parameters of structure I have been deposited with the Cambridge Crystallographic Data Center (no. 730209; deposit@ccdc.cam.ac.uk).

RESULTS AND DISCUSSION

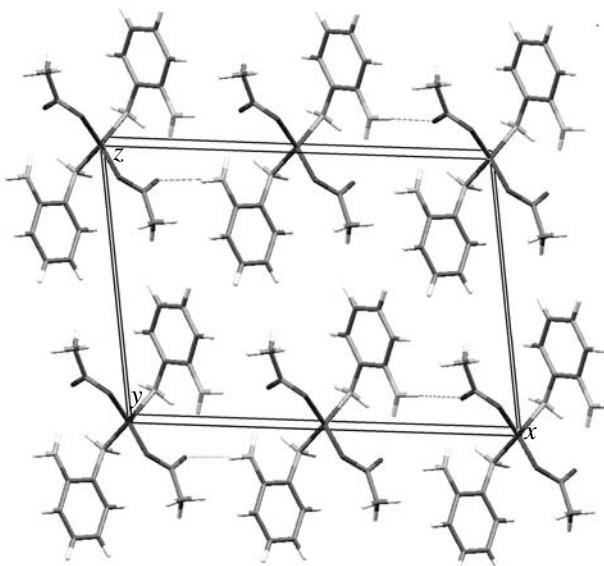
The synthetic route of compound I can be summarized as follows:

**Fig. 1.** Crystal structure of complex I.**Table 2.** Hydrogen bond distances and angles for the complex

Contact D–H…A	Distance, Å			Angle DHA, deg
	D–H	H…A	D…A	
N(2)–H(1B)…O(1)	0.90	2.08	2.948(8)	162(1)
N(2)–H(2D)…O(2)	0.90(2)	2.20(2)	3.091(9)	170(9)



Several interesting observations can be made about the structure from Fig. 1. The complex I was composed of two *o*-diaminobenzene, and $\text{Zn}(\text{OAc})_2$ cores, around the zinc ion is N(1), N(2), O(1) and O(3), with these atoms forming a tetrahedron with the zinc ion in the center. The C(4)–C(9) atoms are coplanar. The bond lengths C–C are in range of 1.368–1.400 Å, and the CCC angles are nearly 120°. The bond distance C(1)–O(2) 1.208 Å, indicating some double-bond characters. Four *o*-diaminobenzene molecules, and two $\text{Zn}(\text{OAc})_2$ cores are connected together to construct a hydrogen-

**Fig. 2.** Packing structure of complex I.

bonded dinuclear structure (Fig. 2). The hydrogen-bond distance N···O of are given in Table 2.

In conclusion, crystalline of $Zn[C_8H_{11}N_2O_2]_2$ was synthesized with a simple, one-pot method. Research is going toward the application to organic reactions such as the Henry reaction and cyaosilylation reaction.

REFERENCES

- Chaudhuri, U.P., Whiteaker, L.R., Mondal, A., et al., *Inorg. Chim. Acta*, 2007, vol. 360, p. 3610.
- Singh, A.K., Kumari, S., and Kumar, K.R., *Polyhedron*, 2008, vol. 27, p. 181.
- Ali, M.A., Bakar, H.J.H.A., Mirza, A.H., and Smith, S.I., *Polyhedron*, 2008, vol. 27, p. 71.
- Wang, Z.M., Zhou, Z.F., Lin, H.K., et al., *Chin. J. Inorg. Chem.*, 2000, vol. 16, p. 267.
- Chen, F.T., Tang, G.R., and Jin, G.X., *J. Org. Chem.*, 2007, vol. 692, p. 3435.
- Sumanta, K.P., Rojalin, S., and Vadivelu, M., *Polyhedron*, 2008, vol. 27, p. 805.
- Chakraborty, D. and Chen, E.Y.X., *Organometallics*, 2003, vol. 22, p. 769.
- Yu, K. and Jones, C.W., *Organometallics*, 2003, vol. 22, p. 2571.
- Sheldrick, G.M., *SHELXS-97, Program for X-Ray Crystal Structure Solution*, Göttingen (Germany): Univ. of Göttingen, 1997.
- Sheldrick, G.M., *SHELXL-97, Program for X-Ray Crystal Structure Refinement*, Göttingen (Germany): Univ. of Göttingen, 1997.
- Stout, G.H. and Jensen, L.H., *X-Ray Structure Determination: a Practical Guide*, New York: MacMillan, 1968.