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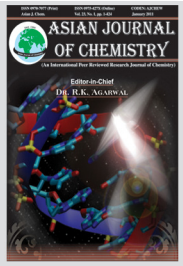

Synthesis, Crystal Structure of Zinc Complex {[$Zn(CH_3CH_2COO)_2(C_7H_6N_2S)_2$]·$CH_3OH$}

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A zinc(II) complex with the formula {[$Zn(CH_3CH_2COO)_2(C_7H_6N_2S)_2$]·$CH_3OH$}was synthesized by the reaction of zinc propionate [$Zn(CH_3CH_2COO)_2$] and 2-aminobenzothiazol ($C_7H_6N_2S$) in methanol medium. The complex was characterized by elemental analysis and IR spectrum. The crystal structure of the complex {[$Zn(CH_3CH_2COO)_2(C_7H_6N_2S)_2$]·$CH_3OH$} was also determined by X-ray single crystal diffraction. The crystal belongs to monoclinic system with space group P2(1)/n and crystallographic data of the compound are: a = 0.89443(14) nm, b = 0.99724 (17) nm, c = 2.8002(3) nm, $\alpha = \gamma = 90°$, $\beta = 96.929(2)°$, V = 2.4795(6) nm^3; D_c = 1.457 g/cm^3; Z = 4; F(000) = 1128; m = 1.197 mm^{-1}.

Key Words: Zn(II) complex, Synthesis, Crystal structure.

INTRODUCTION

Zinc is the significant element in life science and is one of important micro element for human and animals, so there are synthesis of zinc complexes available in literature[1-4]. Propionic acid is the product among metabolic process of human or animals, propionate salts is generally recongnized as safety and effective preservative reagents. However, zinc propionate has double effects on preservative and zinc supply which applied to preservation and nutrition of food and beverage[5]. As an important industry intermediate in medicine, farm insecticide and dyestuff, 2-aminobenzothiazol ($C_7H_6N_2S$) is of biological activitity and good coordination for S atom of benzothiazol ring as well as the N atom of -NH_2[6-8]. Herein the synthesis and X-ray crystal structure of the new mixed complex {[$Zn(CH_3CH_2COO)_2(C_7H_6N_2S)_2$]·$CH_3OH$} is reported.

EXPERIMENTAL

Elemental analysis of C, H and N were carried out with a Perkin-Elmer 240 elemental analyzer. IR spectra were measured by using KBr discs on a spectrum One BFT-IR spectrophotometer. The single crystal structure was determined by Siemens Smart-1000 CCD diffractometer. All starting materials were of chemical purity grade.

Synthesis of the complex: In 40 mL methanol medium, 0.4950 g (2 mmol) zinc propionate and 0.556 g (2 mmol) 2-aminobenzothiazol were added, then the mixed solution was refluxed for 1 h to get a colourless transparent solution. After filtered, the solution was kept at room condition for 10 days and then the colourless block crystals resulted from it. The crystals were suitable for analysis of X-ray single crystal diffraction. IR (KBr, cm^{-1}): 3327s, 3120m, 2978w, 1950w, 1645m, 1614m, 1591s, 1540s,1458s,1354w, 751m, 677w, 560w. Anal. calcd. (%) for $C_{21}H_{26}N_4O_5S_2Zn$: C 46.37, H 4.82, N 10.30. Found: C 46.26, 46.31, H 4.75, 4.78, N 10.25, 10.22 %.

Structure determination: A single crystal of the zinc(II) complex with dimensions of 0.58 mm × 0.29 mm × 0.10 mm was selected for the experiment. X-ray diffraction data collection was performed by Siemens Smart-1000 CCD diffractometer with graphite-monochromatized MoK_α radiation (λ = 0.071073 nm) at 298(2) K, using Φ-ω scand mode. A total of 12572 reflections were collected in the range of $1.48° \le \theta \le 26.41°$, of which 4357 reflections were unique with R_{int} = 0.0507. The crystal structure was solved by the direct methods and fourier synthesis with SHELXS-97 program system[9] and refined by full-matrix least squares techniques on F^2 with SHELXS-97 program system[9]. The non-hydrogen atoms were refined anisotropycally and hydrogen atoms were added according to theoretical models. The final refinement converged at R = 0.0421 and wR = 0.1036 ($\omega = 1/[\sigma^2(F_0^2)^2 + (0.0464P)^2 + 5.5696P]$, where $P = (F_0^2 + 2F_C^2)/3$) for 3412 observed reflections with $I > 2\sigma(I)$. S = 1.039, (Δ/σ) max = 0.00, $(\Delta\rho)$ max = 809 and $(\Delta\rho)$ min = -441 $e{\cdot}nm^{-3}$. Crystallographic data of [$Zn(CH_3CH_2COO)_2(C_7H_6N_2S)_2$]·$CH_3OH$} are listed in Table-1.

TABLE-1
CRYSTALLOGRAPHIC DATA OF THE COMPLEX
{[Zn(CH3CH2COO)2(C7H6N2S)2]·CH3OH}

Empirical	$C_{21}H_{26}N_4O_5S_2Zn$
Formula weight	543.95
Crystal system	Monoclinic
Space group	P2(1)/n
a (nm)	0.89443(14)
b (nm)	0.99724(17)
c (nm)	2.8002(3)
α (°)	90
β (°)	96.929(2)
g (°)	90
V/nm^3	2.4795(6)
Z	4
Dc/(g cm^{-3})	1.457
μ (MoK$_\alpha$)/mm^{-1}	1.197
F(000)	1128
Range of θ/(°)	1.47 to 25.01
Index range	-10 ≤ h ≤ 9, -9 ≤ k ≤ 11, -33 ≤ l ≤ 33
Reflections collected/unique (R(int))	12572/4357(0.0507)
Observed data (I>2σ(I))	3412
R1, wR2 (I>2σ(I))	0.0421, 0.1036
R1, wR2 (all data)	0.0584, 0.1130
GOF	1.039
Largest diff. peak and hole/(e nm^{-3})	809 and -441

RESULTS AND DISCUSSION

In the IR spectrum, symmetric and antisymmetric vibrations of -NH_2 of the 2-aminobenzothiazol in the complex exist at 3327 and 3120 cm^{-1}, respectively. A strong absorption at 1645 cm^{-1} can be attributed to distortion vibration of -NH_2 in 2-aminobenzothiazol, which do not coordinate to the central zinc atom. There are some framework vibrations of 2-aminobenzothiazol at 1591, 1540 and 1458 cm^{-1}. A strong absorption at 751 cm^{-1} means that adjacent double replaced benzene ring (benzene ring of 2-aminobenzothiazol) exist. The weak absorption at 2978 cm^{-1} can be attributed to -CH_3 of the complex, whereas there is a difference of 260 cm^{-1} between symmetric and antisymmetric vibrations of -COO group of propionate in the complex at 1614 and 1354 cm^{-1}, respectively, which indicate the fact of single coordination of propionate.

Crystal structure: Single-crystal X-ray diffraction analysis reveal that mixed complex [Zn(CH3CH2COO)2(C7H6N2S)2]·CH3OH} (**1**) crystallizes in monoclinic system with P2(1)/n space group. The selected important bond parameters are given in Table-2. The molecular structure and packing diagram of the Zn(II) compound in a unit cell are shown in Figs. 1 and 2. From the Fig. 1, the complex [Zn(CH3CH2COO)2(C7H6N2S)2]·CH3OH} (**1**) is a neutral complex. The central zinc atom is coordinated by two O atoms from two propionate and two N atoms from two 2-aminobenzothiazol, where the N atom of -NH_2 do not coordinate to the central zinc atom and one methanol molecule of no-coordination exist, forming a distorted tetrahedral geometry, which bond lengths of Zn(1)-O(1), Zn(1)-O(3), Zn(1)-N(1) and Zn(1)-N(3) are 0.1971(2), 0.1984(2), 0.2058(3) and 0.2066(3) nm, respectively. There are weak interactions between the central zinc atom with another two O atoms from two propionate and its weak interaction lengths of

TABLE-2
SELECTED BOND LENGTHS (nm) AND ANGLES (°) OF
{[Zn(CH3CH2COO)2(C7H6N2S)2]·CH3OH}

Bond	Dist.	Bond	Dist.
Zn(1)-O(1)	0.1984(2)	Zn(1)-O(3)	0.1971(2)
Zn(1)-O(2)	0.2569(3)	Zn(1)-O(4)	0.2681(3)
Zn(1)-N(1)	0.2058(3)	Zn(1)-N(3)	0.2066(3)
Angle	(°)	Angle	(°)
C(8)-N(3)-Zn(1)	125.7(2)	C(2)-N(1)-Zn(1)	120.5(2)
C(9)-N(3)-Zn(1)	122.8(2)	C(18)-O(3)-Zn(1)	108.3(2)
C(18)-O(4)-Zn(1)	76.2(2)	C(15)-O(1)-Zn(1)	104.6(2)
C(15)-O(2)-Zn(1)	78.5(2)	O(3)-Zn(1)-N(1)	109.19(11)
O(3)-Zn(1)-O(1)	131.50(10)	O(1)-Zn(1)-N(1)	104.75(10)
O(3)-Zn(1)-N(3)	103.51(11)	O(1)-Zn(1)-N(3)	105.49(10)
N(1)-Zn(1)-N(3)	97.18(11)	O(3)-Zn(1)-O(2)	87.20(10)
O(1)-Zn(1)-O(2)	55.48(9)	N(1)-Zn(1)-O(2)	160.23(10)
N(3)-Zn(1)-O(2)	89.30(10)	O(3)-Zn(1)-O(4)	53.57(9)
O(1)-Zn(1)-O(4)	91.50(9)	N(1)-Zn(1)-O(4)	93.23(10)
N(3)-Zn(1)-O(4)	156.99(10)	O(2)-Zn(1)-O(4)	87.73(9)
C(1)-N(1)-Zn(1)	127.0(2)	–	–

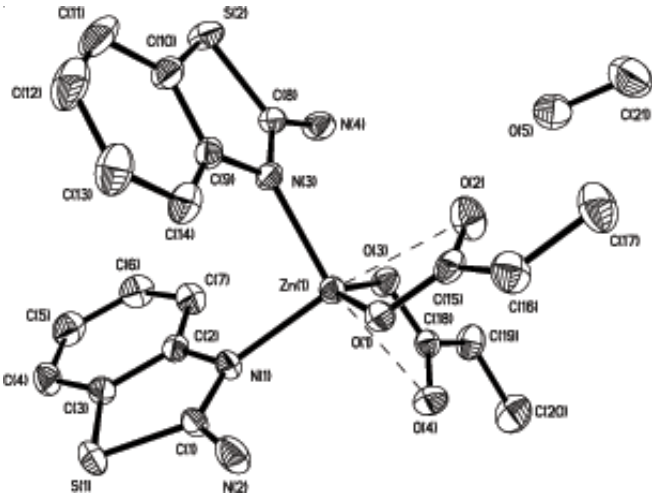

Fig. 1. Stereoview of complex {[Zn(CH3CH2COO)2(C7H6N2S)2]·CH3OH}

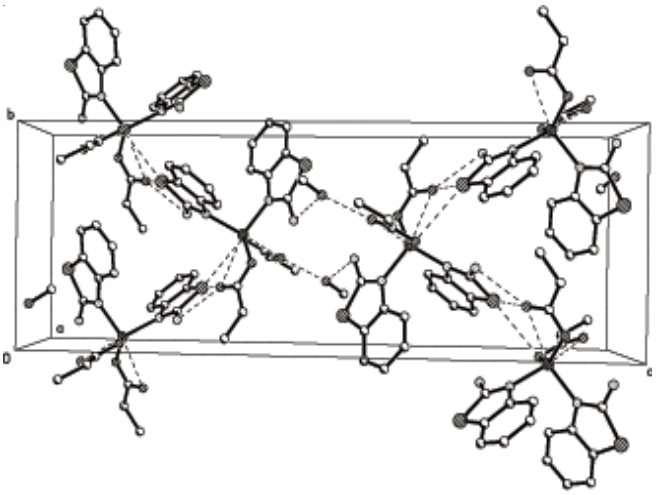

Fig. 2. Cell diagram of complex{[Zn(CH3CH2COO)2(C7H6N2S)2]·CH3OH}

Zn(1)-O(2) and Zn(1)-O(4) are 2.569(3) and 2.681(3) nm. Consideration of weak interactions, the central zinc atom is coordinated by four O atoms from two propionate and two N atoms from two 2-aminobenzothiazol, forming a distorted octahedral coordination structure, obviously different from the complexes[6,7] [Zn(CH3COO)2(C7H6N2S)2] and

TABLE-3
HYDROGEN BONDS OF THE TITLE COMPLEX

D–H···A	d_{D-H} (nm)	$d_{H\cdots A}$ (nm)	θ_{DHA} (°)	$d_{D\cdots A}$ (nm)	Symmetry code
N2-H2A···O1	0.0860	0.2242	146.27	0.2996	
N2-H2B···O4	0.0860	0.2066	156.31	0.2874	[-x+1/2, y-1/2, -z+3/2]
N4-H4A···O3	0.0860	0.2089	152.54	0.2879	
N4-H4B···O5	0.0860	0.2045	149.52	0.2821	[-x+1, -y+1, -z+1]
O5-H5···O2	0.0820	0.1890	171.33	0.2703	

$[Zn(CF_3COO)_2(C_7H_6NS)_2]$. The angles around the zinc atom range from 53.57(9)° to 160.23(10)°. From Fig. 2, the cell diagram of the zinc(II) complex (**1**) consist of four complexes molecules of $[Zn(CH_3CH_2COO)_2(C_7H_6N_2S)_2]\cdot CH_3OH\}$, one O atom of propionate in a title complex molecule acts as a hydrogen-bond donor to the H atom of -OH group in methanol, forming the hydrogen bond of O–H···O with the length of 0.1890 nm, whereas the O atom of -OH group in methanol acts as a hydrogen-bond donor to the H atom of $-NH_2$ group of 2-aminobenzothiazol in another title complex molecule forming the hydrogen bond of N–H···O with bond length from 0.2045 to 0.2242 nm, these hydrogen bonds data were given in Table-3.

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REFERENCES

1. Z.M. Zhang, J. Gao, K.J. Wei, J. Ni and T.T Xu, *J. Synth. Cryst.*, **37**, 1499 (2008).
2. J. Wang, X.Y. Xu, W.X. Ma, H. Zhao, L.D. Lu, X.J. Yang and X. Wang, *J. Synth. Cryst.*, **37**, 1199 (2008).
3. B.H. Qian, W.X. Ma, S.Z. Li, X.Y. Xu, L.D. Lu, X.J. Yang and X. Wang, *J. Synth. Cryst.*, **36**, 1305 (2007).
4. D.B. Dang, Y. Bai and H.Y. Li, *J. Synth. Cryst.*, **36**, 1105 (2007).
5. S.L. Wang and G.T. Chen, *Food Sci. Technol.*, **33**, 234 (2008).
6. W.X. Ma, B.H. Qian, Q.F. Cheng, J. Wang, X.Y. Xu, L.D. Lu, X.J. Yang and X. Wang, *J. Synth. Cryst.*, **35**, 1061 (2006).
7. W.X. Ma, B.H. Qian, S.Z. Li, J. Wang, X.Y. Xu. L.D. Lu and H.B. Song, *Chin. J. Inorg. Chem.*, **22**, 1925 (2006).
8. Z.F. Chen, M. Zhang, S.M. Shi, L. Huang, H. Liang, Q. Xu and K.B. You, *Chin. J. Appl. Chem.*, **22**, 730 (2005).
9. O.H. Hankovszky, K. Hideg, D. Lloyd and H. McNab, *J. Chem. Soc. Chem. Commun.*, 378 (1974).