

КРАТКИЕ СООБЩЕНИЯ

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CRYSTAL STRUCTURE OF DIACETATO-BIS(2-METHYL-2-PROPYLAMINE)ZINC(II)

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The diacetato-bis(2-methyl-2-propylamine)zinc(II) compound crystallizes in the triclinic system, space group $P-1$ with unit cell parameters $a = 10.0144(10) \text{ \AA}$, $b = 10.2687(10) \text{ \AA}$, $c = 10.5149(10) \text{ \AA}$, $\alpha = 115.184(2)^\circ$, $\beta = 97.489(2)^\circ$, $\gamma = 114.066(2)^\circ$, $v = 830.85(14) \text{ \AA}^3$. The obtained solid state structure of $(^t\text{BuNH}_2)_2\text{Zn}(\text{OOCCH}_3)_2$ shows both inter- and intramolecular $\text{NH}\cdots\text{O}$ hydrogen bond interactions which are analyzed.

Key words: zinc acetate, amine, hydrogen bond, $\text{NH}\cdots\text{O}$ interaction.

Introduction. The chemistry of zinc carboxylate has been an interesting area of research for the past three decades [1]. It has many applications in the field of organic reactions as a catalyst and a precursor of zinc oxide related materials and bioscience [2–5]. Examples of Lewis-base (amine, pyridine, phosphine, N-heterocyclic carbene) adduct of zinc acetate are well known together with its application in organic transformations, especially as a catalyst in lactide polymerization and CO_2 copolymerization [6–9]. Also such type of simple zinc acetates was used as secondary building units (SBUs) in porous materials [10]. Extending the example of the Lewis base adduct of zinc acetate, *tert*-butylamine adduct of zinc acetate has been synthesized and characterized by single crystal X-ray diffraction, ^1H NMR, and elemental analysis. Also, weak $\text{NH}\cdots\text{O}$ hydrogen bond interactions are discussed.

Experimental. Anhydrous zinc acetate and $^t\text{Bu}\text{—NH}_2$ were purchased from SD Fine Chemicals, India and used as received. Under the inert atmosphere, a 100-ml flask was charged with anhydrous $\text{Zn}(\text{OOCCH}_3)_2$ (2 mmol, 0.37 g) in toluene (30 ml). To this, 5 ml of $^t\text{Bu}\text{—NH}_2$ was added and the resulting solution was stirred for 3 h. 1/3 of the solvent was removed by vacuum and kept for crystallization at -10°C . Colorless prism-type crystals were obtained after 10 days. Yield (based on $\text{Zn}(\text{OOCCH}_3)_2$): 0.83 g, 84%. Anal. Calcd. for $\text{C}_{12}\text{H}_{28}\text{N}_2\text{O}_4\text{Zn}$ (329.77): C, 43.71; H, 8.56; N, 8.49. Found: C, 43.24; H, 8.32; N, 8.27. ^1H NMR (400 MHz, CDCl_3 , 22°C , TMS): δ 1.15 (s, 18H, $\text{C}(\text{CH}_3)_3$), 2.12 (s, 6H, —OOCCH_3).

^1H NMR spectra were obtained on a JEOL-JNM LAMBDA 400 model spectrometer operating at 400 MHz. The spectra were recorded in the CDCl_3 solution, and the chemical shifts were referenced with respect to TMS. Crystals were coated with light hydrocarbon oil and mounted in the 100 K dinitrogen stream of a Bruker SMART APEX CCD diffractometer equipped with a CRYO Industries low-temperature apparatus, and intensity data were collected using graphite monochromated MoK_α radiation ($k = 0.71073 \text{ \AA}$). The data integration and reduction were processed with the SAINT software [11]. An absorption correction was applied [12]. Structures were solved by the direct method using SHELXS-97 and were refined on F^2 by the full-matrix least-squares technique using the SHELXL-97 software package [13]. Non-hydrogen atoms were refined anisotropically. In the refinement, hydrogen atoms were treated as riding atoms using SHELXL default parameters. The crystallographic fi-

Table 1

Crystal data and data collection parameters for the $({}^t\text{BuNH}_2)_2\text{Zn}(\text{OOCCH}_3)_2$ compound

Identification code	$({}^t\text{BuNH}_2)_2\text{Zn}(\text{OOCCH}_3)_2$
Empirical formula	$\text{C}_{12}\text{H}_{28}\text{N}_2\text{O}_4\text{Zn}$
Formula weight	329.75
Temperature, K	100(2)
Crystal system, space group	Triclinic, $P-1$
Unit cell dimensions $a, b, c, \text{\AA}$; $\alpha, \beta, \gamma, \text{deg.}$	10.0144(10), 10.2687(10), 10.5149(10); 115.184(2), 97.489(2), 114.066(2)
Volume, \AA^3	830.85(14)
Z , calculated density, mg/m^3	2, 1.318
Absorption coefficient, mm^{-1}	1.489
$F(000)$	352
Crystal size, mm	0.04×0.03×0.01
θ range for data collection, deg.	2.30 to 26.00
Index ranges	$-12 \leq h \leq 12, -11 \leq k \leq 12, -12 \leq l \leq 6$
Reflections collected	4739
Independent reflections	3266 [$R(\text{int}) = 0.01741$]
Completeness to $\theta, \%$	97.9
Data / restraints / parameters	3198 / 0 / 180
Goodness-of-fit on F^2	0.725
Final R indices [$I > 2\sigma(I)$] ^a	$R1 = 0.0348,^a$ $wR2 = 0.0941$
R indices (all data)	$R1 = 0.0371,^a$ $wR2 = 0.0969^b$
Largest diff. peak and hole, e/\AA^{-3}	1.176 and -0.663

$$^a \frac{\sum ||F_0| - |F_c||}{\sum |F_0|}$$

$$^b \frac{\sqrt{\sum [w(F_0^2 - F_c^2)^2]}}{\sqrt{\sum w(F_0^2)^2}}$$

figures were generated using the *Diamond 3.1f* software. Crystal data and data collection parameters for the compound are given in Table 1. CCDC 846534 contains the supplementary crystallographic data for diacetato-bis(2-methyl-2-propylamine)zinc. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Results and discussion. ${}^1\text{H}$ NMR spectra of $({}^t\text{BuNH}_2)_2\text{Zn}(\text{OOCCH}_3)_2$ (**1**) were recorded in deuterated chloroform (CDCl_3). The spectra of **1** show resonance peaks at 1.15 ppm for $-\text{CH}_3$ of the *tert*-butyl moiety and at 2.12 ppm for $-\text{CH}_3$ of the acetate moiety in the ratio of 3:1. The NMR spectral analysis supports the molecular structure of **1**.

Single crystals of $({}^t\text{BuNH}_2)_2\text{Zn}(\text{OOCCH}_3)_2$ were grown in a toluene solution at -10°C and a suitable one was subjected to the X-ray structural analysis. The compound crystallizes in the triclinic system, space group $P-1$. Bond lengths and bond angles are shown in Table 2. The solid state structure

Table 2

Important bond distances and angles of $({}^t\text{BuNH}_2)_2\text{Zn}(\text{OOCCH}_3)_2$

Bond Distances (\AA)		Bond Angles (deg.)			
Zn(1)—O(1)	1.9678(16)	O(1)—Zn(1)—O(3)	99.37(7)	N(1)—Zn(1)—N(2)	116.03(7)
Zn(1)—O(3)	1.9695(16)	O(1)—Zn(1)—N(1)	119.64(7)	C(1)—O(1)—Zn(1)	113.31(14)
Zn(1)—N(1)	2.0321(18)	O(3)—Zn(1)—N(1)	110.49(7)	C(3)—O(3)—Zn(1)	122.18(15)
Zn(1)—N(2)	2.0427(18)	O(1)—Zn(1)—N(2)	107.97(7)	C(5)—N(1)—Zn(1)	119.16(14)
		O(3)—Zn(1)—N(2)	100.36(7)	C(9)—N(2)—Zn(1)	125.58(14)

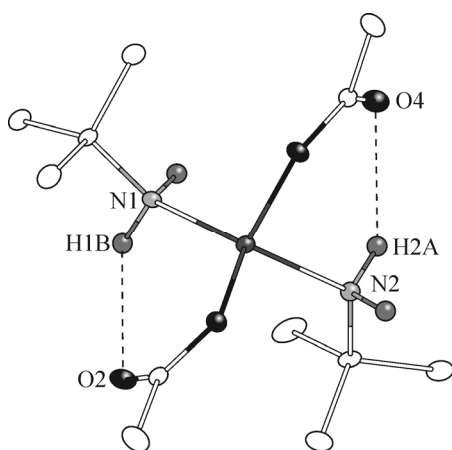


Fig. 1. Molecular structure of $({}^t\text{BuNH}_2)_2\text{Zn}(\text{OOCCH}_3)_2$. Thermal displacement ellipsoids are drawn at the 30 % probability level. Except hydrogen of $-\text{NH}_2$, all hydrogen atoms were omitted for clarity

shows that two molecules of *tert*-butylamine are coordinated to zinc acetate and the zinc center adopts a tetrahedral geometry (Fig. 1). The bond between zinc and nitrogen of *tert*-butylamine, zinc and oxygen of acetate shows two different sets of values. The average Zn—N distance is 2.0374 Å and Zn—O is 1.9686 Å. The O(1)—Zn(1)—O(3) bond angle ($99.37(7)^\circ$) is smaller than N(1)—Zn(1)—N(2) ($116.03(7)^\circ$).

The solid state structure of $({}^t\text{BuNH}_2)_2\text{Zn}(\text{OOCCH}_3)_2$ shows two intramolecular NH---O hydrogen bond interactions between oxygen of the acetate group and —NH from amine.

This hydrogen bond helps to form six-membered rings within the molecule (Fig. 1). The molecule shows two different donor acceptor distances: (N(1)—O(2) 3.139 Å and N(2)—O(4) 3.045 Å).

The interesting feature of the solid state structure of **1** is that two adjacent molecules are connected through the intermolecular NH---O (N(2)—O(1) 3.063 Å) hydrogen bond between oxygen of the acetate group and —NH from amine (Fig. 2). The result of this intermolecular hydrogen bond is the formation of a dimer and an eight-membered supramolecular metallomacrocyclic (Fig. 2). The interatomic distance between two zinc atoms in the eight-membered supramolecular metallomacrocyclic is about 5.0224(6) Å. These dimers are further connected by an intermolecular NH---O (N(1)—O(4) 3.131 Å) hydrogen bond (Fig. 2). The latter weak interaction results in a twelve-membered supramolecular metallomacrocyclic and the interatomic distance between two zinc atoms is 6.8672(8) Å. As a result, 1D supramolecular coordination polymer chains have formed.

Further, the 1D supramolecular coordination polymer chains are connected through another NH---O (N(1)—O(2) 3.139 Å) hydrogen bond and organize a 2D supramolecular coordination polymer (Fig. 3).

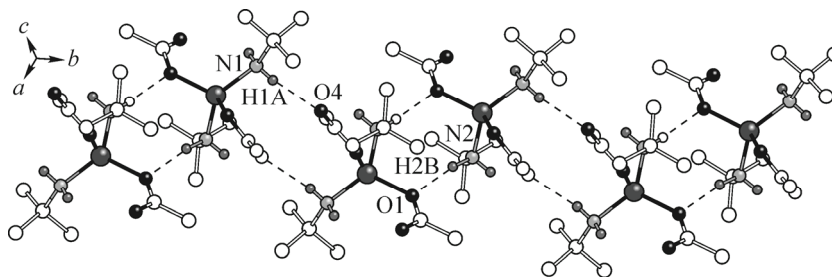


Fig. 2. Illustration of a supramolecular 1D coordination polymer chain in $({}^t\text{BuNH}_2)_2\text{Zn}(\text{OOCCH}_3)_2$ with NH---O interactions

Table 3

Details of inter- and intramolecular hydrogen bonds

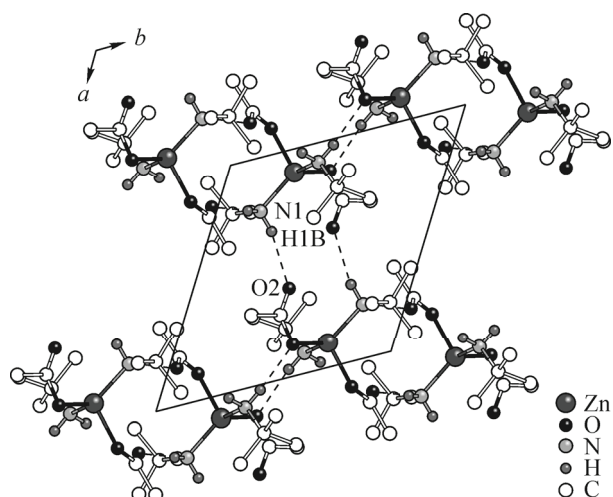
D—H...A	D—H, Å	H...A, Å	D—H...A, deg.	D...A, Å	Type
N1H1B...O2 ^b	0.9	2.655	114.64	3.139	Intra
N2H2A...O4 ^a	0.9	2.388	129.95	3.045	Intra
N1H1A...O4 ^c	0.9	2.242	169.28	3.131	Inter
N1H1B...O2 ^a	0.9	2.286	165.74	3.166	Inter
N2H2B...O1 ^d	0.9	2.168	172.33	3.063	Inter

^a x, y, z; ^b -x+1, -y+1, -z+1, ^c -x+2, -y+2, -z+1, ^d -x+2, -y+1, -z+1.

Fig. 3. Packing of the crystal of $({}^t\text{BuNH}_2)_2\text{Zn}(\text{OOCCH}_3)_2$, viewed along the c axis

Conclusions. Solid state of the structure of diacetato-bis(2-methyl-2-propylamine)zinc(II) has been discussed together with the formation of a 2D supramolecular coordination polymer by different types of $\text{NH}\cdots\text{O}$ weak interactions in the titled compound.

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