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Synthesis and Structural Characterization of (3,5-Me_2-Py)$_2$Zn(S-iPr)$_2$: A precursor for ZnS

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Abstract: Two equivalent of *iso*propylthiol was added in one equivalent of toluene and 3,5-dimethylpyridine solution of diethyl zinc and the reaction mixture yielded the compound (3,5-Me_2-Py)$_2$Zn(S-iPr)$_2$. The structure of (3,5-Me_2-Py)$_2$Zn(S-iPr)$_2$ has confirmed and discussed by single crystal x-ray diffraction studies.

Introduction

Zinc containing materials like ZnO, ZnS, and zinc chalcogenides have attracted great attention due to their potential application in the field of optical, electrical, photovoltaic, catalysis and biological application.[1-5] The presence of wide band gap in ZnO and ZnS helps to construct the variety of optical devices.[6] Doping of other metal oxide, sulfide and chalcogenides with ZnO and ZnS resulted in different types of color emitting devices.[7]

The availability of source for the preparation of ZnO and ZnS nanoparticles are limited. For instance different size of ZnO nanoparticles were synthesized by hydrolysis of $Zn(OAc)_2 \cdot 2H_2O$ in alcoholic medium[8] and some other zinc alkoxides/aryloxides.[9] The aim of the proposed work is to establish a general synthetic approach to the preparation of single molecule precursor and preparation of ZnO and ZnS nanoparticles from the synthesized zinc compounds and then to investigate the chemical and physical properties of all these new materials.

Experimental

Material and Methods

All manipulations were performed either in an inert gas atmosphere of purified dry N_2 with standard Schlenk techniques or in an argon glove box. The glassware was dried at 130 °C, assembled hot and cooled under vacuum. All solvents were dried over appropriate alkali metals, distilled and degassed prior to use. Elemental analyses (C, H, N and S) were carried out at the Mikroanalytisches Labor, Institut für Anorganische Chemie, Universität Göttingen.

Crystallography

The data of **1** was collected with a Bruker D8 three-circle diffractometer equipped with a SMART APEX II CCD detector and an INCOATEC Mo microsource with INCOATEC Quazar mirror optics.[13] The data were integrated with SAINT,[14] and an empirical absorption correction with SADABS[15] was applied. The structure was solved by direct methods (SHELXS-97) and refined against all data by full-matrix least-squares methods on F2 (SHELXL-97).[16] All non-hydrogen atoms were refined with anisotropic displacement parameters. The hydrogen atoms were refined isotropically in calculated positions by using a riding model.

Synthesis

Synthesis of (3,5-Me$_2$-Py)$_2$Zn(S^{i}Pr)$_2$ (4):

3,5-dimethylpyridine (3 mL) was added to hexane (30 mL) solution of $ZnEt_2$ (2 mmole, 0.20 mL) at room temperature and stirred for an hour, then *iso*propylthiol was (4 mmole, 0.40 mL) was added. The reaction mixture was stirred for 6 hrs and the 1/3 volume was reduced and filtered. The filtrate kept at -30 °C. The colourless crystals were formed after 10 days. Yield 0.53 g (62 %). Anal.Calcd. for $C_{20}H_{32}N_2S_2Zn$ (430.01) Found: C, 57.02; H, 7.89; N, 6.29; S, 14.35; requires C, 55.86; H, 7.50; N, 6.51; S, 14.91; %

Results and Discussion

Synthesis

$$ZnEt_2 + 2\ iPr\text{-}SH \xrightarrow[Hexane]{3,5\text{-}Me_2\text{-}Py} (3,5\text{-}Me_2\text{-}Py)_2Zn(S\text{-}iPr)_2$$

Scheme 1: Synthesis of 1

Addition of two equivalent of *iso*propylthiol to either $ZnEt_2$ in mixture of toluene and 3,5-Lutidine in toluene, resulted compound **1**.

Molecular Structures

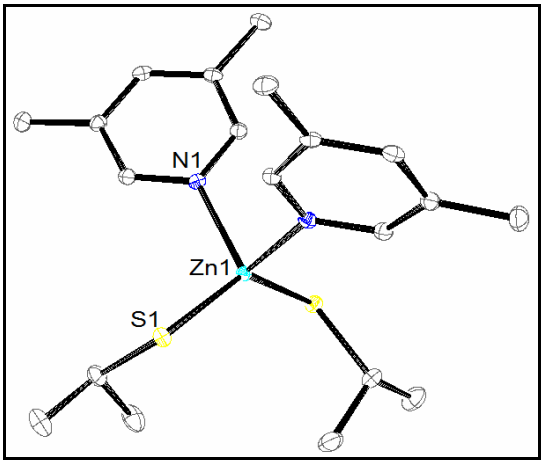

Figure 1: Molecular structure of 1 (All hydrogen atoms are omitted for clarity)

Single crystals of **1** were grown at -30 °C and crystallized in the monoclinic space group *P2/c*. (the molecular structure of **1** is shown in Figure 1). The important bond distances and bond angles are shown in table 1 and the crystal data and structure refinement parameters are given in table 2. The solid state structure of **1** is tetrahedron and two nitrogen from 2-picoline and two sulphur from *iso*propylthiolate ions are coordinated to zinc atom. The bond distance of Zn-S is 2.2694 (5) Å and Zn-N is 2.1023 (17) Å. The angle between S1_Zn1_S2 of **1** is (132.83(3) °). The bond angles between S_Zn_N are 99.51(5) ° and 111.26(5)°.

Table 1: Bond distance and angles of 4

Bond distances (Å)			
Zn(1)-S(1)	2.2695(5)	Zn(1)-N(1)	2.1023(17)
Bond angles (°)			
N(1)#1-Zn(1)-N(1)	97.46(9)	N(1)#1-Zn(1)-S(1)#1	111.26(5)
S(1)#1-Zn(1)-S(1)	132.83(3)	N(1)-Zn(1)-S(1)#1	99.51(5)
N(1)-Zn(1)-S(1)	111.26(5)	N(1)#1-Zn(1)-S(1)	99.51(5)

Table 2: Crystal data and structure refinement parameters of 1

Empirical formula	C20 H32 N2 S2 Zn
Formula weight	430.01
Temperature	100(2) K
Crystal system, Space group	Monoclinic, *P*2/*c*
Unit cell dimensions	a = 18.1967(11) Å, b = 8.3111(5) Å c = 16.1092(10) Å $\alpha = \gamma$ = 90.0°, β = 115.4630(10) °
Volume	2199.6(2) $Å^3$
Z, Calculated density	4, 1.298 mg/m^3
Absorption coefficient	1.312 mm^{-1}
F(000)	1124
Crystal size	0.08 x 0.06 x 0.04 mm^3
θ range for data collection	1.24 to 27.48°
Index ranges	-23<=k<=23, -10<=k<=10, -20<=l<=20
Reflections collected	53090
Independent reflections	5036 [R(int) = 0.0328]
Completeness to theta	99.9%
Data / restraints / parameters	5036 / 0 / 235
Goodness-of-fit on F^2	0.670
Final *R* indices [$I>2\sigma(I)$]	R1 = 0.0291, wR2 = 0.0705
R indices (all data)	R1 = 0.0342, wR2 = 0.0725
Largest diff. peak and hole	0.428 and -0.314 e.$Å^{-3}$

Summary

The $(3,5\text{-}Me_2\text{-}Py)_2Zn(S\text{-}iPr)_2$ was synthesized and characterized. The single crystal of **1** was analyzed and the important bond distances and angles were discussed. The compound can be suitable precursor to synthesis of ZnS.

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