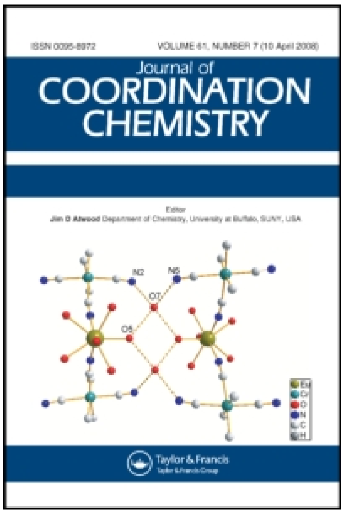

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Synthesis and crystal structure of a dinuclear zinc(II)-dithiocarbamate complex, <i>bis</i>{[(μ^2-pyrrolidinedithiocarbamato-S,S')(pyrrolidinedithiocarbamato-S,S')zinc(II)]}

Mariam Shahid[a]; Tobias Rüffer[b]; Heinrich Lang[b]; Shafique Ahmed Awan[c]; Saeed Ahmad[a]
[a] Department of Chemistry, University of Engineering and Technology, Lahore 54890, Pakistan [b] Technische Universitat Chemnitz, Institut fur Chemie, Lehrstuhl fur Anorganische Chemie, Chemnitz, Germany [c] PAEC, Islamabad, GPO 44000, Pakistan

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Synthesis and crystal structure of a dinuclear zinc(II)-dithiocarbamate complex, *bis*{[(μ^2-pyrrolidinedithiocarbamato-S,S′)(pyrrolidinedithiocarbamato-S,S′)zinc(II)]}

MARIAM SHAHID†, TOBIAS RÜFFER‡, HEINRICH LANG‡,
SHAFIQUE AHMED AWAN§ and SAEED AHMAD*†

†Department of Chemistry, University of Engineering and Technology,
Lahore 54890, Pakistan
‡Technische Universitat Chemnitz, Institut fur Chemie, Lehrstuhl fur Anorganische Chemie,
Straße der Nationen 62, 09111, Chemnitz, Germany
§PAEC, P.O. Box # 1114, Islamabad, GPO 44000, Pakistan

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A new zinc(II) complex of pyrrolidinedithiocarbamate (PDTC), *bis*[(μ^2-pyrrolidinedithiocarbamato-S,S′)(pyrrolidinedithiocarbamato-S,S′)zinc(II)], [$Zn_2(PDTC)_4$] (**1**) has been prepared by reaction of $ZnCl_2$ with ammonium pyrrolidinedithiocarbamate in 1 : 1 and 1 : 2 ratio, respectively. The complex has been characterized by IR, NMR and X-ray crystallography. Compound **1** crystallizes in the triclinic space group $P\bar{1}$ in the form of a centrosymmetric dimer. The solid-state structure contains two crystallographically equivalent Zn^{+2} centers in a tetrahedrally distorted ion sphere. A mixed-ligand complex, $[Zn(PDTC)(MSC)]^-$ (MSC = mercaptosuccinate) was also prepared but the structure of the resulting complex was found to be the same as **1**, suggesting that the thiolate ligand was replaced on addition of PDTC.

Keywords: Zinc(II); Pyrrolidinedithiocarbamate; Mercaptosuccinate; Crystal structure

1. Introduction

Zinc-dithiocarbamate complexes have a wide range of industrial and biological applications, widely used in the rubber vulcanization process [1–4]. Zinc(II)-dibutyldithiocarbamato is a primary accelerator in rubber production and acts as an antioxidant in rubber-based adhesives [5, 6]. Zinc(II)-polythiocarbamato complexes that have one or more sulfurs inserted in the Zn-dithiocarbamato bond such as [$Zn(Me_2NCS_3)_2$] are very important intermediates in the vulcanization process [7, 8]. Zinc-dithiocarbamate complexes and salts thereof are also used as fungicides [9, 10]. ZnS, a technologically important material as phosphor and as a white pigment, can be prepared from Zn(II)-diethyldithiocarbamate [11]. In addition, dithiocarbamates,

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*Corresponding author. Email: saeed_a786@hotmail.com

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in particular diethyldithiocarbamate and pyrrolidinedithiocarbamate, are strong inhibitors of NF-kB signaling pathway with their activity thought to be due to chelating of zinc or copper present in serum supplemented in the culture medium [12–14]. A number of zinc(II)-dithiocarbamates have been prepared and characterized [15–20]. The importance of such compounds motivated us to investigate their structural properties and consequently, we attempted to prepare three zinc(II)-pyrrolidinedithiocarbamate complexes, $[Zn(PDTC)Cl_2]^-$, $[Zn(PDTC)_2]$ and $[Zn(PDTC)(MSC)]^-$ (MSC = mercaptosuccinate). However, the X-ray analysis showed that the product of all three reactions is *bis*[(μ^2-pyrrolidinedithiocarbamato-S,S′) (pyrrolidinedithiocarbamato-S,S′)zinc(II)], the crystal structure of which is being reported.

2. Experimental

2.1. *Chemicals*

Ammonium pyrrolidinedithiocarbamate was purchased from Sigma Chemical Company. $ZnCl_2$ was obtained from Fluka Chemical Co., Switzerland, and 2-mercaptosuccinic acid was purchased from Acros Organics, Belgium.

2.2. *X-ray structure determination*

X-ray diffraction data of **1** were collected on an Oxford Gemini S diffractometer [Mo-Kα ($\lambda = 0.71073$ Å)] at 100 K. The structure of **1** was solved by direct methods with SHELXS-97 [21] and refined by full-matrix least squares procedures on F^2 using the program SHELXL-97 [22]. All non-hydrogen atoms were refined anisotropically. Hydrogen atoms on carbon were included in calculated positions and refined using a riding model. Crystal data and refinement details are presented in table 1.

2.3. *IR and NMR measurements*

IR data were obtained with a Perkin–Elmer FTIR 180 spectrophotometer in the frequency range 4500–400 cm^{-1} using KBr pellets. The ^1H NMR spectra of PDTC and its zinc complex in DMSO-d_6 were obtained on a Bruker Avance 250 MHz NMR spectrometer operating at a frequency of 250.00 MHz at 300 K. The $^{13}C\{^1H\}$ NMR spectra were obtained at frequency of 62.90 MHz with ^1H broadband decoupling. The spectral conditions were: 32 K data points, 2.084 s acquisition time, 2.00 s pulse delay and 6.00 µs pulse width. The ^{13}C chemical shifts were measured relative to TMS.

2.4. *Synthesis of complexes*

Compound **1** was prepared by reaction of $ZnCl_2$ (0.14 g, 1.00 mmol) in methanol with 1 or 2 mmoles (0.164 g or 0.328 g) of ammonium pyrrolidinedithiocarbamate (PDTC) in methanol. The addition of PDTC in the colorless metal ion solution resulted in the formation of white precipitate immediately. After stirring for half an hour, the

Table 1. Crystal data and refinement details for **1**.

Formula	$C_{10}H_{16}N_2S_4Zn$
Formula weight	357.86
Crystal system	Triclinic
Space group	$P\bar{1}$
Unit cell dimensions (Å, °)	
a	7.758(2)
b	7.906(2)
c	12.267(4)
α	74.92(9)
β	73.36(8)
γ	88.28(11)
V (Å^3)	695.3(3)
Z	2
ρ (Calcd) (g cm^{-3})	1.709
Crystal color/habit	Yellow/block
Crystal dimensions (mm^3)	0.4 × 0.4 × 0.4
Temperature (K)	100
Radiation (λ, Å)	0.71073
Absorption correction	Empirical from equivalents [30]
Maximum, minimum transmission	1.00000, 0.87145
μ (Mo-Kα) (mm^{-1})	2.345
F(000)	368
θ range (°)	3.59–26.06
h, k, l limits	$-7:9; -9:9; -15:15$
Reflections collected	4309
Unique reflections	2675 ($R_{\text{int}} = 0.0110$)
Completeness to θ max (%)	97.3
Data, restraints, params.	2675/0/154
R_1, wR_2 ($I > 2\sigma(I)$)	0.0173, 0.0438
R_1, wR_2 (all data)	0.0191, 0.0447
GOF	1.062
Largest diff. peak, hole (e Å^{-3})	0.604, −0.250

precipitate was filtered off and dried. The precipitate (0.05 g) was dissolved in 5 mL DMSO and the resulting solution yielded crystals after a week.

A mixed-ligand complex, $[Zn(PDTC)(MSC)]^-$ (MSC = mercaptosuccinate), was also attempted by adding first 1 mmolar solution of mercaptosuccinate to $ZnCl_2$ followed by addition of PDTC. However, the reaction followed by crystallization in DMSO resulted in **1**.

3. Results and discussion

3.1. *X-ray structure description*

The molecular structure of **1**, together with the atomic labeling, is shown in figure 1. Selected bond lengths and angles are presented in table 2. The complex is dinuclear with each zinc coordinated to one terminal and two bridging PDTC ligands. The dimeric structure is centrosymmetric and features an 8-membered $[\text{–S–C–S–Zn–}]_2$ ring with a Zn–Zn separation of 3.73 Å. The Zn^{+2} is distorted tetrahedral. Two of the four S–Zn–S bond angles show significant distortions from tetrahedral (table 2). The average bond lengths of 2.33 Å and 1.73 Å for the Zn–S and C–S bonds, respectively, are similar to those observed in other Zn-dithiocarbamate complexes [11, 23, 24]. The two Zn–S_2–C four-membered rings are almost planar [highest deviation of a calculated mean plane of

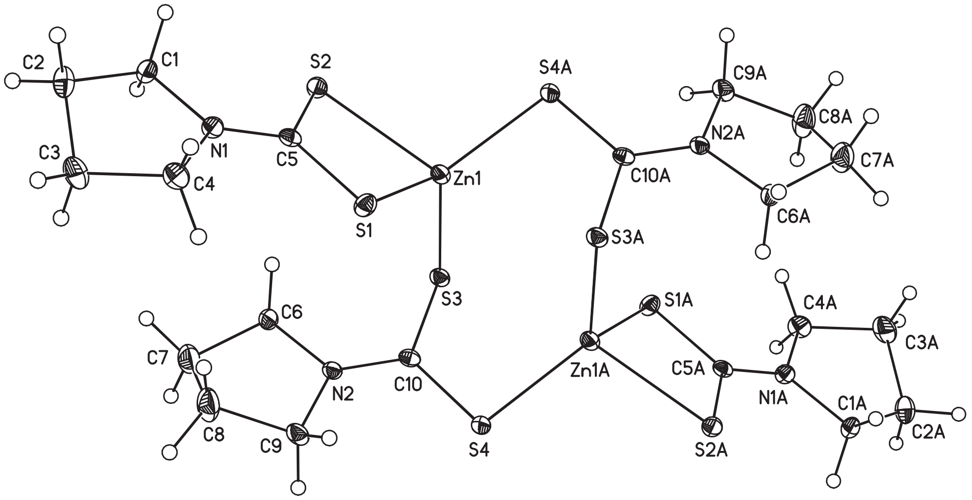

Figure 1. Ortep plot (50% probability level) of the molecular structure of the centrosymmetric dimer of **1** in the solid state. Symmetry transformations used to generate equivalent atoms, A: $-x$, $-y$, $-z+1$.

Table 2. Selected geometric parameters for **1**.

Zn1–S4A	2.319(2)	S1–Zn1–S3	113.99(7)
Zn1–S1	2.3362(14)	S1–Zn1–S2	76.15(10)
Zn1–S2	2.477(2)	S1–Zn1–S4A	133.91(3)
Zn1–S3	2.3664(16)	S2–Zn1–S3	112.48(5)
Zn1A–S4	2.319(2)	S2–Zn1–S4A	107.01(9)
S1–C5	1.730(3)	S3–Zn1–S4A	107.03(7)
S2–C7	1.725(2)	C5–S1–Zn1	84.57(10)
S3–C10	1.7439(18)	C5–S2–Zn1	80.39(12)
S4–C10	1.720(3)	C10–S3–Zn1	98.67(10)
N1–C5	1.318(2)	C10–S4–Zn1A	95.36(10)
N1–C1	1.475(3)	N1–C5–S1	120.58(13)
N1–C4	1.477(2)	N1–C5–S2	120.87(14)
N2–C10	1.315(2)	S1–C5–S2	118.55(13)
N2–C6	1.480(3)	N2–C10–S3	120.43(14)
N2–C9	1.482(2)	N2–C10–S4	119.70(13)
C1–C2	1.525(2)	S3–C10–S4	119.86(13)

Symmetry transformations used to generate equivalent atoms, A: $-x$, $-y$, $-z+1$.

Zn1, S1, S2, and C5 is observed for C5 with 0.046 Å; the dihedral angle Zn1–S1–C5–N1 is 173.7(1)°]. The N–CS_2 moiety of the terminal and bridging dithiocarbamate ligands show planar geometry with sp^2-hybridized carbon. The smaller N–C(S_2) bond lengths (1.318 and 1.315 Å) compared to the other N–C bond distances (1.476 and 1.481 Å) are in agreement with a marked double bond character in the N–C(S_2) bond.

3.2. *IR and NMR studies*

For dithiocarbamate compounds, three main regions are of interest: the 1580–1450 cm^{-1} region, primarily associated with the stretching of the C–N of N–CSS^-; the 1060–940 cm^{-1} region, associated with ν(–CSS); and the 420–250 cm^{-1} region which is associated with ν(M–S) [25]. In **1**, ν(N–CSS) is shifted to higher energies compared to free PDTC ($1480\,cm^{-1}$ *versus* $1410\,cm^{-1}$) showing an increase of the carbon–nitrogen double bond character. The ν(N–CSS) is comparable to the pyrrolidinedithiocarbamate complexes of Pd^{2+}; $[Pd(PDTC)_2] = 1500\,cm^{-1}$ [26] and Cu^{2+}; $[Cu(PDTC)_2] = 1500\,cm^{-1}$ [27]. A band at $1005\,cm^{-1}$ ($995\,cm^{-1}$ for PDTC) belongs to the ν(−CSS) stretching mode and is indicative of bidentate dithiocarbamate [28].

In the ^{1}H NMR spectrum of **1**, the $N(CH_2)_2$ and the ring $(CH_2)_2$ protons appear at 3.58 ppm (triplet) and 1.96 ppm (quintet), respectively. For the free ligand they are observed at 3.65 and 1.84 ppm, respectively, along with two weak signals at 3.21 and 2.08 ppm. The $^{13}C\{^1H\}$ NMR spectrum of PDTC exhibits signals at 25.72, 52.89 and 208.20 ppm for the ring CH_2, N–CH_2 and CS_2 carbons, respectively. In **1**, these resonances appear at 26.75, 54.74 and 199.64 ppm, respectively. A significant upfield shift in CS_2 resonance is attributed to lowering of the C=S bond order upon coordination and a shift of N→C electron density producing partial double bond character in the C–N bond; a deshielding effect is observed in other carbon atoms. The ^{1}H and ^{13}C NMR chemical shift values are in accord with literature reports [26, 29]. In the ^{13}C NMR spectrum of free ligand two less intense peaks at 23.98 and 44.49 ppm were also observed, showing that both the CH_2 and N–CH_2 carbons are non-equivalent, but only one set of signals is observed for the methylene protons and carbons in both ^{1}H and $^{13}C\{^1H\}$ NMR of **1**, suggesting that both $N(CH_2)$ groups are equivalent in the complex at 300 K.

The present study provides information about Zn–S bonding in Zn–PDTC complexes; PDTC has a strong preference for zinc(II) and on addition of PDTC, other labile ligands such as mercaptosuccinate are dissociated from Zn^{+2} forming the more stable $[Zn(PDTC)_2]_2$.

Supplementary material

Supplementary crystallographic data of **1** (CCDC No. 676540) can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif by e-mailing data_request@ccdc.cam.ac.uk or by contacting the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK [Fax: +44(0)1223-336033].

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