

Scientific paper

The Crystal Structure of *bis*-(μ -*N*-ethyl-*N*-phenyldithiocarbamato-*S,S'*)-*bis*[(*N*-ethyl-*N*-phenyldithiocarbamato- κ^2 *S,S'*)zinc(II)]

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Abstract

The title material crystallises in the triclinic crystal system in space group *P*-1 with *Z* = 2. The unit cell dimensions are *a* = 8.7365(6) Å, *b* = 10.6009(7) Å, *c* = 12.0210(8) Å with α = 66.343(1)°, β = 79.566(1)°, γ = 83.150(1)° and *V* = 1001.6(1) Å³. The final *R* value is 0.0307 (3905 observed reflections: *I* > 2σ(*I*)). The compound is best described as a species in which each metal atom is coordinated to two dithiocarbamato groups, one of which forms a secondary bridging interaction (through a *S*-atom) to a second [Zn(S₂CNEtPh)₂] unit. Thus, the title material is in the form of a dimeric aggregate. This complex is compared to related materials which contain *N*-atoms within the dithiocarbamato ligand that are derived from secondary amines containing two different organic functionalities.

Keywords: Zinc dithiocarbamate, X-ray structure analysis, dithiolate, zinc(II), dimer

1. Introduction

The zinc dithiocarbamates (ZDTC) represent an important sub-class of the Group XII dithiolates.^{1,2} These materials have historically found application as pesticides, most notably the fungicide ZIRAM (*i.e.*, [Zn₂(S₂CNMe₂)₄]), in addition to their widespread use as radical scavenging agents and as additives to commercial pavement asphalt. In addition, ZDTC are used in combination with high stress industrial lubricants to impart improved stability to the lubricant formulation; they can also promote the vulcanisation of rubber and act as Lewis acid frameworks in coordination chemistry.^{1–5} More recent investigations of ZDTC include their evaluation as potential precursors in chemical vapour deposition technology (*e.g.*, ZnS thin film production)^{6–9} and in other materials science applications.¹⁰ Although there are a number of complexes of general formula [Zn(S₂CNRR')₂]_n found in the CCDC database, relatively few of these are of the class where R ≠ R'. In this report, we detail the structural characterisation of

one of these derivatives, *viz.* *bis*-(μ -*N*-ethyl-*N*-phenyldithiocarbamato-*S,S'*)-*bis*[(*N*-ethyl-*N*-phenyl-dithiocarbamato- κ^2 *S,S'*)zinc(II)] (**1**).

2. Experimental

2.1. General

Compound **1** (purity > 98%) was obtained commercially from TCI Chemicals Co. Ltd. of Tokyo, Japan. Crystals of the title material that were suitable for X-ray diffraction work were obtained by suspending crude **1** (~10 g) in 140 mL of petroleum spirit (bp 90–120 °C). The mixture was heated on a steam bath to a temperature of about 80 °C and the solids quickly filtered off from the supernatant solution. This procedure was repeated four times. On cooling, the filtrates yielded copious quantities of well-formed crystals. One such crystal, with approximate dimensions 0.05 × 0.11 × 0.20 mm³, was selected and mounted on a glass fibre for characterisation by X-ray diffraction.

2. 2. X-ray diffraction study of 1

Data were collected at $-50\text{ }^{\circ}\text{C}$ on a Bruker-AXS SMART 1K CCD diffractometer, and were processed using SMART/SAINT V5.059; a semi-empirical absorption correction was applied using SADABS. The structure was solved with SHELXS-97 using the heavy atom method with full-matrix least squares refinement on F^2 using SHELXL-97.^{10–15} All non-hydrogen atoms were refined anisotropically and H atoms were refined as riding on their constituent atoms. An approximate 60:40 disorder in the ethyl group bound to N1 was modelled with free variables on the occupancies of each atom; the major component constituted 61.2%. In the final cycles of refinement, $R^1 = 3.07\%$ and $wR^2 = 5.88\%$; the largest residual peak at $0.298\text{ }\text{\AA}^3$ was associated with Zn1. Details of the experimental parameters can be found in Tables 1 and 2.¹⁶

Table 1. Crystal data, data collection and structure refinement for compound 1.

Empirical formula	$\text{C}_{18}\text{H}_{18}\text{N}_2\text{S}_4\text{Zn}$
M_r	455.95
Wavelength	0.71073 \AA
Crystal system	Triclinic
Space group	$P-1$, No. 2
a (\AA)	8.7365(6)
b (\AA)	10.6009(7)
c (\AA)	12.0210(8)
α ($^{\circ}$)	66.343(1)
β ($^{\circ}$)	79.566(1)
γ ($^{\circ}$)	83.150(1)
V (\AA^3)	1001.6(1)
Z	2
ρ (Mg m^{-3})	1.519 (calc.)
T (K)	223(2) K
Absorption coefficient	1.647 mm^{-1}
$F(000)$	472
θ range for data collection	1.87 to 26.00° .
Index ranges	$-10 \leq h \leq 10$; $-13 \leq k \leq 13$; $-14 \leq l \leq 14$
Reflections collected	8090
Independent reflections	3905 [$R_{\text{int}} = 0.0218$]
Completeness to $\theta = 25.00^{\circ}$	99.4 %
Absorption correction	Semi-empirical from equivalents
Data / restraints / parameters	3905 / 0 / 242
Goodness-of-fit on F^2	0.918
Final R indices [$I > 2\sigma(I)$]	$R1 = 0.0307$, $wR2 = 0.0588$
R indices (all data)	$R1 = 0.0534$, $wR2 = 0.0627$
Largest diff. peak and hole ($\text{e.}\text{\AA}^{-3}$)	0.298 and -0.214

Table 2. Selected Bond Lengths (\AA) and Angles ($^{\circ}$) for Compound 1.

Zn(1)-S(4)	2.3516(7)
Zn(1)-S(2)	2.3655(7)
Zn(1)-S(3)#1	2.4033(7)

Zn(1)-S(1)	2.4437(7)
Zn(1)-S(3)	2.7512(7)
S(1)-C(1)	1.709(3)
S(2)-C(1)	1.725(2)
S(3)-C(11)	1.736(3)
S(4)-C(11)	1.718(2)
N(1)-C(1)	1.338(3)
N(1)-C(4)	1.443(3)
N(1)-C(2)	1.497(6)
N(1)-C(2')	1.620(7)
N(2)-C(11)	1.328(3)
N(2)-C(14)	1.447(3)
N(2)-C(12)	1.482(3)
C(2)-C(3)	1.512(7)
C(2')-C(3')	1.486(9)
C(4)-C(5)	1.377(4)
C(4)-C(9)	1.381(4)
C(5)-C(6)	1.380(4)
C(6)-C(7)	1.372(4)
C(7)-C(8)	1.370(4)
C(8)-C(9)	1.376(4)
C(12)-C(13)	1.516(3)
C(14)-C(19)	1.373(3)
C(14)-C(15)	1.382(3)
C(15)-C(16)	1.368(3)
C(16)-C(17)	1.377(4)
C(17)-C(18)	1.379(4)
C(18)-C(19)	1.376(4)
S(4)-Zn(1)-S(2)	136.18(3)
S(4)-Zn(1)-S(3)#1	104.11(3)
S(2)-Zn(1)-S(3)#1	117.50(3)
S(4)-Zn(1)-S(1)	107.35(3)
S(2)-Zn(1)-S(1)	75.50(2)
S(3)#1-Zn(1)-S(1)	105.31(2)
S(4)-Zn(1)-S(3)	70.60(2)
S(2)-Zn(1)-S(3)	95.99(2)
S(3)#1-Zn(1)-S(3)	88.86(2)
S(1)-Zn(1)-S(3)	165.61(2)
C(1)-S(1)-Zn(1)	82.12(9)
C(1)-S(2)-Zn(1)	84.21(9)
C(11)-S(3)-Zn(1)#1	100.95(8)
C(11)-S(3)-Zn(1)	78.78(8)
Zn(1)#1-S(3)-Zn(1)	91.14(2)
C(11)-S(4)-Zn(1)	91.72(9)
C(1)-N(1)-C(4)	122.8(2)
C(1)-N(1)-C(2)	124.3(3)
C(4)-N(1)-C(2)	110.9(3)
C(1)-N(1)-C(2')	112.8(3)
C(4)-N(1)-C(2')	122.7(2)
C(2)-N(1)-C(2')	30.4(2)
C(11)-N(2)-C(14)	121.1(2)
C(11)-N(2)-C(12)	123.0(2)
C(14)-N(2)-C(12)	115.9(2)
N(1)-C(1)-S(1)	121.2(2)
N(1)-C(1)-S(2)	120.7(2)
S(1)-C(1)-S(2)	118.1(2)
N(1)-C(2)-C(3)	103.7(4)
C(3')-C(2')-N(1)	102.6(6)
C(5)-C(4)-C(9)	120.5(3)
C(5)-C(4)-N(1)	119.6(3)

C(9)-C(4)-N(1)	119.9(3)
C(4)-C(5)-C(6)	119.2(3)
C(7)-C(6)-C(5)	120.6(3)
C(8)-C(7)-C(6)	119.7(3)
C(7)-C(8)-C(9)	120.6(3)
C(8)-C(9)-C(4)	119.4(3)
N(2)-C(11)-S(4)	120.94(19)
N(2)-C(11)-S(3)	120.67(18)
S(4)-C(11)-S(3)	118.35(15)
N(2)-C(12)-C(13)	112.5(2)
C(19)-C(14)-C(15)	120.1(3)
C(19)-C(14)-N(2)	120.4(2)
C(15)-C(14)-N(2)	119.4(2)
C(16)-C(15)-C(14)	119.8(3)
C(15)-C(16)-C(17)	120.6(3)
C(16)-C(17)-C(18)	119.3(3)
C(19)-C(18)-C(17)	120.5(3)
C(14)-C(19)-C(18)	119.6(3)

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

3. Results and Discussion

A schematic representation of the title complex appears in Figure 1 and an ORTEP version, with select atoms and atomic labelling, appears in Figure 2.

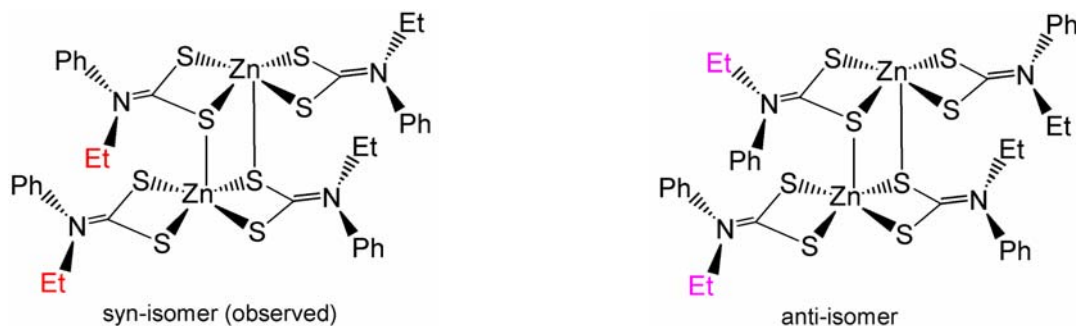


Figure 1. Schematic representation of the observed form of compound **1** and a possible anti-isomer.

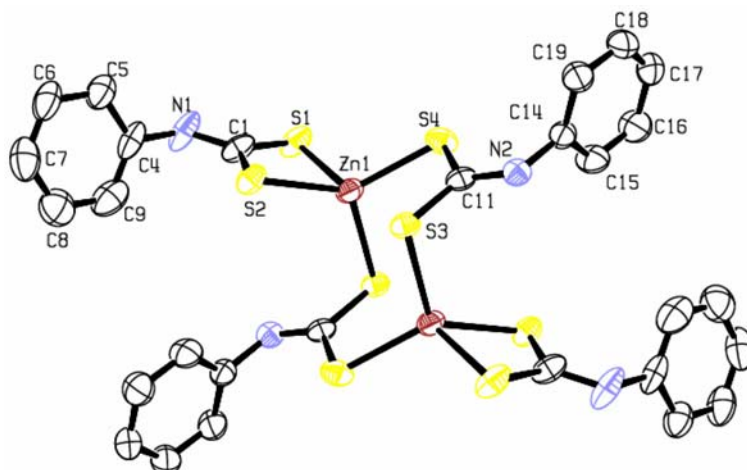


Figure 2. ORTEP representation of a molecule of **1** with selected atomic numbering; ethyl groups have been removed for clarity.

Each Zn atom is coordinated by two chelating dithiocarbamate units; one of these forms a secondary bonding interaction with a second $[\text{Zn}(\text{S}_2\text{CNRR}')_2]$ moiety via S3. This forms a dimeric aggregate situated on a centre of crystallographic inversion. The chelating $\text{S}_2\text{CN}(\text{Et})\text{Ph}$ groups form a highly distorted square pyramidal array around the metal atom with one long (~ 2.75 Å) and three short (between ~ 2.35 – 2.45 Å) Zn–S bonds, where the smallest angle is between S4–Zn1–S3 at $70.60(2)^\circ$; the coordination sphere surrounding the Zn1 atom is completed by a further bridging Zn1–S3' bond (~ 2.40 Å). Within each moiety there is a distinct angle between the planes formed by S1–C1–S2 and S3–C11–S4 of $40.59(5)^\circ$ and a twist of $49.57(3)^\circ$ between S1–Zn1–S4 and S2–Zn1–S3. The coordination motif can be best described as being midway between trigonal bipyramidal and square pyramidal ($\tau = 0.491$).¹⁷ Such a bonding pattern is also seen for related complexes such as $[\text{Zn}_2(\text{S}_2\text{CN}\{\text{R}\}\text{Et})_4]$, (R = Et, ⁱPr, ⁿBu or Cy),^{18–21} $[\text{Zn}_2(\text{S}_2\text{CN}\{\text{Ph}\}\text{Me})_4]$,²² $[\text{Zn}_2(\text{S}_2\text{CN}\{\text{R}\}\text{H})_4]$ (R = Et, ⁿPr, ⁱPr or ⁿBu),²³ $[\text{Zn}_2(\text{S}_2\text{CN}\{\text{CH}_2\text{CH}_2\text{OH}\}\text{R})_4]$ (R = Me or Et)²⁴ and $[\text{Zn}_2(\text{S}_2\text{CN}\{\text{Ph}\}\{\text{C}_{14}\text{H}_{29}\})_4]$.²⁵

The core of the molecule of **1** adopts a “twisted chair” conformation in relation to the eight-membered $[-\text{S}-\text{M}-\text{S}-\text{C}-]_2$ (M = Zn, Cd or Hg) ring system. Therefore, compound **1** is a representative of what has been refer-

red to by Tiekink, in his seminal review on the structural properties of Group XII dithiolates, as *Dithiolate Bonding Motif Type III*.² This motif is also found in the complexes referred to above and is characterised by the observation that the bridging dithiolates are found on opposite sides of the eight-membered ring.^{18–25} Symmetry restrictions also impose that the molecule can be described as the *syn*-isomer, in relation to the orientation of opposing Ph or Et groups, of a possible *syn*- or *anti*-conformational pair (Figure 1). This *syn* isomeric form is also displayed in, for example, the complexes of general formula $[\text{Zn}_2(\text{S}_2\text{CN}\{\text{R}\}\text{H})_4]$ where R = Et, ⁿPr, ⁱPr or ⁿBu).²³

Although the Cd analogue of **1** does not appear to have been structurally characterised, a Hg²⁺ derivative containing the $[\text{S}_2\text{CN}(\text{Et})\text{Ph}]$ anion has been reported.^{26–28} The complex $[\text{Hg}(\text{S}_2\text{CN}\{\text{Et}\}\text{Ph})_2]$ (**2**) is not however, isostructural to the Zn material described here.²⁸ Complex **2** contains a metal atom in which the coordination environment is distinctly more pronounced towards square pyramidal ($\tau = 0.201$)¹⁷ although a similar twisted chair conformation of the $[-\text{S}-\text{Hg}-\text{S}-\text{C}-]_2$ ring system is clearly visible (Figure 3). This distortion precludes the establishment of a definitive *syn* or *anti* structural isomer in contrast to that observed for **1**.

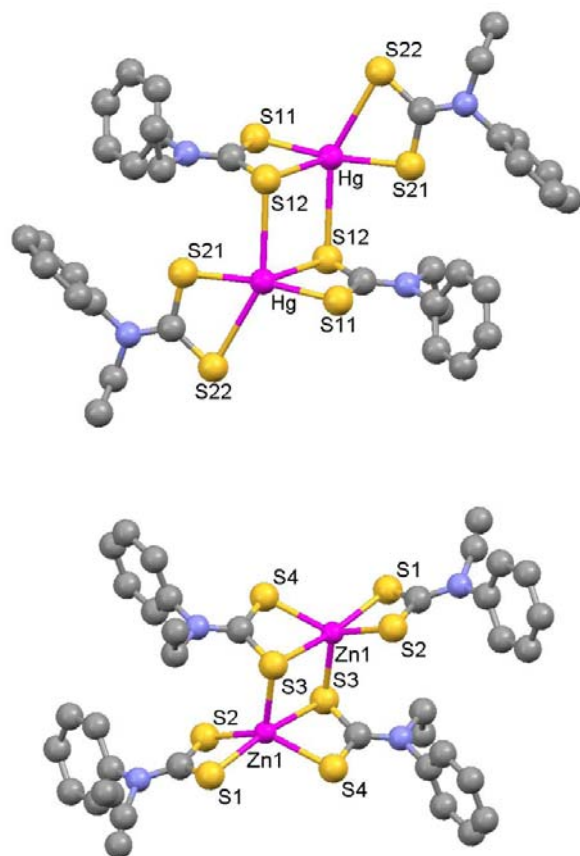


Figure 3. Mercury representations of Hg compound **2** (left) and Zn derivative **1** (right).

4. Conclusions

The solid-state characterisation of $[\text{Zn}(\text{S}_2\text{CN}\{\text{Et}\}\text{Ph})_2]_n$ (**1**) by single crystal X-ray diffraction reveals the compound to be a dimeric aggregate (*i.e.* $n = 2$) that may be described as the *syn*-isomer in relation to the orientation of ethyl and phenyl groups. In addition, compound **1** is a member of Tiekink's Dithiolate Bonding Motif Type III.² The title material is also shown not to be isostructural with the Hg analogue reported previously.^{26–28}

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6. References

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Povzetek

Opisana spojina kristalizira v triklinski prostorski skupini $P-1$ z osnovno celico $a = 8.7365(6)\text{Å}$, $b = 10.6009(7)\text{Å}$, $c = 12.0210(8)\text{Å}$, $\alpha = 66.3430(10)^\circ$, $\beta = 79.5660(10)^\circ$, $\gamma = 83.1500(10)^\circ$ in $V = 1001.56(12)\text{Å}^3$, $Z = 2$, $R = 0.0209$ (3522 opaženih uklonov, $I > 2\sigma(I)$). V strukturi je kovinski atom koordiniran z dvema ditiokarbamatnima skupinama, ena od obeh ditiokarbamatnih skupin daje sekundarno interakcijo (preko S-atoma) do druge $[\text{Zn}(\text{S}_2\text{CNEtPh})_2]$ enote z nastankom dimere. Strukturno spojine primerjamo s podobno spojino z dušikovim atomom v ditiokarbamatnem ligandu.