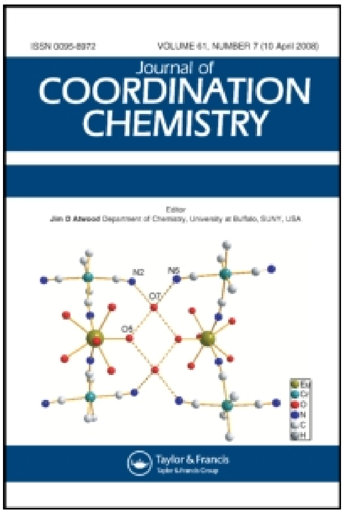

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CRYSTAL STRUCTURE AND THERMAL ANALYSIS OF A 4,4′-BIPY-BRIDGED BINUCLEAR ZINC(II) COMPLEX, $2[R_2NCS_2]_2 \cdot Zn(4,4'\text{-BIPY})$ (R=PIPERIDYL)

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The crystal structure of the title complex $2[R_2NCS_2]_2 \cdot Zn(4,4'\text{-bipy})$ (R = Piperidyl), 1, revealed that it consists of dimers made up from two crystallographically independent molecules. Each zinc atom in 1 forms a 5-coordinate *pseudo*-square-based pyramidal arrangement (with four Zn–S and one Zn–N interactions). Bondlengths to Zn with the coordinating atoms are comparable to those in other Zn(II) dithiocarbamate complexes. The piperidine ring has a chair conformation. To allow improved packing, the title complex molecules form an approximately linear arrangement extending along both *a* and *b*. TGA showed that 1 is decomposed in two close steps to produce ZnS as identified by residual weight. The complex 1 crystallizes in the monoclinic space group $C2/c$ with cell parameters: $a = 22.021(5)$, $b = 22.215(3)$, $c = 17.537(2)$ Å, $\beta = 93.49(2)°$, $V = 8563(3)$ Å^3 and $Z = 8$. The structure was refined by full-matrix least-squares methods to $R = 0.067$, $R_w = 0.114$.

Keywords: Binuclear; Zinc(II); 4,4′-bipy; Crystal structure; Thermal analysis

INTRODUCTION

Recently, *bis*(dialkyldithiocarbamates) of zinc and cadmium have found use as precursors in the growth of Group II–Group VI materials by low-pressure metal organic chemical vapour deposition (LP-MOCVD), leading to a renewed interest in their chemistry and further crystallographic

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investigations [1]. Simple dialkyldithiocarbamates of zinc and cadmium have dimeric structures in the solid state. The parent dimeric dithiocarbamates can be broken into monomeric species by adduct formation, as illustrated by recent structural studies of the 2,2′-bipyridyl [2], 1,10-phenanthroline [2] and triethylphosphine [3] adducts of $Cd(S_2CNEt_2)_2$ and 1,2-*bis*(diethylphosphino)ethane adducts of zinc and cadmium *bis*(diethyldithiocarbamates) [3]. However, this is not the case for the *N*,*N*,*N*′, *N*′-tetramethylethylenediamine (TMED) adduct of the asymmetric dithiocarbamate species $Zn(S_2CNMe^iPr)_2$ which was reported as consisting of two *bis*(*N*-methylisopropyldithiocarbamato)zinc molecules bridged by a TMED molecule [4]. Although 4,4′-bipy is a more common bridging ligand, the structural consequences of employing it for adduct formation of dithiocarbamate complex are unknown. Here we report the synthesis crystal structure and thermal analysis of the title complex **1**.

EXPERIMENTAL

Materials and Reagents

All chemicals are of analytical grade and used without further purification. The ligand sodium *N*-piperidyldithiocarbamate (L) was synthesized according to a literature method [5]. The starting reactant ZnL_2 was prepared by a literature method [6] and recrystallized twice from boiling benzene.

Preparation of Complex 1

ZnL_2(386 mg, 1 mmol) was dissolved in the minimum amount of DMF, and then to the clear DMF solution was added 4,4′-biby[$(C_5H_4N)_2 \cdot 2H_2O$] (96 mg, 0.5 mmol) in small portions over a 30 minute period at room temperature. The mixed solution turned yellow, a crude yellow solid appeared, and then the mixture was refluxed for one hour. Yellow microcrystals were collected by concentrating the DMF solution of **1**. Yellow crystals suitable for X-ray analysis were obtained by slow evaporation of a CH_3CN solution at room temperature over one week. Found: C, 43.87; H, 5.69; N, 9.15(%). Calc. for $C_{34}H_{48}N_6S_8Zn_2$(%): C, 44.00; H, 5.18; N, 9.06. The IR of **1** showed peaks at 3042(w), 2976(m), 2929(m), 1597(m), 1485(s), 1458(w), 1422(s), 1375(m), 1355(s), 1299(m), 1269(s), 1205(s), 1141(s), 1093(w), 1069(m), 987(s), 910(s), 836 (m), 804(m), 776 (w),732(w), 619(m), 562(m), 507(w), 471(w), 457(w), 431(w).

Physical Measurements

Elemental analyses were performed on a Perkin-Elmer 240C instrument. The IR spectrum was recorded on a Nicolet FT-IR 170SX spectrophotometer in a KBr pellet. TGA-DTA measurements were performed by heating the sample from 50 to 600°C at a rate of 20°C min^{-1} under a dinitrogen purge on a SDT 2960 simultaneous TGA-DTA instrument.

Crystallography

The intensities were collected on a Siemens P4 four-circle diffractometer with monochromated radiation Mo-Kα($\lambda = 0.71073$ Å) radiation at room temperature. The data were corrected for Lorentz and polarization effects during data reduction using XSCANS [7]. A total of 7368 reflections, of which 7159 reflections were unique ($R_{\text{int}} = 0.051$), were collected in the range $3.56 \leq 2\theta \leq 50.02°$ using the $\omega/2\theta$ scan mode with a variable scan speed of $5.0-50.0° \text{min}^{-1}$ in ω. The structure was solved by direct methods and refined on F^2 by full-matrix least-squares methods using SHELXTL version 5.0 [8]. Complex 1 crystallizes in the monoclinic space group $C2/c$ with $a = 22.021(5)$, $b = 22.215(3)$, $c = 17.537(2)$Å, $\beta = 93.49(2)°$, $V = 8563(3)$Å^3, $Z = 8$; $M_w = 928.00$, $D_{\text{calc}} = 1.440\,\text{g}\,\text{cm}^{-3}$, $F(000) = 3856$ and $\mu = 1.543\,\text{mm}^{-1}$. The C(15), C(16), C(17) atoms (site occupancy factors 0.5) and C(26), C(27), C(28), C(29) and C(30) atoms (site occupancy factors 0.67) were found to be disordered.

All the non-hydrogen atoms were refined anisotropically. Hydrogen atoms were placed in calculated positions (C-H, 0.96 Å), assigned fixed isotropic thermal parameters at 1.2 times the equivalent isotropic U of the atoms to which they are attached (1.5 times for methyl groups) and allowed to ride on their respective parent atoms. The contributions of these hydrogen atoms were included in the structure-factors calculations. All computation were carried out using the SHELXTL-Pc Program Package [8]. The final cycle of refinement included 527 parameters and converged with unweighted and weighted agreement factors of $R = 0.067$ and $R_w = 0.114$; GOF = 1.013 (on F^2) (The weighting scheme was $w^{-1} = \sigma^2(F_0^2) + (0.06P)^2$, $P = (F_0^2 + 2F_c^2)/3$). The maximum and minimum peaks in the final difference Fourier map corresponded to 0.422 and $-0.378\,\text{e}\text{Å}^{-3}$,

TABLE I Selected bond distances (Å) and angles (°) for **1**

Zn(1)—N(2)	2.105(9)	Zn(1)—S(2)#	2.385(3)	Zn(1)—S(2)	2.385(3)
Zn(1)—S(1)	2.521(2)	Zn(1)—S(1)#	2.521(2)	Zn(2)—N(3)	2.103(9)
Zn(2)—S(3)#	2.349(2)	Zn(2)—S(4)#	2.568(2)	Zn(2)—S(4)	2.568(2)
Zn(2)—S(3)	2.349(2)	Zn(3)—S(8)	2.347(2)	Zn(3)—S(5)	2.355(2)
Zn(3)—S(6)	2.572(2)	Zn(3)—S(7)	2.575(2)	Zn(3)—N(7)	2.083(6)
S(1)—C(6)	1.693(8)	S(2)—C(6)	1.719(8)	N(1)—C(6)	1.334(10)
N(1)—C(5)	1.458(9)	N(1)—C(1)	1.466(8)	N(2)—C(7)	1.332(9)
N(2)—C(7)#	1.332(9)	C(1)—C(2)	1.483(10)	C(7)—C(8)	1.380(10)
C(9)—C(10)	1.487(14)				
N(2)—Zn(1)—S(2)#	112.80(8)	N(2)—Zn(1)—S(2)	112.8(8)	S(2)#—Zn(1)—S(2)	134.41(16)
N(2)—Zn(1)—S(1)	101.23(6)	S(2)#—Zn(1)—S(1)	98.12(8)	S(2)—Zn(1)—S(1)	73.01(8)
N(2)—Zn(1)—S(1)#	101.23(6)	S(2)#—Zn(1)—S(1)#	73.01(8)	S(2)—Zn(1)—S(1)#	98.12(8)
S(1)—Zn(1)—S(1)#	157.53(12)	C(7)#—N(2)—Zn(1)	121.3(5)	C(6)—S(2)—Zn(1)	86.4(3)
C(6)—S(1)—Zn(1)	82.7(3)	C(7)—N(2)—Zn(1)	121.3(5)	N(3)—Zn(2)—S(3)#	116.60(7)
S(3)#—Zn(2)—S(4)#	73.00(8)	N(3)—Zn(2)—S(4)	100.51(7)	S(3)—Zn(2)—S(4)	73.00(8)
C(13)—S(3)—Zn(2)	88.0(3)	N(3)—Zn(2)—S(3)	116.60(7)	N(3)—Zn(2)—S(4)#	100.51(7)
S(3)—Zn(2)—S(4)#	97.40(9)	S(3)#—Zn(2)—S(4)	97.40(9)	S(4)#—Zn(2)—S(4)	158.97(14)
C(13)—S(4)—Zn(2)	81.1(3)	C(12)—N(3)—Zn(2)	121.8(5)	C(12)#—N(3)—Zn(2)	121.8(5)
S(3)#—Zn(2)—S(3)	126.79(14)	N(7)—Zn(3)—S(7)	99.0(2)	N(7)—Zn(3)—S(8)	114.27(19)
S(8)—Zn(3)—S(5)	124.55(9)	C(24)—S(5)—Zn(3)	88.0(3)	S(8)—Zn(3)—S(6)	97.97(8)
S(5)—Zn(3)—S(7)	97.47(8)	N(7)—Zn(3)—S(6)	100.5(2)	S(5)—Zn(3)—S(6)	72.80(8)
S(8)—Zn(3)—S(7)	73.24(8)	S(6)—Zn(3)—S(7)	160.47(8)	C(24)—S(6)—Zn(3)	81.2(3)
C(25)—S(7)—Zn(3)	81.2(3)	C(35)—N(7)—Zn(3)	121.8(5)	C(25)—S(8)—Zn(3)	87.7(3)
C(31)—N(7)—Zn(3)	121.5(5)	N(7)—Zn(3)—S(5)	121.18(19)		

Symmetry related atoms at $-x, y, 1/2-z$.

TABLE II Atomic coordinates [$\times 10^4$] and equivalent isotropic displacement parameters [$Å^2 \times 10^3$]. $U(eq)$ is defined as one third of the trace of the orthogonalized U_{ij} tensor

	x/a	*y/b*	*z/c*	*U(eq)*
Zn (1)	0	8973 (1)	2500	43 (1)
Zn (2)	0	3895 (1)	2500	45 (1)
Zn (3)	−2450 (1)	6397 (1)	2489 (1)	41 (1)
S (1)	−1112 (1)	9194 (1)	2634 (1)	54 (1)
S (2)	−86 (1)	9389 (1)	3743 (2)	69 (1)
S (3)	−42 (1)	3422 (1)	3693 (1)	60 (1)
S (4)	1102 (1)	3684 (1)	2991 (2)	64 (1)
S (5)	−1833 (1)	6331 (1)	3631 (1)	49 (1)
S (6)	−2225 (1)	5275 (1)	2731 (1)	48 (1)
S (7)	−2280 (1)	7523 (1)	2227 (1)	51 (1)
S (8)	−2080 (1)	6465 (1)	1265 (1)	54 (1)
N (1)	−1207 (3)	9739 (4)	3974 (4)	59 (2)
N (2)	0	8025 (4)	2500	41 (2)
N (3)	0	4842 (4)	2500	38 (2)
N (4)	1037 (4)	3082 (4)	4288 (5)	75 (3)
N (5)	−1393 (3)	5226 (3)	3886 (4)	55 (2)
N (6)	−1847 (5)	7586 (4)	858 (5)	112 (4)
N (7)	−3396 (2)	6398 (3)	2500 (4)	39 (2)
C (1)	−1858 (3)	9837 (5)	3796 (5)	69 (3)
C (2)	−2217 (4)	9590 (6)	4414 (6)	99 (4)
C (3)	−2024 (4)	9855 (6)	5181 (6)	106 (5)
C (4)	−1350 (5)	9774 (5)	5342 (5)	78 (3)
C (5)	−1000 (4)	10008 (5)	4703 (5)	81 (4)
C (6)	−851 (4)	9462 (4)	3496 (5)	47 (2)
C (7)	−492 (4)	7714 (3)	2664 (5)	45 (2)
C (8)	−510 (4)	7093 (3)	2659 (5)	45 (2)
C (9)	0	6772 (5)	2500	39 (3)
C (10)	0	6103 (5)	2500	34 (3)
C (11)	−519 (4)	5785 (3)	2278 (4)	40 (2)
C (12)	−500 (3)	5161 (4)	2276 (4)	40 (2)
C (13)	733 (4)	3359 (4)	3718 (5)	57 (3)
C (14)	743 (5)	2775 (5)	4907 (6)	101 (5)
C (15)	974 (11)	2146 (8)	4747 (16)	102 (13)
C (16)	1652 (12)	2040 (13)	4680 (20)	112 (16)
C (17)	1961 (10)	2406 (8)	4106 (14)	82 (9)
C (15′)	692 (13)	2116 (8)	5080 (20)	134 (16)
C (17′)	1700 (20)	2317 (9)	4480 (18)	140 (20)
C (16′)	1369 (13)	1994 (11)	5100 (18)	102 (10)
C (18)	1701 (5)	2992 (6)	4313 (7)	105 (5)
C (19)	−943 (4)	5468 (5)	4458 (5)	76 (3)
C (20)	−960 (5)	5142 (5)	5196 (6)	83 (4)
C (21)	−896 (5)	4468 (4)	5101 (5)	78 (3)
C (22)	−1365 (4)	4246 (4)	4503 (5)	64 (3)
C (23)	−1324 (4)	4574 (3)	3765 (5)	54 (2)
C (24)	−1776 (3)	5571 (3)	3469 (4)	39 (2)
C (25)	−2029 (4)	7237 (4)	1402 (5)	59 (3)
C (26)	−1849 (7)	8266 (5)	845 (10)	51 (4)
C (27)	−1199 (8)	8433 (10)	819 (11)	76 (7)
C (28)	−981 (13)	8230 (13)	53 (13)	99 (12)
C (29)	−1057 (10)	7553 (13)	21 (15)	89 (9)
C (30)	−1712 (9)	7401 (8)	59 (7)	67 (5)
C (26′)	−1650 (30)	8176 (10)	1199 (13)	170 (30)
C (27′)	−1480 (20)	8519 (17)	517 (18)	76 (14)

TABLE II (Continued)

	x/a	*y/b*	*z/c*	*U(eq)*
C (28′)	−1210 (20)	8259 (16)	−180 (20)	62 (15)
C (29′)	−1300 (30)	7587 (16)	−282 (19)	61 (14)
C (30′)	−1390 (30)	7248 (18)	430 (30)	220 (50)
C (31)	−3704 (3)	5905 (4)	2682 (5)	46 (2)
C (32)	−4323 (3)	5884 (4)	2684 (5)	46 (2)
C (33)	−4660 (3)	6397 (4)	2488 (4)	37 (2)
C (34)	−4345 (3)	6907 (4)	2304 (5)	49 (2)
C (35)	−3720 (4)	6878 (4)	2309 (5)	53 (2)

respectively. Selected bond lengths and angles are listed in Table I, and final atomic coordinates in Table II.

DISCUSSION

DTA and DTA of Complex 1

The TGA-DTA curve of complex **1** exhibits two endotherms at ca. 300 and 347°C. TGA data also show that the Zn−N (from 4,4′-bipy) bonds are labile in the solid state. Upon heating, the 4,4′-bipy ligand dissociates from the metal centre before 300°C to form the starting material, ZnL$_2$ (weight loss obs. 17.00; calc. 16.81%). In the next step which begins at 347°C, complex **1** decomposes to ZnS (residual obs. 19.15, calc. 20.90%).

Description of the Structure

An ORTEP drawing of complex **1**, giving the atom numbering scheme, is shown in Figure 1. Each Zn atom in **1** has a distorted rectangular pyrimidal geometry linked to two bidentate S$_2$CNR$_2$ ligand in the basal plane and bridged by a 4,4′-bipy at the apex. There are two shorter and two longer bondlengths for Zn(1) in **1**, very similar to those in other related compounds. For example, there are two shorter [2.349(2) Å] and two longer [2.5460(7) Å and 2.6103(7) Å] for 2[Me^{i}PrNCS$_2$]$_2$Zn·Me$_2$(CH$_2$)$_2$Me$_2$ [4]; two shorter [2.3362(7) Å and 2.3498(7) Å] and two longer [2.586(2) Å and 2.588(2) Å] for [Me^{i}PrNCS$_2$]Zn$_2$·C$_5$H$_5$N [4]; two shorter [2.319(2) Å and 2.325(4) Å] and two longer [2.672(3) Å and 2.591(1) Å] for [Me$_2$NCS$_2$]$_2$Zn [9]. The Zn(2)−S and Zn(3)−S bond lengths are similar.

Compared to the Zn−N bondlength [2.137(5)Å] in 2 [Me^{i}PrNCS$_2$]$_2$Zn·Me$_2$(CH$_2$)$_2$Me$_2$, the Zn−N bond in **1** is shorter. This difference is probably attributable to the very different steric character of the *N*-containing

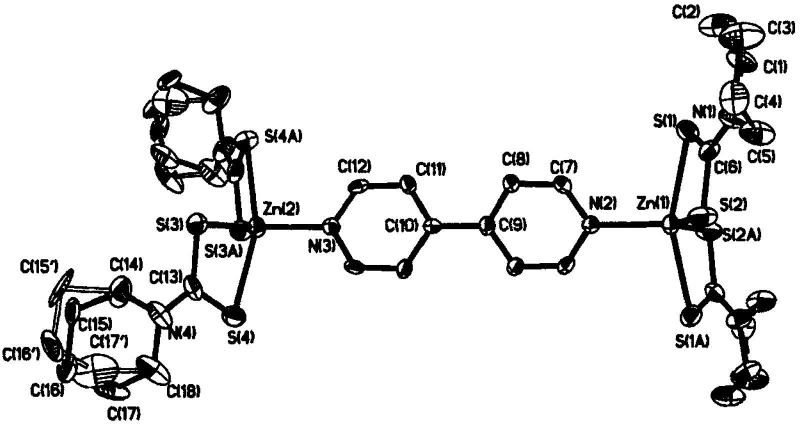

FIGURE 1 ORTEP drawing of molecule 1 (30% probability ellipsoids) showing the atom numbering scheme.

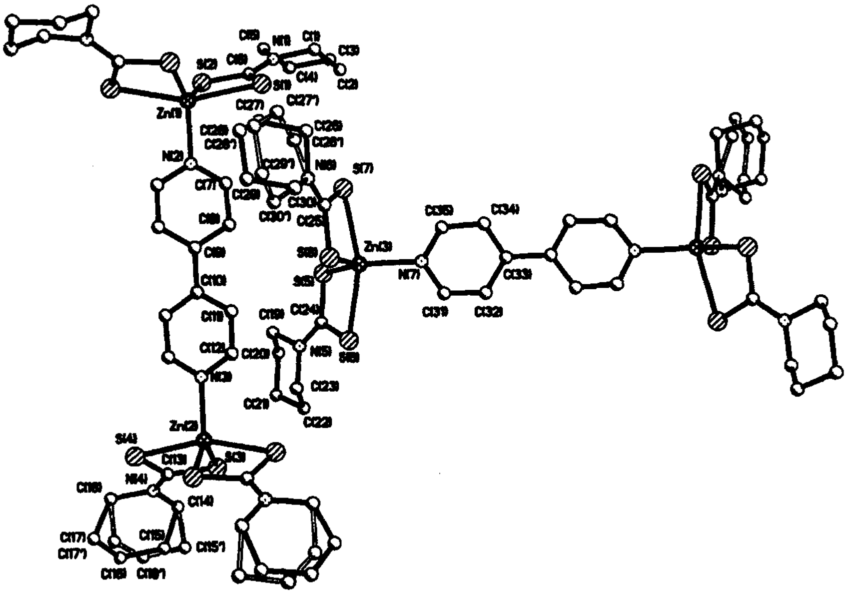

FIGURE 2 ORTEP drawing of molecule 2 (30% probability ellipsoids) showing the atom numbering scheme.

bridging ligands. The bulkiness of the dimethylamino unit of TMED in $2[\mathrm{Me}^{i}\mathrm{PrNCS}_2]_2\mathrm{Zn}\cdot\mathrm{Me}_2(\mathrm{CH}_2)_2\mathrm{Me}_2$ may inhibit the approach of ligand to the zinc atom and result in a longer Zn–N bond, whereas in complex **1**, the less bulky surroundings of the nitrogen atom of 4,4′-bipy facilitate a closer interaction with the Zn atom, resulting in a shorter Zn−N bond.

There are two asymmetric molecules in the unit cell. Molecule 1 has both Zn atoms and the bridging 4,4′-bipy on a 2-fold axis while molecule 2 lies across the 2-fold axis at the mid-point of the 4,4′-bipy ligand. The two molecules are mutually orthogonal to each other. The bond distances and angles of 4,4′-bipy ligands are normal, but the 4,4′-bipy linking the two zinc atoms is not planar. Interplanar angles between the pyridine rings of the bridging 4,4′-bipy ligands are almost the same [33.8° for molecule 1 and 33.1° for molecule 2]. Molecules of **1** form an approximately linear arrangement extending in both *a* and *b* directions. Presumably, this allows improved packing. It is worthwhile noting that the piperidine rings in **1** are disordered. Three carbon atoms in molecule 1 [C(15), C(16) and C(17)] are disordered while in molecule 2 the disorder involves five carbon atoms [C(26), C(27), C(28), C(29) and C(30)]. Although the disorder in the two molecules is not the same, the piperidine rings have the chair conformation as found in *bis*(piperidine-1-dithiocarbamato)nickel(II) and *bis*(piperidine-1-dithiocarbamato)copper(II) [10].

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Supplementary Data

Full lists of crystallographic data are available from the authors upon request.

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