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An Unusual Coordination Mode in a Bis(dialkyldithiocarbamato)zinc(II) Adduct with *N,N,N′,N′*-Tetramethylethylenediamine: X-ray Crystal Structures of $2[\mathrm{Me^{i}PrNCS_2}]_2\mathrm{Zn{\cdot}Me_2N(CH_2)_2NMe_2}$ and $[\mathrm{Me^{i}PrNCS_2}]_2\mathrm{Zn{\cdot}C_5H_5N}$

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Introduction

Several papers have reported the synthesis and characterization of adducts of simple group 12 bis(dialkyldithiocarbamates) of the type $[\mathrm{R_2NCS_2}]_2\mathrm{M{\cdot}L}$ (R = Me, Et; M = Zn, Cd; L = 2,2-bipyidyl, $\mathrm{PEt_3}$, etc.)[1,2] and include the structural studies of $(\mathrm{Et_2NCS_2})_2\mathrm{Cd{\cdot}2,2\text{-}bipy}$[1] and $(\mathrm{Et_2NCS_2})_2\mathrm{Cd{\cdot}PEt_3}$.[2]

In general, the formation of the adduct breaks the parent dimeric dithiocarbamate into a monomeric species. In the present note, we report that the *N,N,N′,N′*-tetramethylethylenediamine (TMED) adduct of the asymmetric dithiocarbamate species $\mathrm{Zn(S_2CNMe^{i}Pr)_2}$ gives the first example of a bridging TMED molecule in a 1:2 adduct of a group 12 metal bis(dialkyldithiocarbamate) (compound **1**). The more common 1:1 adduct stoichiometry is exemplified by the pyridine adduct of $\mathrm{Zn(S_2CNMe^{i}Pr)_2}$ (compound **2**).

Results and Discussion

The two adducts reported in this work are both white crystalline solids which are soluble in most common organic solvents. The compounds were synthesized from a solution of $\mathrm{Zn(S_2CNMe^{i}Pr)_2}$ in warm TMED or pyridine followed by evaporation of the ligand to give a crude white product subsequently recrystallized from acetone.

The X-ray crystal structures of single crystals of each compound have been determined. The structure of compound **2** is as expected, the pyridine molecule forcing the zinc atom into a 5-coordinate pseudo-square-based-pyramidal arrangement (with four Zn−S interactions and one Zn−N interaction). The compound is monomeric.

Compound **1** is unusual and consists of two bis(*N*-methylisopropyldithiocarbamato)zinc molecules bridged by a TMED molecule. This is a common coordination mode with group 13 alkyls and hydrides, where the metal center requires only one more interaction to achieve pseudotetrahedral symmetry, e.g. the TMED adducts of trimethylaluminum,[3] gallane,[4,5] and bis(tris(trimethylsilyl)methyl)gallium.[6]

However, for group 12 metals, both donor atoms might well be expected to bind to the same metal atom as in $\mathrm{Me_2Zn{\cdot}TMED}$,[7] $[\mathrm{(CH_3)_3CCH_2}]_2\mathrm{Zn{\cdot}TMED}$,[7] $(\mathrm{Et_2NCS_2Zn})_2\mathrm{{\cdot}TMED}$,[2] and $(\mathrm{Et_2NCO_2})_2\mathrm{Zn.TMED}$.[8]

There is no significant difference in the average Zn−S bond lengths between compounds **1** and **2**, both having two shorter Zn−S bond lengths (two at 2.349(2) Å for compound **1** and at 2.3362(7) and 2.3498(7) Å for compound **2**) and two longer Zn−S bond lengths (2.586(2) and 2.588(2) Å for compound **2** and 2.5460(7) and 2.6103(7) Å for compound **1**).

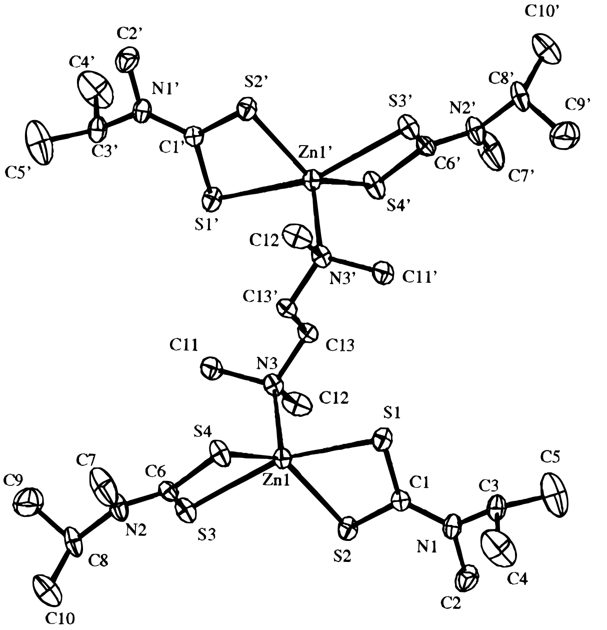

Figure 1. Molecular structure of $2(\mathrm{Me^{i}PrNCS_2})_2\mathrm{Zn{\cdot}(CH_3)_2N(CH_2)_2N(CH_3)_2}$.

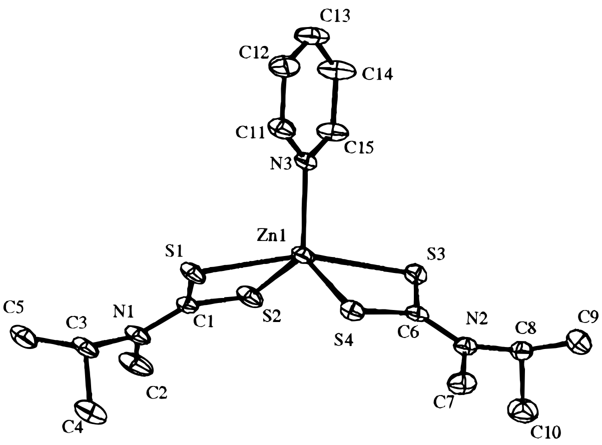

Figure 2. Molecular structure of $(\mathrm{Me^{i}PrNCS_2})_2\mathrm{Zn{\cdot}NC_5H_5}$.

The most significant differences are in the Zn−N bond lengths. The bulkiness of the dimethylamino unit of TMED may inhibit the approach of the ligand to the zinc atom and result in a longer Zn−N bond (2.137(5) Å), as opposed to the case of compound **2** where the less bulky surroundings of the nitrogen atom of pyridine facilitate a closer interaction with the zinc atom (although there are basicity differences), resulting in a shorter Zn−N bond (2.069(2) Å) (which compares favorably with a Zn−N bond length of 2.079 Å in $\{\mathrm{Me_2NCS_2}\}_2\mathrm{Zn{\cdot}NC_5H_5}$).[9]

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Table 1. Selected Bond Lengths (Å) and Angles (deg) for Compound **1**

Zn(1)−N(3)	2.137(5)	Zn(1)−S(1)	2.586(2)
Zn(1)−S(2)	2.349(2)	Zn(1)−S(3)	2.588(2)
Zn(1)−S(4)	2.349(2)		

N(3)−Zn(1)−S(2)	113.2(2)	S(1)−Zn(1)−S(3)	159.97(7)
N(3)−Zn(1)−S(4)	112.5(2)	C(1)−S(1)−Zn(1)	81.4(2)
S(2)−Zn(1)−S(4)	134.19(8)	C(1)−S(2)−Zn(1)	88.8(2)
N(3)−Zn(1)−S(1)	101.98(13)	C(6)−S(3)−Zn(1)	81.1(2)
S(2)−Zn(1)−S(1)	72.75(6)	C(6)−S(4)−Zn(1)	88.3(2)
S(4)−Zn(1)−S(1)	100.53(6)	C(11)−N(3)−Zn(1)	112.0(4)
N(3)−Zn(1)−S(3)	98.00(13)	C(12)−N(3)−Zn(1)	104.9(4)
S(2)−Zn(1)−S(3)	98.01(6)	C(13)−N(3)−Zn(1)	114.2(3)
S(4)−Zn(1)−S(3)	72.80(5)		

Table 2. Selected Bond Lengths (Å) and Angles (deg) for Compound **2**

Zn(1)−N(3)	2.069(2)	Zn(1)−S(1)	2.5460(7)
Zn(1)−S(4)	2.3362(7)	Zn(1)−S(3)	2.6103(7)
Zn(1)−S(2)	2.3498(7)		

N(3)−Zn(1)−S(4)	119.35(5)	S(2)−Zn(1)−S(3)	99.52(3)
N(3)−Zn(1)−S(2)	114.26(5)	S(1)−Zn(1)−S(3)	162.21(2)
S(4)−Zn(1)−S(2)	126.37(3)	C(1)−S(1)−Zn(1)	81.01(7)
N(3)−Zn(1)−S(1)	100.29(5)	C(1)−S(2)−Zn(1)	86.88(7)
S(4)−Zn(1)−S(1)	97.35(2)	C(6)−S(3)−Zn(1)	80.33(7)
S(2)−Zn(1)−S(1)	73.89(2)	C(6)−S(4)−Zn(1)	88.56(7)
N(3)−Zn(1)−S(3)	97.49(5)	C(15)−N(3)−Zn(1)	119.6(2)
S(4)−Zn(1)−S(3)	72.93(2)	C(11)−N(3)−Zn(1)	123.1(2)

Both compounds have also been characterized by NMR (^{1}H and ^{13}C) spectra. ^{1}H NMR spectra gave a singlet for the *N*-methyl protons, a doublet for the methyl protons, and a septet for the methyne protons of the isopropyl group. Chemical shifts of these protons were similar in both compounds. Pyridine shows characteristic signals in the aromatic region, and TMED gives two intense singlets in midfield. ^{13}C NMR spectra showed seven signals for compound **1** and six for compound **2**, as expected. NMR data with the chemical shift assignments are given in the following section.

Experimental Section

N,N,N′,N′-Tetramethylethylenediamine and pyridine were purchased from the Aldrich Chemical Co. Ltd., and solvents were obtained from BDH. NMR spectra were recorded using a Bruker AM250 pulsed Fourier transform instrument. Microanalyses were performed at the University of London service at UCL. The synthesis of the parent bis(*N*-methylisopropyldithiocarbamato)zinc has been reported elsewhere.[10]

Synthesis of 2(Me^{i}PrNCS$_2$)$_2$Zn·(CH$_3$)$_2$N(CH$_2$)$_2$N(CH$_3$)$_2$. Bis(*N*-methylisopropyldithiocarbamato)zinc was dissolved in *N,N,N′,N′*-tetramethylethylenediamine, and as the excess solvent evaporated, a crude white solid appeared, which was recrystallized from acetone to give colorless crystals, mp 175 °C. Anal. Calcd for $C_{26}H_{56}N_6S_8Zn$: C, 37.17; H, 6.72; N, 10.00; S, 30.54. Found: C, 37.31; H, 6.40; N, 9.97; S, 30.14.

Synthesis of (Me^{i}PrNCS$_2$)$_2$Zn·NC$_5$H$_5$. Bis(*N*-methylisopropyldithiocarbamato)zinc was dissolved in warm pyridine, and as the excess solvent evaporated, a crude white solid appeared, which was recrystallized from acetone to give colorless, cubic crystals, mp 175 °C. Anal. Calcd for $C_{15}H_{25}N_3S_4Zn$: C, 40.85; H, 5.71; N, 9.53; S, 29.08. Found: C, 40.32; H, 5.37; N, 9.38; S, 29.64.

Table 3. Crystal Data and Structure Refinement Details

	1	2
empirical formula	$C_{13}H_{28}N_3S_4Zn_2$	$C_{15}H_{25}N_3S_4Zn$
fw	419.99	440.99
temp, K	293(2)	293(2)
wavelength, Å	0.710 69	0.710 69
crystal system	monoclinic	triclinic
space group	$P2_1/a$	$P\bar{1}$
unit cell dimens		
a, Å	11.312(10)	9.171(10)
b, Å	25.616(4)	10.335(2)
c, Å	7.056(10)	12.318(2)
α, deg	90	102.99(10)
β, deg	104.02(10)	78.19(10)
γ, deg	90	114.02(10)
V, Å^3	1983.7(5)	1030.7(3)
Z	4	2
d(calcd), g cm^{-3}	1.406	1.421
μ, mm^{-1}	1.656	1.598
F(000)	884	460
R^a	0.0568	0.0279
$R_w{}^b$	0.1926	0.0769

^{a} $R = \sum||F_o| - |F_c||/\sum|F_o|$. ^{b} $R_w = [\sum w(|F_o| - |F_c|)^2/\sum wF_o{}^2]^{1/2}$.

X-ray Studies. X-ray measurements were made on a sample mounted in a glass capillary with an Enraf-Nonius CAD4 diffractometer operating in the $\omega/2\theta$ scan mode with graphite-monochromated Mo Kα radiation as described previously.[11] The structures were solved via standard heavy-atom procedures and refined by using full-matrix least-squares methods[12] with scattering factors calculated by using the data from ref 13. All non-hydrogen atoms were refined with anisotropic displacement factors; for compound **1** hydrogen atoms were geometrically idealized (using riding model), and for compound **2** hydrogen atoms were identified in different maps and included with isotropic displacement factors.

Crystal data and details of the intensity measurements and refinement are given in Table 3; atomic coordinates, full lists of bond lengths and angles, and anisotropic displacement factor coefficients are included in the Supporting Information.

NMR Data. 2(Me^{i}PrNCS$_2$)$_2$Zn·(CH$_3$)$_2$N(CH$_2$)$_2$N(CH$_3$)$_2$ (1). ^{1}H NMR ([^{2}H$_6$]C$_6$H$_6$, 250.1 MHz): δ 1.22 (24H, d, NCH(CH_3)$_2$), 2.42 (12H, s, N(CH_3)$_2$), 2.53 (4H, s, N(CH_2)$_2$N), 3.26 (12H, s, NCH_3), 5.36 (4H, septet, NCH(CH$_3$)$_2$). ^{13}C NMR ([^{2}H$_6$]C$_6$H$_6$, 62.9 MHz): 19.62 (NCH(CH$_3$)$_2$), 34.28 (NCH$_3$), 46.26 (N(CH$_3$)$_2$), 55.11 (N(CH$_2$)$_2$N), 57.03 (NCH(CH$_3$)$_2$), 203.57 (CS$_2$).

(Me^{i}PrNCS$_2$)$_2$Zn·NC$_5$H$_5$ (2). ^{1}H NMR ([^{2}H$_6$]C$_6$H$_6$, 250.1 MHz): δ 1.22 (6H, d, NCH(CH_3)$_2$), 3.27 (3H, s, NCH_3), 5.37 (1H, septet, NCH(CH$_3$)$_2$), 7.42, 7.81, 8.91 (5H, NC$_5\mathit{H}_5$). ^{13}C NMR ([^{2}H$_6$]C$_6$H$_6$, 62.9 MHz): 19.57 (NCH(CH$_3$)$_2$), 34.31 (NCH$_3$), 55.13 (NCH(CH$_3$)$_2$), 124.53, 137.99, 149.57 (NC_5H$_5$), 203.57 (CS$_2$).

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Supporting Information Available: Complete listings of data collection parameters, bond distances and angles, thermal parameters, and atomic coordinates for compounds **1** and **2** (16 pages). Ordering information is given on any current masthead page.

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