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Chalcogenolato-di-thiocarbamato-complexes of zinc: The X-ray single crystal structures of pyridine adducts

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Abstract

Novel mixed complexes 2,4,6-$Me_3C_6H_2SZnS_2CNEt_2$ (**1**), 2,4,6-$Me_3C_6H_2SeZnSe_2CNEt_2$ (**2**) and their pyridine adducts **(**$[Zn(SC_6H_2Me_3\text{-}2,4,6)_2(C_5H_5N)_2]$ **(3),** $[Zn(SeC_6H_2Me_3\text{-}2,4,6)_2(C_5H_5N)_2]$ (**4**) and $(Et_2CNSe_2)_2Zn.NC_5H_5$ **(5)** and $(Et_2CNS_2)_2Zn.NC_5H_5$ **(6)** have been synthesised and characterised. The X-ray single crystal structures of (**4**), (**5**) and (**6**) have been determined. © 1999 Elsevier Science Ltd. All rights reserved.

Keywords: Cadmium complexes; Zinc complexes; Chalcogenides; Pyridine adducts

1. Introduction

Arene-thiolato or -selenolato complexes of cadmium or zinc are usually crystalline solids with infinite lattices in which the metal centre is bridged by the chalcogenolato ligands to give pseudo-tetrahedral co-ordination at the metal [1–4]. The structures of metal-arene chalcogenalato complex are strongly influenced by packing arrangements and the nature of the substituents [5] on the arene-chalcogenalato ligands is crucial. The mesityl (2,4,6-trimethylphenyl) chalogens form one dimensional chain structures whereas the related 2,4,6-trimethylphenyl complexes MER_2 (M=Cd or Zn; E=S or Se) are polymeric solids which only dissolve in co-ordinating solvents [6]. Other than for $Cd(SR)_2$ ($R=C_6H_2Me_3$-2,4,6), which forms a unstable crystalline pyridine adduct, $[Cd(SR)_2.(py)_2]$, no defined pyridine adducts have been obtained [6]. The bulkier *tert*-butyl analogue of the mesityl aryl group forms dimers in the solid state [7] which are air-stable, sublime under reduced pressure, dissociate to monomers and hence are useful precursors for film deposition by MOCVD.

We report the synthesis and characterisation of several novel compounds, derived from these chalcogenides. The compounds synthesised include: the mixed complexes 2,4,6-$Me_3C_6H_2SZnS_2CNEt_2$ (**1**), 2,4,6-$Me_3C_6H_2SeZnSe_2CNEt_2$ (**2**) and their pyridine adducts **(**$[Zn(SC_6H_2Me_3\text{-}2,4,6)_2(C_5H_5N)_2]$ **(3),** $[Zn(SeC_6H_2Me_3\text{-}2,4,6)_2(C_5H_5N)_2]$ (**4**) and $(Et_2CNSe_2)_2Zn.NC_5H_5$ **(5)** and $(Et_2CNS_2)_2Zn.NC_5H_5$ **(6)** The X-ray single crystal structures of (**4**), (**5**) and **(6)** have been determined.

2. Experimental

2.1. Chemicals

Dimethylzinc was supplied by Epichem Ltd. Carbon disulphide, diethylamine, diethyl ether, toluene, thf were purchased from Aldrich Chemical Co. Ltd, solvents were dried (distilled after boiling with sodium metal and benzophenone for two hours under nitrogen) and degassed by freeze and thawing. This process was repeated three times before use. Carbon diselenide was prepared using the literature method [12].

2.2. Physical measurements

NMR spectra were recorded using a Bruker AM250 pulsed Fourier transform instrument. Infra red spectra were carried out using Matteson Polaris FT-IR spectrometer as nujol mulls, mass spectra were recorded by a micromass Auto-spec-Q using micromass OPUS software. An electron impact energy of 70 eV at 10^{-7} Torr was used to initiate mass fragmentation. Melting points were measured

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in sealed tubes with an electrothermal melting point apparatus and are uncorrected. Microanalyses were carried out by the Imperial College London service.

2.3. X-ray crystallography

The structures of compounds **(4)**, **(5)** and **(6)** were determined by single crystal X-ray methods. Measurements were made on a sample mounted in a glass capillary. The intensity data were collected with a CAD4 diffractometer in $\omega/2\theta$ scan mode with graphite-monochromated Mo Kα, and corrected for absorption by the empirical method (ψ-scan**)** [8]. The unit cell parameters were determined by a least-squares refinement on diffractometer angles for automatically centred reflections. The structure was solved by the heavy-atom method using the SHELX-97 program package [9] and than refined anisotropically (non-hydrogen atoms) by a full-matrix least-square on F^2. All hydrogen atoms were calculated geometrically (riding model) using the AFIX command of the SHELX-97 program. The program ORTEP-3 for Windows [10] was used for drawing molecular structures. Crystal data and details of the intensity measurements and refinements are given in Table 1.

Atomic co-ordinates, thermal parameters and bond lengths and angles have been deposited at the Cambridge Crystallographic Data Center (CCDC).

2.4. Synthesis

All reactions were performed under dry nitrogen using standard Schlenck techniques. 2,4,6-$Me_3C_6H_2SH$, 2,4,6-$Me_3C_6H_2SeH$ [11,6], CSe_2 [12] $MeZnS_2CNEt_2$ [13] and $MeZnSe_2CNEt_2$ were prepared as described in the literature [14].

2.4.1. 2,4,6-$Me_3C_6H_2SZnS_2CNEt_2$ **(1)**

2,4,6-$Me_3C_6H_2SH$ (0.20 g, 1.4 mmol) and $MeZnS_2CNEt_2$ (0.33 g, 1.4 mmol) in toluene (20 cm^3) were stirred and heated at 80°C for 0.5 h. The mixture on concentration gave white powder which was separated by decanting the solvent. The product, m.p. >260°C (0.40 g, 1.1 mmol, 79%) was insoluble in most organic solvents and hence could not be recrystallised. (Found: C, 45.38; H, 5.68; N, 3.93; S, 26.42. Calculated: C, 46.08; H, 5.80; N, 3.84; S, 26.36). ^1H NMR ([$^2H_6$]C_6H_6), 250 MHz) δ (ppm) 1.30 [6H, t, CH_3], 3.84 [4H, q, CH_2], 1.55 [6H, s, CCH_3], 2.24 [3H, s, CCH_3], 6.71 [2H, s, C_6H_2-]. ^{13}C-{^1H} NMR

Table 1
Crystal data and structure refinement

	(**4**)	(**5**)	(**6**)
Formula	$C_{28}H_{32}N_2Se_2Zn$	$C_{15}H_{25}N_3Se_4Zn$	$C_{15}H_{25}N_3S_4Zn$
Molecular weight	619.85	628.59	440.99
Crystal system	Monoclinic	Monoclinic	Monoclinic
Crystal size, mm	0.4×0.3×0.25	0.35×0.23×0.2	0.30×0.25×0.2
Space group	P21/a	P21/c	P21/c
a, Å	16.410(3)	10.392(5)	10.140(2)
b, Å	12.425(1)	32.796(8)	31.794(5)
c, Å	13.546(2)	13.186(4)	13.48191)
α/°	90	90	90
β/°	99.68(2)	105.41(4)	107.17(1)
γ/ °	90	90	90
Volume (Å^3)	2722.6(7)	4332(3)	4152.5(2)
Z	4	8	8
D_{calc} (g cm^{-3})	1.512	1.927	1.411
F(000)	1248	2416	1840
Temperature (K)	293(2)	293(2)	293(2)
λ, Å	Mo Kα	Mo Kα	Mo Kα
μ, mm^{-1}	3.594	7.855	1.58
20 range (°)	1.52/26.97	1.72/24.97	1.28/24.98
Data/restraints/parameters	5926/0/316	7608/0/441	7274/0/441
Observed reflections[I>2σ(I)]	3012	4134	3959
Refinement method	Full-matrix least squares on F^2	Full-matrix least squares on F^2	Full-matrix least squares on F^2
Goodness of fit on F^2	0.878	0.966	1.054
Calculated weights[a]	a=0.0569, b=0.00	a=0.1308, b=0.00	a=0.0626, b=0.00
Final R[b]	0.0484	0.0567	0.0497
Final $_wR_2$ [c]	0.0.0979	0.1680	0.1194

[a] $w=1[\sigma^2(F_o^2)+(aP)^2+bP]$ where $P=(F_o^2+2F_c^2)/3$.

[b] $R=\Sigma||F_o|-|F_C||/\Sigma|F_o|$.

[c] $_wR_2=[\Sigma[w(F_O^2-F_C^2)^2]/\Sigma[w(F_O^2)^2]]^{1/2}$.

($[^2H_6]C_6H_6$), 62.9 MHz) δ (ppm) 12.09 [CH_3], 49.21 [CH_2], 26.51 [$(CH_3)_2$], 20.72 [CCH_3], 128.3 [meta-C], 138.9 [ortho-], 142.2 [ipso-C], 128.4 [para-C], 202.2 [CS_2]. IR major bands and tentative assignments) 559, 557 cm^{-1} (υ(Zn–S), 987cm^{-1} (υ(C=S), 1489 cm^{-1} (υ(C=N). Mass spectrum (m/z): M^+ 362 [$Me_3C_6H_2SZnS_2CNEt_2$], base peak 116 [$SCNEt_2$], 244 [$SZnS_2CNEt_2$], 212 [ZnS_2CNEt_2], 148 [S_2CNEt_2], 119 [$Me_3C_6H_2$], 96 [ZnS], 72 [NEt_2], 44 [HNEt].

2.4.2. 2,4,6-$Me_3C_6H_2SeZnSe_2CNEt_2$ (**2**)

A mixture of 2,4,6-$Me_3C_6H_2SeH$ (0.85 g, 4.3 mmol) and $MeZnSe_2CNEt_2$ (1.40 g, 4.3 mmol) in toluene (20 cm^3) were stirred and heated at 80°C for 0.5 h. On cooling a yellowish powdery material settled in a yellow solution. The product was separated by decanting the solvent and dried under vacuum, m.p. >260°C (1.51 g, 3.0 mmol, 87%). Several attempts to recrystallise from ordinary organic solvent were unsuccessful as the product was insoluble in most of them. (Found: C, 33.11; H, 4.13; N, 2.86. Calculated: C, 33.26; H, 4.18; N, 2.77). ^1H NMR ($[^2H_6]C_6H_6$), 250 MHz) δ (ppm) 1.35 [6H, t, CH_3], 3.79 [4H, q, CH_2], 1.48 [6H, s, CCH_3], 2.20 [3H, s, CCH_3], 6.69 [2H, s, C_6H_2–]. ^{13}C-{^1H} NMR ($[^2H_6]C_6H_6$), 62.9 MHz) δ (ppm) 11.7 [CH_3], 52.1 [CH_2], 27.2 [$(CCH_3)_2$], 19.9 [CCH_3], 122.6 [meta-C], 136.5 [ortho-C], 143.1 [ipso-C], 126.7 [para-C], 191.3 [CSe_2].

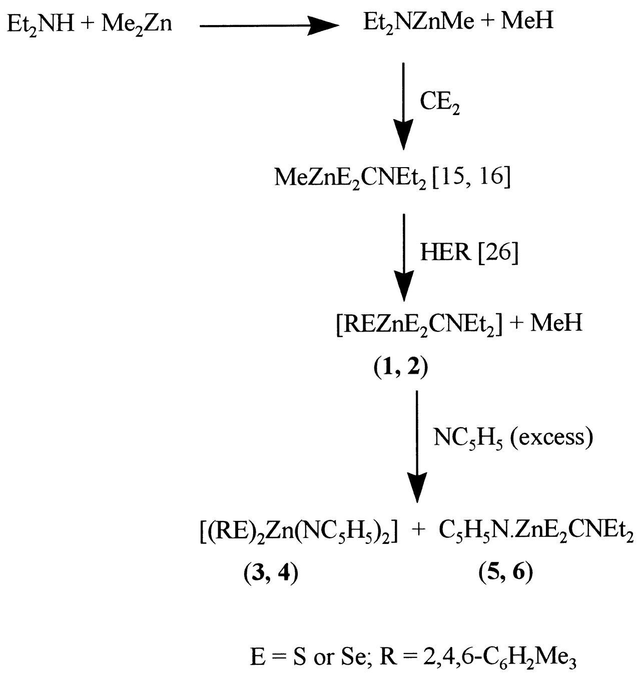
IR (major bands and tentative assignments) 472, 503 cm^{-1} (υ(Zn–Se), 850 cm^{-1} (υ(C=Se), 1503 cm^{-1} (υ(C=N). Mass spectrum (m/z): M^+ 507 [$Me_3C_6H_2SeZnSe_2CNEt_2$], base peak 44 [HNEt], 388 [$SeZnSe_2CNEt_2$], 308[$ZnSe_2CNEt_2$], 244 [Se_2CNEt_2], 119 [$Me_3C_6H_2$], 144 [ZnSe], 72 [NEt_2].

2.4.3. 2,4,6-$Me_3C_6H_2SNC_5H_5$ (**3**) and 2,4,6-$Me_3C_6H_2SeNC_5H_5$ (**4**), $(Et_2CNSe_2)_2Zn.NC_5H_5$ (**5**) and $(Et_2CNS_2)_2Zn.NC_5H_5$ (**6**)

All four compounds were prepared by the reaction of compounds (**1**) or (**2**) with an excess of pyridine. The mixture was heated to obtain a clear solution, concentrated under vacuum, and left in the fridge to crystallise. Crystalline products were obtained for all compounds, (Scheme 1).

Compound (**3**): m.p. 255°C (decomp.), 89%, (Found: C, 56.06; H, 5.39; N, 4.89; S, 10.90. Calculated: C, 56.86; H, 5.45; N, 4.78; S, 10.84). NMR data: ^1H NMR ($[^2H_6]C_6H_6$), 250 MHz) δ (ppm) 2.11 [3H, s, CH_3], 2.66 [6H, s, $(CH_3)_2$], 6.71 [2H, s, C_6H_2–], 6.39, 6.72, 8.45 [5H, m, NC_5H_5]. ^{13}C-{^1H} NMR ($[^2H_6]C_6H_6$), 62.9 MHz) δ (ppm) 21.1 [CH_3], 27.4 [$(CH_3)_2$], 128.0 [meta-C], 131.5 [ortho-C], 142.8 [ipso-C], 133.2 [para-C], 124.5, 138.0, 149.3 [NC_5H_5]. IR (major bands and tentative assignments) 557 cm^{-1} (υ(Zn–S), 866 cm^{-1} (υ(C–S).

Compound (**4**): m.p. 245°C (decomp.), 67% (Found: C, 47.98; H, 4.64; N, 4.15. Calculated: C, 49.08; H, 4.71; N, 4.09;). NMR data: ^1H NMR ($[^2H_6]C_6H_6$), 250 MHz) δ (ppm) 2.10 [3H, s, CH_3], 2.66 [6H, s, $(CH_3)_2$], 6.71 [2H, s, C_6H_2–], 6.37, 6.68, 8.45 [5H, m, NC_5H_5]. ^{13}C-{^1H} NMR ($[^2H_6]C_6H_6$), 62.9 MHz) δ (ppm) 20.89 [CH_3], 27.20 [$(CH_3)_2$], 122.0 [meta-C], 134.1 [ortho-C], 142.3 [ipso-C], 133.0 [para-C],, 123.9, 139.2, 149.6 [NC_5H_5]. IR (major bands and tentative assignments) 476 cm^{-1} (υ(Zn–Se), 798 cm^{-1} (υ(C–Se).



Scheme 1.

Compound (**5**) : (Found: C, 28.72; H, 4.0; N, 6.75. Calculated: C, 28.65; H, 3.98; N, 6.68). ^1H NMR ($[^2H_6]C_6H_6$), 250 MHz) δ (ppm) 1.23 [6H, t, CH_3], 3.95 [4H, q, CH_2], 7.43, 7.78, 8.88 [5H, m, NC_5H_5]. ^{13}C-{^1H} NMR ($[^2H_6]C_6H_6$), 62.9 MHz) δ (ppm) 11.7 [CH_3], 52.6 [CH_2], 124.6, 138.3, 149.1 [NC_5H_5], 189.9 [CSe_2]. IR (major bands and tentative assignments) 447 cm^{-1} (υ(Zn–Se), 837 cm^{-1} (υ(C–Se), 1508 cm^{-1} (υ(C=N).

Compound (**6**): (Found: C, 41.23; H, 5.73; N, 9.71. Calculated: C, 40.87; H, 5.68; N, 9.54;). ^1H NMR ($[^2H_6]C_6H_6$), 250 MHz) δ (ppm) 1.29 [6H, t, CH_3], 3.87 [4H, q, CH_2], 7.45, 7.84, 8.98 [5H, m, NC_5H_5]. ^{13}C-{^1H} NMR ($[^2H_6]C_6H_6$), 62.9 MHz) δ (ppm) 12.1 [CH_3], 49.1 [CH_2], 124.4, 137.8, 149.5 [NC_5H_5], 203.3 [CS_2]. IR (major bands and tentative assignments) 463 cm^{-1} (υ(Zn–S), 973 cm^{-1} (υ(C–S), 1510 cm^{-1} (υ(C=N).

3. Results and discussion

3.1. Structure of $[Zn(SeC_6H_2Me_3\text{-}2,4,6)_2(C_5H_5N)_2]$ (**4**)

The structure of the pyridine adduct (**4**) was determined

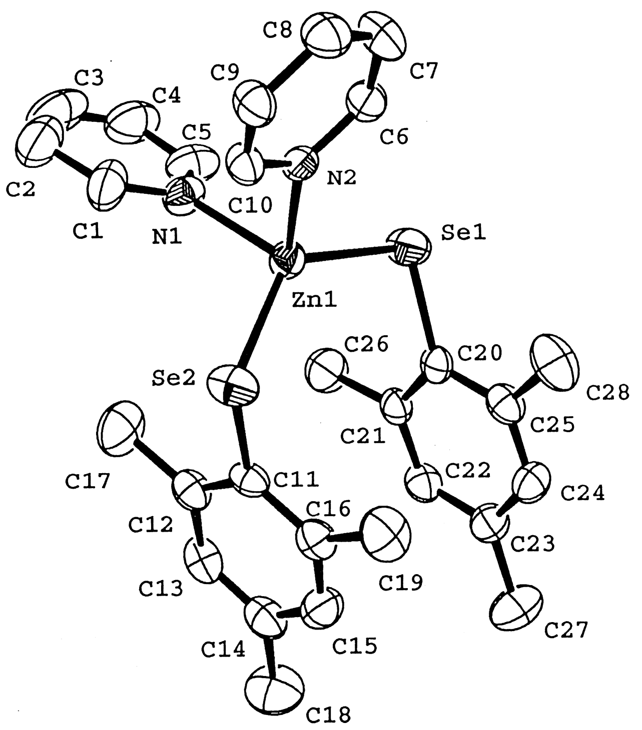


Fig. 1. The molecular structure of $[\mathrm{Zn(SeC_6H_2Me_3\text{-}2,4,6)_2(C_6H_5N)_2}]$.

by single crystal X-ray diffraction methods. The molecular structure is shown in Fig. 1 and selected bond distances and angles are given in Table 2. The structure is based on monomeric units where the zinc atom is four co-ordinated through two nitrogen atoms of pyridine and two selenium atoms of the mesitylselenolato group. The co-ordination can be defined as distorted tetrahedral. Zn–N bond distances in adducts such as $\mathrm{Me_2Zn[(CH_2NMe)_3]_2}$ [15,16] (2.410(4) Å), $\mathrm{Me_2Zn[(Me_2N(CH_2)_2NMe_2]_2}$ [17] (2.260(8) Å), $\mathrm{[Me_2N(CH_2)_3]Zn}$ [18] (2.307(4) Å), $\mathrm{(Me_3CCH_2)_2Zn[Me_2N(CH_2)_2NMe_2]_2}$ [17] (2.411(4) Å), $\mathrm{[(Et_2NCO_2)_2Zn(Me_2NCH_2)_2]}$ [19] (2.208(9), 2.179(6) Å), are much larger than those observed in this structure (2.112(4), 2.125(3) Å). The bond distances in other adducts e.g. $\mathrm{C_5H_5N.Zn[S_2CNMe_2]_2}$ [20] (2.079 (9) Å), $\mathrm{[(CNS)ZnS_2CNMe_2)_2]^-}$ [21] (1.954(9) Å), $\mathrm{[(Et_2NCO_2)_3MeZn_2\ NC_5H_5)_2]}$ [19] (2.057(6) Å), $\mathrm{[2,4,6\text{-}CF_3(C_6H_2)Se]ZnHN(SiMe_3)_2}$ [22] (2.070(4) Å), $\mathrm{[Zn_2(C_{10}N_2H_8)\{(i\text{-}C_4H_9)_2NCS_2\}_4]}$ [23] (2.076(5) Å), and $\mathrm{[(Me^iPrNCS^2)_2ZnNC_5H_5]}$ [24] (2.067(2) Å) are slightly shorter but are comparable in $\mathrm{[(Me^iPrNCS^2)_2ZnMe_2N(CH_2)_2NMe_2]}$ [24] (2.137(5) Å).

The Zn–Se distance (2.377(9), 2.378(8) Å) is shorter than those reported for selenocarbamates such as $\mathrm{MeZnSe_2CNEt_2}$ [14], (2.581(4), 2.467(3), 2.634(3) Å), $\mathrm{EtZnSe_2CNEt_2}$ [14], (2.590(9), 2.484(8), 2.617(3) Å), $\mathrm{MeZnCdSe_2CNEt_2}$ [14], (2.682(4), 2.575(4), 2.742(4) Å), and $\mathrm{Zn(Se_2CNEt_2)_2}$ [25], (2.57, 2.45, 2.44, 2.49 Å), slightly longer than that of $\mathrm{Zn(SeBu_3C_6H_2\text{-}2,4,6)_2.(OSC_4H_8)}$ [25] (2.313(3) Å) and is close to that in $\mathrm{[2,4,6\text{-}CF_3(C_6H_2)Se]ZnHN(SiMe_3)_2}$ [22] (2.350(8), 2.368(8)Å). Se–Zn–Se angle (130.16(3)°) is very close to that reported for $\mathrm{Zn(SeBu_3C_6H_2\text{-}2,4,6)_2.(OSC_4H_8)}$ [26].

Table 2
Selected bond lengths [Å] and angles [°]

Compound (**4**)	
Zn(1)–N(1)	2.112(4)
Zn(1)–N(2)	2.125(3)
Zn(1)–Se(2)	2.3768(9)
Zn(1)–Se(1)	2.3775(8)
Se(1)–C(20)	1.926(4)
Se(2)–C(11)	1.925(4)
N(1)–Zn(1)–N(2)	93.94(14)
N(1)–Zn(1)–Se(2)	110.61(12)
N(2)–Zn(1)–Se(2)	100.92(10)
N(1)–Zn(1)–Se(1)	106.82(13)
N(2)–Zn(1)–Se(1)	108.18(10)
Se(2)–Zn(1)–Se(1)	130.16(3)
Compound (**5**)	
Zn(1)–N(1)	2.054(10)
Zn(1)–Se(2)	2.430(2)
Zn(1)–Se(3)	2.4329(19)
Zn(1)–Se(1)	2.737(2)
Zn(1)–Se(4)	2.749(2)
N(1)–Zn(1)–Se(2)	112.2(3)
N(1)–Zn(1)–Se(3)	109.8(3)
Se(2)–Zn(1)–Se(3)	137.89(8)
N(1)–Zn(1)–Se(1)	96.4(3)
Se(2)–Zn(1)–Se(1)	75.84(6)
Se(3)–Zn(1)–Se(1)	102.44(7)
N(1)–Zn(1)–Se(4)	94.0(3)
Se(2)–Zn(1)–Se(4)	98.14(7)
Se(3)–Zn(1)–Se(4)	75.95(6)
Se(1)–Zn(1)–Se(4)	169.34(7)
Compound (**6**)	
Zn(1)–N(1)	2.072(4)
Zn(1)–S(3)	2.3561(17)
Zn(1)–S(1)	2.3691(17)
Zn(1)–S(2)	2.5292(17)
Zn(1)–S(4)	2.5566(18)
N(1)–Zn(1)–S(3)	109.32(14)
N(1)–Zn(1)–S(1)	110.38(14)
S(3)–Zn(1)–S(1)	140.28(7)
N(1)–Zn(1)–S(2)	96.53(14)
S(3)–Zn(1)–S(2)	102.90(6)
S(1)–Zn(1)–S(2)	73.72(6)
N(1)–Zn(1)–S(4)	95.63(14)
S(3)–Zn(1)–S(4)	73.37(6)
S(1)–Zn(1)–S(4)	101.51(6)
S(2)–Zn(1)–S(4)	167.84(6)

3.2. Structures of $(\mathrm{Et_2CNSe_2})_2\mathrm{Zn.NC_5H_5}$ (5) and $(\mathrm{Et_2CNS_2})_2\mathrm{Zn.NC_5H_5}$ (6)

Compounds (**5**) and (**6**) are isostructural and the structure of both compounds (**5**) and (**6**) is based on monomeric molecular units $[\mathrm{Zn(E_2CNEt_2)_2.Py}]$ (E=S, Se) in which each zinc atom is five co-ordinate through two diseleno- or dithio-carbamato which chelate through sulphur (**6**) or selenium (**5**) atoms and an additive bond from nitrogen atom of pyridine. The co-ordination is close to trigonal bipyramidal. There are two unsymmetrical molecular units in a unit cell in each of these structures. The structure of compound (**6**) is shown in Fig. 2 and the selected bond distances and angles are given in Table 2.

The Zn–N bond distance (2.054(1) Å (**5**), 2.072(4) Å (**6**) in both structures is very similar and is close to those in $C_5H_5N.Zn[S_2CNMe_2]_2$ [20] (2.079 (9) Å), $[(Et_2NCO_2)_3MeZn_2\ NC_5H_5)_2]$ [19] (2.057(6) Å), $[2,4,6\text{-}CF_3(C_6H_2)Se]ZnHN(SiMe_3)_2$ [22] (2.070(4) Å), $[Zn_2(C_{10}N_2H_8)\{(i\text{-}C_4H_9)_2NCS_2\}_4]$ [23] (2.076(5) Å), and $[(Me^iPrNCS^2)_2ZnNC_5H_5]$ [24] (2.067(2) Å). These distances are much shorter than other adducts [15–18] formed through nitrogen co-ordination. The Zn–Se bond distances in compound (**5**), as usual, encompass short and long bonds (2.430(2), 2.433(1), 2.737(2), 2.749(2) Å). The shorter Zn–Se distances are close to those reported for bis(di-ethyl-di-selenocarbamato)zinc [28] (2.45, 2.44Å) but the longer distances (2.49, 2.57 Å) are considerably longer in compound (**5**). These bond lengths are also longer than those observed in $MeZnSe_2CNEt_2$ [14], (2.581(4), 2.467(3), 2.634(3) Å), $EtZnSe_2CNEt_2$ [14], (2.590(9), 2.484(8), 2.617(3) Å), $MeZnCdSe_2CNEt_2$ [14], (2.682(4), 2.575(4), 2.742(4) Å), $[2,4,6\text{-}CF_3(C_6H_2)Se]\text{-}ZnHN(SiMe_3)_2$ [22] (2.350(8), 2.368(8)Å) and $Zn(SeBu_3\text{-}C_6H_2\text{-}2,4,6)_2.(OSC_4H_8)$ [26] (2.313(3) Å). But the Zn–S bond distances in compound (**6**) (2.356(1), 2.369(1), 2.529(1), 2.556(1) Å) show a small variation as compared to those in $EtZnS_2CNEt_2$ [27] (2.481(7), 2.375(9), 2.509(9) Å) and $MeZnS_2CNEt_2$ [13] (2.512(4), 2.501(4), 2.370(3) Å).

3.3. Spectroscopic studies

The ^1H NMR spectra of compounds (**1**) and (**2**) gave four signals at high field, two for the methyl (triplet) and methylene (quartet) protons of the ethyl groups and two for the ethyl protons (singlets with different intensity) of the aryl group and only one signal (a singlet) at lower field corresponding to equivalent aryl protons. The ^{13}C NMR appear as nine line spectra as expected (see Section 2). The ^1H NMR and ^{13}C NMR spectra of pyridine adducts ((**3**) and (**4**)) and **(5)** and **(6)** give spectra as expected. Infra red spectra showed clear bands for C–E and Zn–E (E=S, Se) in all compounds. Compounds (**1**) and (**2**) were further characterised by mass spectrometry. Section 2 shows the assignment of all major peaks to different fragments. Both compounds show a similar trend in their fragmentation behaviour.

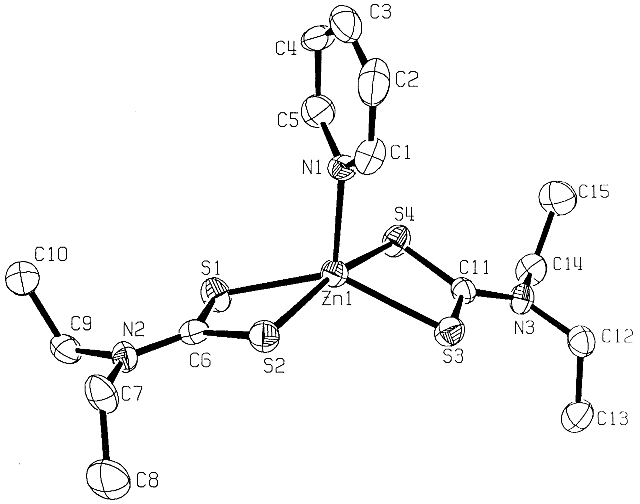


Fig. 2. The molecular structure of $[(Et_2CNS_2)_2Zn.NC_5H_5]$.

Supplementary material

Complete bond lengths and angles, coordinates and displacement parameters have been deposited at the Cambridge Crystallographic Data Centre. Supplementary data are available from the CCDC, 12 Union Road, Cambridge CB2 1EZ, UK on request, quoting the deposition numbers for compound (**4**)–103201; compound (**5**)–103199; and compound (**6**)–103200.

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