Bis(μ-diethyldithiocarbamato)-1κS,1:2κ²S';2κS,1:2κ²S'-bis(ethylzinc)

M. Azad Malik,[a] Paul O'Brien[a] and Majid Motevalli[b]

[a]*Department of Chemistry, Imperial College, London SW7 2AY, England, and* [b]*Department of Chemistry, Queen Mary and Westfield College, Mile End Road, London E1 4NS, England. E-mail: p.obrien@ic.ac.uk*

Abstract

The structure of the title compound consists of $[Zn(C_2H_5)(C_5H_{10}NS_2)]_2$ units in which each dithiocarbamate group chelates one Zn atom and bridges to the other.

Comment

Interest in single-molecule precursors for the deposition of compound semiconductors by metallo-organic chemical vapour deposition (MOCVD) has grown substantially in recent years. Suitable molecules for the deposition of III/V materials, such as InP and GaAs, have been developed by Andrews *et al.* (1988), Cowley *et al.* (1988) and Cowley & Jones (1989).

A number of reports have also appeared concerning single-molecule precursors for the deposition of II/VI materials and systems studied include thiophosphinates (Takahashi, Yuki, Motojima & Sugiyama, 1980; Evans & Williams, 1982), thiocarbamates (Saunders, Vecht & Tyrell, 1986), selenocarbamates (Hursthouse, Malik, Motevalli & O'Brien, 1992*a*), thiolates (Osaka & Yamamoto, 1991; Bochmann, Webb, Harman & Hursthouse, 1990; Bochmann, Webb, Hursthouse & Mazid, 1991), 2,4,6-tri('butyl)phenylchalcogenides (Bochmann, Webb, Harman & Hursthouse, 1990; Bochmann, Webb, Hursthouse & Mazid, 1991), silicon-based systems (*e.g.* $[M\{ESi(SiCH_3)_3\}_2]$, M = Zn, Cd, Hg and E = Se or Te) (Dabbousi, Bonasia & Arnold, 1991) and alkylmetal–thio- or selenocarbamates (Hursthouse, Malik, Motevalli & O'Brien, 1991; Hursthouse, Malik, Motevalli & O'Brien, 1992*a,b*; Malik, Motevalli, Walsh & O'Brien, 1992). Alkylmetal–thio- or selenocarbamates have been found to exist as dimers with the empirical formula $[RME_2CNR'_2]_2$, and a wide range of derivatives of dimethylzinc, diethylzinc or dimethylcadmium have been prepared (*e.g.* R = Me, R' = Me, Et, M = Cd, Zn, $Cd_{0.5}/Zn_{0.5}$, E = S, or R = Me, Et, E = Se, or R = neo, 'Bu, E = S, Se). X-ray crystal structures of $[MeZnS_2CNEt_2]_2$ (Hursthouse, Malik, Motevalli & O'Brien, 1991), $[MeZnSe_2CNEt_2]_2$, $[EtZnSe_2CNEt_2]_2$, $[MeCd_{0.5}/Zn_{0.5}Se_2CNEt_2]_2$ (Hursthouse, Malik, Mote-

valli & O'Brien, 1992*b*) and $[Me_3CCH_2ZnSe_2CNEt_2]_2$ have established a common dimeric structure in which each carbamate group chelates one metal atom and bridges to the other. In this paper, we report the structure of the title compound, (I), another member of this series of compounds.
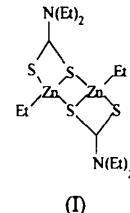
(I)

The structure consists of discrete centrosymmetric dimeric $[EtZnS_2CNEt_2]_2$ molecules in which each dithiocarbamate group chelates one Zn atom and bridges to the other. The Zn atoms are four coordinate and the coordination geometry can be described as distorted tetrahedral. The structure is similar to those recently reported for a neopentylzincdiselenocarbamate dimer (Malik, Motevalli, Walsh & O'Brien, 1992), a methylzincdithiocarbamate dimer (Hursthouse, Malik, Motevalli & O'Brien, 1991) and methyl- or ethylzincdiselenocarbamate dimers (Hursthouse, Malik, Motevalli & O'Brien, 1992*a*). The structure also resembles the dimeric units found in bis(thiocarbamates) and bis(selenocarbamates) (Bonamico, Mazzone, Vaciago & Zambonelli, 1965; Bonamico & Dessy, 1971; Domenico, Torelli, Vaciago & Zambonelli, 1968; Hursthouse, Malik, Motevalli & O'Brien, 1992*b*) but with the alkyl group replacing the chelating-only carbamate group. The bond distances and angles are similar to those in other alkylzincdithiocarbamates. Zn—S distances [2.481 (7), 2.375 (9) and 2.509 (9) Å] are slightly smaller than those observed in ethylzincdiselenocarbamate (Hursthouse, Malik, Motevalli & O'Brien, 1992*a*) [Zn—Se 2.590 (9), 2.484 (8) and 2.617 (7) Å]. Similarly Zn—C [1.956 (3) Å], S—C [1.750 (2), 1.708 (2) Å] and C—N [1.320 (3) Å] distances are all smaller than the corresponding selenocarbamate Zn—C [1.974 (47) Å], Se—C [1.901 (32), 1.795 (32) Å] and C—N distances [1.401 (44) Å] (Hursthouse, Malik, Motevalli & O'Brien, 1992*a*), which is as expected on the basis of the accepted difference in radii between S (r_{ion} = 1.70, r_{cov} = 1.02 Å) and Se atoms (r_{ion} = 1.84, r_{cov} = 1.17 Å). Some problems were encountered in the crystallographic study of ethylzincdiethylselenocarbamate (Hursthouse, Malik, Motevalli & O'Brien, 1992*a*): the ethyl groups bonded to the Zn atom were disordered, which adversely affected the refinement of the structure, and during the course of the data collection the $h0l$, $h + l = 2n + 1$ reflections, which should be absent for $P2_1/n$, began to take on significant values. However, none of these problems were encountered with the present compound.
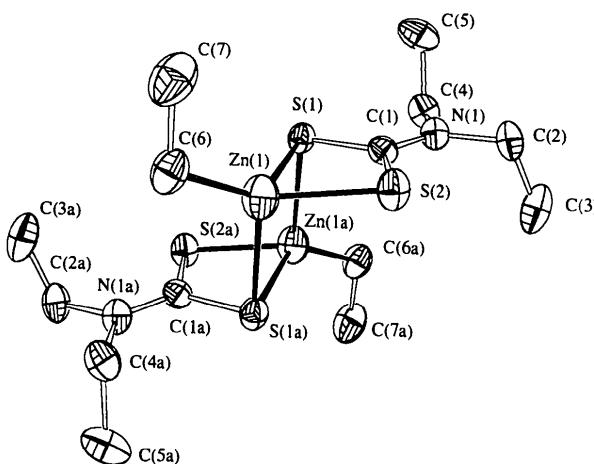
Fig. 1. The structure of the title compound showing the labelling of the atoms and displacement ellipsoids at the 50% probability level for non-H atoms (*ORTEX*; McArdle, 1994). H atoms have been omitted for clarity.

Experimental

The title compound was prepared by the method of Hursthouse, Malik, Motevalli & O'Brien (1991). Recrystallization from hot toluene gave transparent cubic crystals.

Crystal data
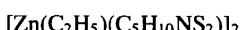
[Zn(C₂H₅)(C₅H₁₀NS₂)]₂
$M_r = 485.38$
Monoclinic
$P2_1/a$
$a = 14.605 (3)$ Å
$b = 9.877 (2)$ Å
$c = 7.5690 (10)$ Å
$\beta = 92.44 (2)°$
$V = 1090.9 (3)$ Å^3
$Z = 2$
$D_x = 1.478$ Mg m^{-3}

Mo $K\alpha$ radiation
$\lambda = 0.71069$ Å
Cell parameters from 25 reflections
$\theta = 12$–$14°$
$\mu = 2.579$ mm^{-1}
$T = 293 (2)$ K
Transparent rhombic
$0.38 \times 0.35 \times 0.25$ mm
Colourless

Data collection

Enraf–Nonius CAD-4 four-circle diffractometer
$2\theta/\omega$ scans
Absorption correction:
  ψ scan (North, Phillips & Mathews, 1968)
  $T_{min} = 0.970$, $T_{max} = 0.985$
2577 measured reflections
2382 independent reflections

1820 observed reflections
  $[I > 2\sigma(I)]$
$R_{int} = 0.0082$
$\theta_{max} = 26.98°$
$h = -1 \rightarrow 18$
$k = 0 \rightarrow 12$
$l = -9 \rightarrow 9$
3 standard reflections
  frequency: 60 min
  intensity decay: none

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.0337$
$wR(F^2) = 0.0886$
$S = 1.138$
2382 reflections
109 parameters
H atoms riding
$w = 1/[\sigma^2(F_o^2) + (0.0619P)^2]$
  where $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{max} = 0.004$
$\Delta\rho_{max} = 0.483$ e Å^{-3}
$\Delta\rho_{min} = -0.713$ e Å^{-3}
Extinction correction: none
Atomic scattering factors from *International Tables for Crystallography* (1992, Vol. C, Tables 4.2.6.8 and 6.1.1.4)

Table 1. *Fractional atomic coordinates and equivalent isotropic displacement parameters (Å²)*

$$U_{eq} = (1/3)\Sigma_i\Sigma_j U_{ij}a_i^* a_j^* \mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	U_{eq}
Zn1	0.49906 (2)	0.09123 (3)	0.19295 (4)	0.05421 (13)
S1	0.52303 (4)	0.15450 (7)	-0.11884 (7)	0.0468 (2)
S2	0.66049 (4)	0.10491 (8)	0.17073 (8)	0.0547 (2)
C1	0.6382 (2)	0.1410 (2)	-0.0475 (3)	0.0415 (5)
N1	0.70403 (13)	0.1583 (2)	-0.1596 (3)	0.0462 (4)
C2	0.8015 (2)	0.1564 (3)	-0.1004 (4)	0.0595 (7)
C3	0.8427 (2)	0.0182 (4)	-0.1079 (5)	0.0824 (10)
C4	0.6857 (2)	0.1822 (3)	-0.3506 (3)	0.0550 (6)
C5	0.6834 (3)	0.3281 (4)	-0.3963 (4)	0.0791 (10)
C6	0.4153 (2)	0.1719 (3)	0.3582 (4)	0.0635 (7)
C7	0.4295 (2)	0.3206 (4)	0.3892 (5)	0.0845 (10)

Table 2. *Selected geometric parameters (Å, °)*

Zn1—C6	1.956 (3)	S1—C1	1.750 (2)
Zn1—S2	2.3746 (9)	S1—Zn1^i	2.5088 (9)
Zn1—S1	2.4805 (7)	S2—C1	1.708 (2)
Zn1—S1^i	2.5088 (9)	C1—N1	1.320 (3)
C6—Zn1—S2	132.21 (9)	C1—S1—Zn1^i	96.22 (8)
C6—Zn1—S1	128.56 (10)	Zn1—S1—Zn1^i	86.96 (2)
S2—Zn1—S1	74.78 (3)	C1—S2—Zn1	86.09 (8)
C6—Zn1—S1^i	117.33 (10)	N1—C1—S2	122.3 (2)
S2—Zn1—S1^i	99.08 (2)	N1—C1—S1	120.6 (2)
S1—Zn1—S1^i	93.04 (2)	S2—C1—S1	117.07 (13)
C1—S1—Zn1	81.97 (8)		

Symmetry code: (i) $1 - x, -y, -z$.

All non-H atoms were refined with anisotropic displacement factors; H atoms were identified in difference maps and included at geometrically idealized positions.

Data collection: *CAD-4/PC* (Enraf–Nonius, 1993). Cell refinement: *CAD-4/PC*. Data reduction: *CAD-4/PC*. Program(s) used to solve structure: *SHELXS86* (Sheldrick, 1990). Program(s) used to refine structure: *SHELXL93* (Sheldrick, 1993). Molecular graphics: *ORTEX* (McArdle, 1994). Software used to prepare material for publication: *SHELXL93*.

References

Andrews, D. A., Davies, G. J., Bradley, D. C., Faktor, M. M., Frigo, D. M. & White, E. A. D. (1988). *Semicond. Sci. Technol*, **3**, 1053–1056.

Bochmann, M., Webb, K., Harman, M. & Hursthouse, M. B. (1990). *Angew. Chem. Int. Ed. Engl.* **29**, 638–639.

Bochmann, M., Webb, K. J., Hursthouse, M. B. & Mazid, M. (1991). *J. Chem. Soc. Dalton Trans.* pp. 2317–2323.

Bonamico, M. & Dessy, G. (1971). *J. Chem. Soc. A*, pp. 264–269.

Bonamico, M., Mazzone, G., Vaciago, A. & Zambonelli, L. (1965). *Acta Cryst.* **19**, 898–909.

Cowley, A. H., Benac, B. L., Ekerdt, J. G., Jones, R. A., Kidd, K. B., Lee, J. Y. & Miller, J. E. (1988). *J. Am. Chem. Soc.* **110**, 6248–6249.

Cowley, A. H. & Jones, R. A. (1989). *Angew. Chem. Int. Ed. Engl.* **28**, 1208–1218.

Dabbousi, B. O., Bonasia, P. J. & Arnold, J. (1991). *J. Am. Chem. Soc.* **113**, 3186–3188.

Domenico, A., Torelli, L., Vaciago, A. & Zambonelli, L. (1968). *J. Chem. Soc. A*, 1351–1361.

Enraf–Nonius (1993). *CAD-4/PC Software*. Version 1.2. Enraf–Nonius, Delft, The Netherlands.

Evans, M. A. H. & Williams, J. O. (1982). *Thin Solid Films*, **87**, L1–L2.

Hursthouse, M. B., Malik, M. A., Motevalli, M. & O'Brien, P. (1991). *Organometallics*, **10**, 730–732.

Hursthouse, M. B., Malik, M. A., Motevalli, M. & O'Brien, P. (1992*a*). *Polyhedron*, **11**, 45–48.

Hursthouse, M. B., Malik, M. A., Motevalli, M. & O'Brien, P. (1992*b*). *J. Mater. Chem.* **2**, 949–955.

McArdle, P. (1994). *J. Appl. Cryst.* **27**, 438–439.

Malik, M. A., Motevalli, M., Walsh, J. R. & O'Brien, P. (1992). *Organometallics*, **11**, 3136–3139.

North, A. C. T., Phillips, D. C. & Mathews, F. S. (1968). *Acta Cryst.* A**24**, 351–359.

Osaka, K. & Yamamoto, T. (1991). *Inorg. Chem.* **30**, 2328–2332.

Saunders, A., Vecht, A. & Tyrell, G. (1986). *Ternary Multiary Cmpd. Proc. 7th Int. Conf.* (publ. 1987); *Chem. Abs.* (1988), **108**, 66226h.

Sheldrick, G. M. (1990). *Acta Cryst.* A**46**, 467–473.

Sheldrick, G. M. (1993). *SHELXL93. Program for the Refinement of Crystal Structures*. University of Göttingen, Germany.

Spek, A. L. (1993). *PLUTON93. Molecular Graphics Program*. University of Utrecht, The Netherlands.

Takahashi, Y., Yuki, R., Motojima, M. & Sugiyama, K. (1980). *J. Cryst. Growth*, **50**, 491–497.

Acta Cryst. (1996). C**52**, 1933–1935

(Thiocyanato-*N*)tris(triphenylphosphine)-silver(I) Chloroform Solvate

Abdul Hamid Othman,[a] Hoong-Kun Fun,[b] Kandasamy Sivakumar,[b] Yang Farina[a] and Ibrahim Baba[a]

[a]*Department of Chemistry, Universiti Kebangsaan Malaysia, 43600 Bangi, Selangor, Malaysia, and* [b]*X-ray Crystallography Unit, School of Physics, Universiti Sains Malaysia, 11800 Penang, Malaysia. E-mail: hamie@pkrisc.cc.ukm.my*

Abstract

Crystals of [Ag(NCS)(C$_{18}$H$_{15}$P)$_3$].CHCl$_3$ consist of discrete [Ag(PPh$_3$)$_3$(NCS)] molecules, in which the Ag atom is tetrahedrally surrounded by three P atoms of the PPh$_3$ groups and the N atom of the isothiocyanate ligand, and chloroform molecules. The coordination polyhedron around the Ag atom is distorted with angles at Ag ranging from 102.58(10) to 114.73(3)°. The Ag—N—C angle is 159.6(3)°.

Comment

During our study of the reactions of the dimer bis-[acetato(triphenylphosphine)silver(I)], we have reacted the dimer with *N*-pyrrolidine carbodithioate (Othman,

Fun & Sivakumar, 1996), bis(2-hydroxyethyl)dithiocarbamate (Drew, Othman, Baba, Farina & Ng, 1996), 8-hydroxyquinoline (Othman, Goh, Fun & Sivakumar, 1996) and 2-hydroxy-3,5-dinitrobenzoate ligands, all of which are potentially bidentate (Othman, Effendy & White, 1996). Crystallographic studies of the products of these reactions showed that the Ag atoms are in tetrahedral environments except in the dimeric benzoate complex, in which the Ag atom is in a trigonal environment, essentially retaining the structure of the parent acetate. The title compound, (1), is the product of an attempt to prepare a complex between the dimer and thiosemicarbazide.

(1)
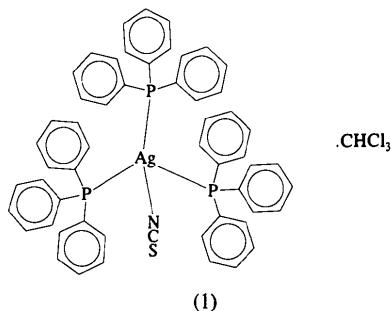
The geometry about the Ag atom in (1) is tetrahedral, with three P atoms of the triphenylphosphine ligands and the N atom of the isothiocyanate ligand bonded to the Ag atom. The angles about the Ag atom deviate significantly from the ideal 109.5°, but to a lesser extent than those in [Ag(PPh$_3$)$_3$Cl] (Cassel, 1981). The difference can be attributed to the different electronegativities of the N and Cl donor atoms of the anionic ligands, rather than to the Ag—N distance [2.319(4) Å] being shorter than the Ag—Cl distance of 2.552(1) Å. The π-acceptor nature of the NCS ligand enhances the bonding of the PPh$_3$ ligands to the Ag atom.
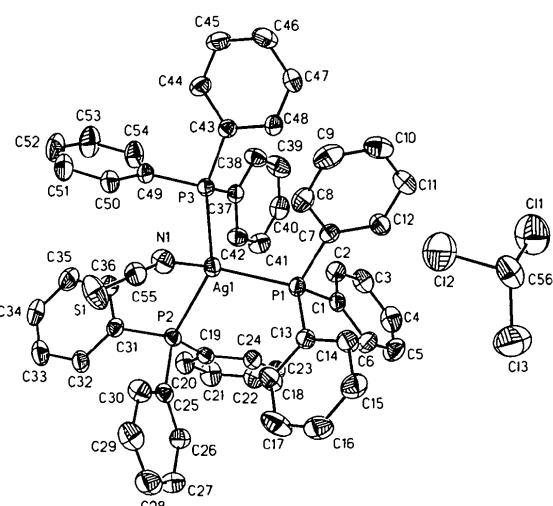

Fig. 1. A 30% displacement ellipsoid plot of (1) with the atomic numbering scheme.