

wR = 0.041
S = 1.42
2328 reflections
118 parameters
All H atoms were refined isotropically

$\Delta\rho_{\max} = 2.00 \text{ e } \text{\AA}^{-3}$
 $\Delta\rho_{\min} = -0.65 \text{ e } \text{\AA}^{-3}$
Atomic scattering factors from *International Tables for X-ray Crystallography* (1974, Vol. IV)

Table 1. Fractional atomic coordinates and equivalent isotropic displacement parameters (\AA^2)

$$U_{\text{eq}} = (1/3) \sum_i \sum_j U_{ij} a_i^* a_j^* a_i \cdot a_j$$

	Occupancy	x	y	z	U_{eq}
Cd1	1/2	1/2	0.13139 (2)	1/4	0.0281 (1)
Ni1	1/2	0	0	0	0.0309 (3)
N1	1	0.2739 (5)	0.1167 (2)	0.1018 (3)	0.046 (1)
N2	1	0.3055 (4)	0.0499 (2)	0.3444 (3)	0.043 (1)
C1	1	0.1704 (4)	0.0738 (2)	0.0606 (3)	0.035 (1)
C2	1	0.1904 (4)	0.0292 (2)	0.4031 (3)	0.034 (1)
N11	1	0.3341 (4)	0.2421 (2)	0.3075 (2)	0.035 (1)
C11	1	0.4069 (5)	0.3114 (2)	0.2807 (3)	0.035 (1)
C12	1	0.3125 (7)	0.3790 (2)	0.3096 (4)	0.052 (3)
C13	1	0.1407 (7)	0.3750 (3)	0.3673 (4)	0.060 (3)
C14	1	0.0679 (6)	0.3043 (3)	0.3939 (4)	0.052 (3)
C15	1	0.1663 (5)	0.2389 (2)	0.3626 (3)	0.046 (1)

Table 2. Selected geometric parameters (\AA , $^\circ$)

Cd1—N1	2.392 (3)	Ni1—C2 ⁱ	1.856 (3)
Cd1—N2	2.273 (3)	N1—C1	1.135 (4)
Cd1—N11	2.336 (3)	N2—C2	1.139 (4)
Ni1—C1	1.869 (3)		
N1—Cd1—N1 ⁱⁱ	167.8 (2)	C1—Ni1—C1 ⁱⁱⁱ	180
N1—Cd1—N2	87.9 (1)	C1—Ni1—C2 ⁱ	89.2 (1)
N1—Cd1—N2 ⁱⁱ	84.6 (1)	C1—Ni1—C2 ^{iv}	90.8 (1)
N1—Cd1—N11	91.0 (1)	C2 ⁱ —Ni1—C2 ^{iv}	180
N1—Cd1—N11 ⁱⁱ	99.0 (1)	Cd1—N1—C1	143.1 (3)
N2—Cd1—N2 ⁱⁱ	103.6 (2)	Cd1—N2—C2	160.0 (3)
N2—Cd1—N11	93.3 (1)	Ni1—C1—N1	176.8 (3)
N2—Cd1—N11 ⁱⁱ	162.3 (1)	Ni1—C2 ⁱ —N2 ⁱ	177.5 (3)
N11—Cd1—N11 ⁱⁱ	70.4 (1)		

Symmetry codes: (i) $-x, y, \frac{1}{2} - z$; (ii) $1 - x, y, \frac{1}{2} - z$; (iii) $-x, -y, -z$; (iv) $x, -y, z - \frac{1}{2}$.

All non-H atoms were refined anisotropically. All H atoms were located from the difference Fourier map and refined isotropically without a special damping factor for each parameter. In the weighting scheme, $\sigma^2(F_o^2) = [S^2(C+R^2B) + (pF_o^2)^2]/Lp^2$, where S = scan rate, C = total integrated peak count, R = ratio of scan time to background counting time, B = total background count, Lp = Lorentz-polarization factor, p = p factor. Data collection: *MSC/AFC Diffractometer Control Software* (Molecular Structure Corporation, 1988). Cell refinement: *MSC/AFC Diffractometer Control Software*. Data reduction: *TEXSAN* (Molecular Structure Corporation, 1985). Program(s) used to solve structure: *TEXSAN*. Molecular graphics: *ORTEPII* (Johnson, 1976).

Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 71738 (28 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England. [CIF reference: AS1078]

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(Hexasulfanediy)di(pyridine-N)zinc

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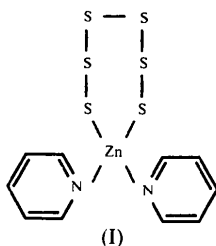
(Received 20 May 1993; accepted 7 October 1993)

Abstract

The title compound {[hexasulfido(2-)-S¹, S⁶]di(pyridine-N)zinc, [Zn(S₆)(C₅H₅N)₂]} contains a distorted tetrahedrally coordinated core of ZnS₂N₂, in which the bond lengths Zn—S and Zn—N are 2.286 (1) and 2.064 (3) Å, respectively.

Comment

In recent years, zinc compounds containing sulfur and nitrogen ligands have attracted much attention because of their bioinorganic relevance. For example, it has been suggested recently (Corwin & Koch, 1988) that [Zn(cysteine-S)₂(histidine)₂] is the active centre of the transcription factor IIIA. Several polysulfido metal complexes containing S₂²⁻, S₄²⁻, S₅²⁻ and S₇²⁻ ligands have been synthesized (Wu, Lu, Zhu, Wu & Lu, 1987; Du, Zhu, Wu & Lu, 1992) but compounds with an S₆²⁻ ligand are rare. The title compound (I) is similar to [ZnS₆(N-methylimidazole)₂] reported by Dev, Ramli, Rauchfuss & Stern (1990).



The crystal structure of the title compound consists of four neutral molecules per unit cell in the $C2/c$ space group. The central Zn atom has distorted tetrahedral coordination by two S and two N atoms, with the angles varying from $103.3(2)$ to $125.21(7)^\circ$.

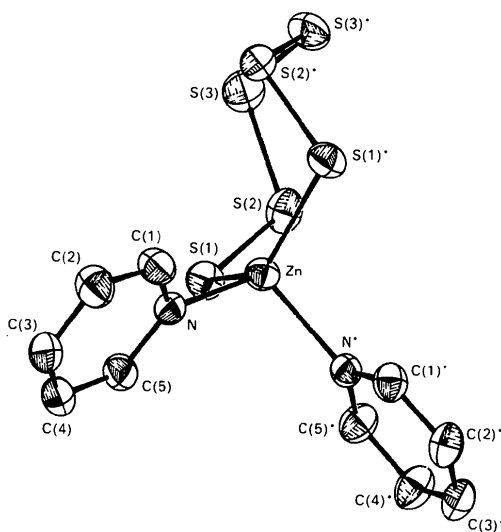


Fig. 1. An ORTEPII (Johnson, 1976) plot of $[Zn(S_6)(C_5H_5N)_2]$.

Experimental

The title compound was obtained by refluxing a mixture of zinc and sulfur powders in pyridine for 6 h.

Crystal data

$[Zn(S_6)(C_5H_5N)_2]$

$M_r = 415.94$

Monoclinic

$C2/c$

$a = 13.608(8) \text{ \AA}$

$b = 8.998(6) \text{ \AA}$

$c = 15.334(8) \text{ \AA}$

$\beta = 118.61(4)^\circ$

$V = 1648(2) \text{ \AA}^3$

$Z = 4$

Data collection

Rigaku AFC-5R diffractometer

$D_x = 1.68 \text{ Mg m}^{-3}$

Mo $K\alpha$ radiation

$\lambda = 0.71069 \text{ \AA}$

Cell parameters from 25 reflections

$\theta = 6-27.5^\circ$

$\mu = 2.243 \text{ mm}^{-1}$

$T = 296 \text{ K}$

Prism

Yellow

$R_{\text{int}} = 0.0774$

$\theta_{\text{max}} = 30.05^\circ$

ω - 2θ scans

Absorption correction:

empirical

$T_{\text{min}} = 0.72$, $T_{\text{max}} = 1.0$

2664 measured reflections

2564 independent reflections

1599 observed reflections

$[I > 3\sigma(I)]$

$h = 0 \rightarrow 21$

$k = 0 \rightarrow 14$

$l = -24 \rightarrow 24$

3 standard reflections

monitored every 150

reflections

intensity variation: none

Refinement

Refinement on F

$R = 0.050$

$wR = 0.059$

$S = 1.57$

1599 reflections

88 parameters

H-atom parameters not

refined

$w = 1/\sigma^2(F_o)$

$(\Delta/\sigma)_{\text{max}} = 0.010$

$\Delta\rho_{\text{max}} = 0.52 \text{ e \AA}^{-3}$

$\Delta\rho_{\text{min}} = -0.51 \text{ e \AA}^{-3}$

Extinction correction: none

Atomic scattering factors

from *International Tables*

for *X-ray Crystallography*

(1974, Vol. IV)

Table 1. Fractional atomic coordinates and equivalent isotropic displacement parameters (\AA^2)

$$B_{\text{eq}} = (4/3)\sum_i \sum_j \beta_{ij} a_i \cdot a_j$$

	x	y	z	B_{eq}
Zn	1	0.18998 (6)	3/4	4.08 (3)
S(1)	1.12367 (9)	0.07310 (11)	0.71182 (8)	4.97 (4)
S(2)	1.03522 (10)	-0.10828 (13)	0.63216 (7)	5.46 (4)
S(3)	1.06481 (11)	-0.27283 (13)	0.73292 (10)	6.35 (5)
N	1.0952 (3)	0.3321 (4)	0.8658 (3)	3.9 (1)
C(1)	1.0786 (5)	0.3434 (6)	0.9444 (4)	5.1 (2)
C(2)	1.1417 (5)	0.4344 (7)	1.0236 (4)	5.9 (2)
C(3)	1.2233 (4)	0.5198 (7)	1.0219 (4)	5.5 (2)
C(4)	1.2416 (5)	0.5089 (7)	0.9410 (4)	5.5 (2)
C(5)	1.1763 (4)	0.4143 (6)	0.8659 (4)	4.8 (1)

Table 2. Selected geometric parameters (\AA , $^\circ$)

Zn—S(1)	2.286 (1)	N—C(1)	1.335 (4)
Zn—N	2.064 (3)	N—C(5)	1.327 (5)
S(1)—S(2)	2.049 (2)	C(1)—C(2)	1.373 (6)
S(2)—S(3)	2.036 (2)	C(2)—C(3)	1.367 (6)
S(3)—S(3)*	2.067 (3)	C(3)—C(4)	1.376 (6)
C(4)—C(5)	1.364 (6)		
N—Zn—N*	103.3 (2)	S(2)—S(3)—S(3)*	108.04 (8)
N—Zn—S(1)	105.7 (1)	C(5)—N—C(1)	117.2 (3)
N*—Zn—S(1)*	107.51 (9)	N—C(1)—C(2)	122.6 (4)
S(1)—Zn—S(1)*	125.21 (7)	N—C(5)—C(4)	123.5 (4)
S(2)—S(1)—Zn	102.99 (7)	C(2)—C(3)—C(4)	118.0 (4)
C(1)—N—Zn	121.1 (3)	C(3)—C(2)—C(1)	119.6 (4)
C(5)—N—Zn	121.7 (2)	C(5)—C(4)—C(3)	119.1 (4)
S(3)—S(2)—S(1)	106.30 (8)		

* Symmetry-related atoms.

The structure was solved by direct methods using *MITHRIL* (Gilmore, 1983); the heavy atom Zn was located in an *E* map and the remaining non-H atoms were located using the *DIRDIF* (Beurskens, 1984) program. H atoms were placed in geometrically calculated positions with $C-H = 0.95 \text{ \AA}$, but were not included in the refinement. The structure was refined by full-matrix least-squares techniques with anisotropic displacement parameters for all atoms. Data collection: *CONTROL* (Molecular Structure Corporation, 1986) software. All calculations were performed on a VAX 785 computer using the *TEXSAN* (Molecular Structure Corporation, 1985) package.

This research was supported by grants from the State Key Laboratory of Structural Chemistry, Fujian Institute of Research on the Structure of Matter, Chinese Academy of Science, People's Republic of China.

Lists of structure factors, anisotropic displacement parameters and H-atom coordinates have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 71747 (18 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England. [CIF reference: AL1062]

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Acta Cryst. (1994). **C50**, 500-502

μ -(*O,O'*-Diethyl dithiophosphato-2 κ S:3 κ S')-oxo-1 κ O-tri- μ_3 -sulfido-1:2:3 κ^3 S;1:2:4 κ^3 S;-1:3:4 κ^3 S-tris(triphenylphosphine)-2 κ P;3 κ P;4 κ P-tricoppertungsten

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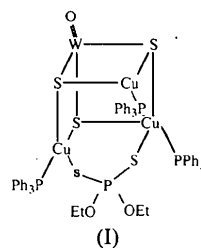
Abstract

The structure of the title compound, [WCu₃(O)S₃(C₄H₁₀O₂PS₂)(C₁₈H₁₅P)₃], contains an incom-

plete cubane-like cluster core, [WCu₃S₃{S₂P(OCH₂CH₃)₂}]²⁺, in which the two S atoms of the diethyl dithiophosphato ligand coordinate to two Cu atoms with bond lengths of 2.472 (3) Å [Cu(1)—S(4)] and 2.337 (3) Å [Cu(3)—S(5)].

Comment

Several different structural types of *M*—Cu—S complexes (*M* = Mo, W) have been found during recent years. For example, clusters containing the cores [M₃CuS₄]⁵⁺ (Lu, Zhu, Wu, Wu & Lu, 1989; Zhan, Zheng Wu & Lu, 1989), [M₂Cu₂S₄]⁴⁺ (Zhu, Zheng & Wu, 1990) and *MCu*₃S₃*X* (*X* = Cl, Br) (Müller, Bögge & Schimanski, 1983) have been prepared. The structure of the title compound (I) is similar to that of [WCu₃(O)S₃Cl(Ph₃P)₃], except that the chloride anion is replaced by a bidentate diethyl dithiophosphato ligand.



Mean bond lengths of W—Cu 2.775 (2), Cu—(μ_3 -S) 2.347 (3), W—(μ -S) 2.250 (2) and W=O 1.715 (6) Å are found. The W atom is tetrahedrally coordinated by three S atoms and one O atom; the Ph₃P ligands complete the tetrahedral geometry at each Cu atom. The Cu(2)···S(4) distance (2.640 Å) is too long to be considered as a bond.

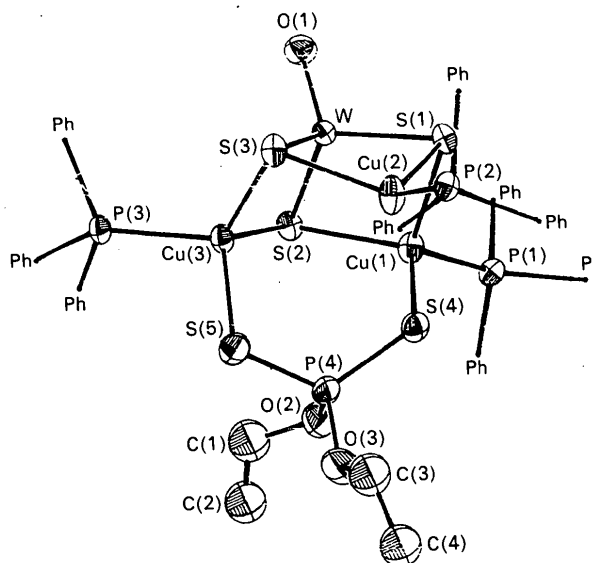


Fig. 1. View of the title structure showing the non-H atoms. Displacement ellipsoids are shown at the 30% probability level.