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μ-(4,4′-Bipyridine)-*N*:*N*′-bis[bis(pyrrolidinedithiocarboxylato-*S*,*S*′)zinc(**II**)]

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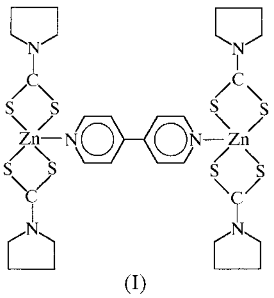
The title compound, $[Zn_2(C_5H_8NS_2)_4(C_{10}H_8N_2)]$, consists of two bis(pyrrolidinedithiocarboxylato)zinc molecules bridged by a 4,4′-bipyridine molecule, and has a 222 symmetry. Each Zn atom forms a five-coordinate pseudo-square-based pyramidal arrangement, with four Zn—S interactions and one Zn—N interaction; the Zn—N distance is 2.085 (3) Å and the Zn—S distances are in the range 2.3319 (8)–2.6290 (9) Å.

Comment

Recently, bis(dialkyldithiocarbamates) of zinc and cadmium have found use as single-molecule 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 investigations (O'Brien *et al.*, 1996). In general, the formation of the adduct breaks the parent dimeric dithiocarbamate into a monomeric species (Airolidi *et al.*, 1990; Zeng *et al.*, 1994). 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 (Malik *et al.*, 1997). We report here the crystal structure of μ-(4,4′-bipyridine)-*N*:*N*′-bis[bis(pyrrolidinedithiocarboxylato-*S*,*S*′)zinc(II)], (I), composed of two bis(pyrrolidinedithiocarboxylato)zinc(II) moieties bridged by a 4,4′-bipyridine (4,4′-bipy) molecule.



(I)

Compound (I) (Fig. 1) has a 222 symmetry and each Zn atom has a distorted rectangular pyramidal geometry. Zn atoms are linked to two bidentate $–S_2CNR_2$ ligands in the basal plane and are bridged by a 4,4′-bipy ligand at the apex. The 4,4′-bipy ligand is not planar and the dihedral angle between the two pyridine rings is 38.6°. There are two short [2.3319 (8) Å] and two long Zn—S bond lengths [2.6290 (9) Å], which are similar to the distances found in $[Zn(Me^iPrNCS_2)_2]_2$·TMED (Malik *et al.*, 1997) of 2.349 (2) and 2.5640 (7)/2.6103 (7) Å, respectively. The short Zn—S bonds are associated with the longer S—C distances. This indicates that the dithiocarbamate ligand is asymmetrically linked to zinc. The Zn—N bond length [2.085 (3) Å] is shorter than that of $[Zn(Me^iPrNCS_2)_2]_2$·TMED [2.137 (5) Å] and longer than that of $[Zn(Me^iPrNCS_2)]$·pyridine [2.069 (2) Å; Malik *et al.*, 1997]. This difference may be attributed to the very different steric characters of the N-containing bridged ligands.

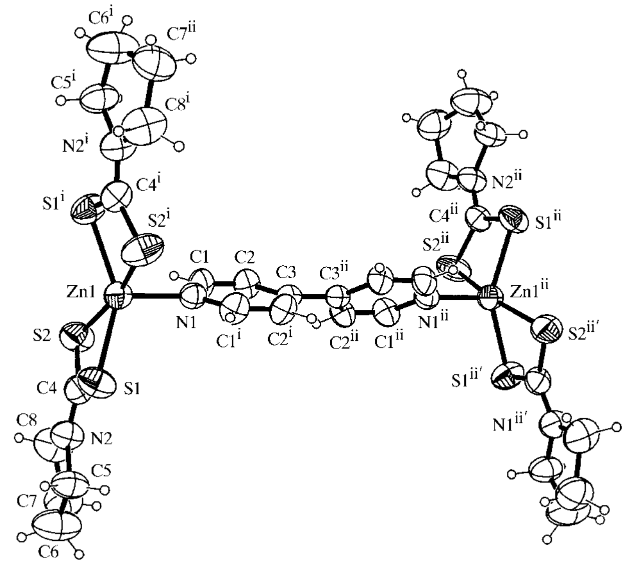


Figure 1
View of the title compound with the atomic numbering scheme and 30% probability ellipsoids.

Experimental

Bis(pyrrolidinedithiocarboxylate)zinc (Wang & Marshall, 1974) and 4,4′-bipyridine were dissolved in dimethylformamide (DMF) and refluxed for 1 h. The yellow microcrystals which formed were collected by concentrating the DMF solution. Single crystals suitable for X-ray analysis were obtained by recrystallization from CH_3CN.

Crystal data

$[Zn_2(C_5H_8NS_2)_4(C_{10}H_8N_2)]$
$M_r = 871.90$
Orthorhombic, *Fddd*
$a = 11.7643$ (2) Å
$b = 19.9965$ (3) Å
$c = 32.9889$ (3) Å
$V = 7760.5$ (2) Å^3
$Z = 8$
$D_x = 1.493$ Mg m^{-3}

Mo *K*α radiation
Cell parameters from 6152 reflections
$\theta = 2.10–29.37°$
$\mu = 1.70$ mm^{-1}
$T = 293$ (2) K
Cut hexagonal block, yellow
0.20 × 0.20 × 0.18 mm

Data collection

Siemens SMART CCD diffractometer
ω scans
Absorption correction: empirical (*SADABS*; Sheldrick, 1996)
$T_{\min} = 0.644$, $T_{\max} = 0.737$
11 821 measured reflections
2497 independent reflections
2009 reflections with $I > 2\sigma(I)$
$R_{\rm int} = 0.024$
$\theta_{\max} = 29.37°$
$h = -15 \rightarrow 8$
$k = -27 \rightarrow 27$
$l = -45 \rightarrow 43$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.046$
$wR(F^2) = 0.121$
$S = 1.078$
2497 reflections
115 parameters
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0532P)^2 + 18.0531P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max} < 0.001$
$\Delta\rho_{\max} = 0.62$ e Å^{-3}
$\Delta\rho_{\min} = -0.33$ e Å^{-3}

Table 1
Selected geometric parameters (Å, °).

Zn1—N1	2.085 (3)	N2—C5	1.476 (4)
Zn1—S1	2.3319 (8)	C1—C2	1.369 (4)
Zn1—S2	2.6290 (9)	C2—C3	1.392 (3)
S1—C4	1.729 (3)	C3—C3$^{\rm i}$	1.479 (7)
S2—C4	1.714 (3)	C5—C6	1.502 (5)
N1—C1	1.340 (3)	C6—C7	1.437 (10)
N2—C4	1.318 (4)	C7—C8	1.535 (9)
N2—C8	1.474 (4)		
N1—Zn1—S1	107.23 (3)	S1—Zn1—S2	73.10 (3)
S1—Zn1—S1$^{\rm ii}$	145.53 (5)	S1$^{\rm ii}$—Zn1—S2	103.28 (3)
N1—Zn1—S2	95.92 (2)	S2$^{\rm ii}$—Zn1—S2	168.17 (5)

Symmetry codes: (i) $\frac{3}{4} - x, y, -\frac{1}{4} - z$; (ii) $\frac{3}{4} - x, \frac{3}{4} - y, z$.

The C7 atom was found to be disordered and was refined as C7 and C7*A* with occupancies of 0.55 and 0.45, respectively.

Data collection: *SMART* (Siemens, 1996*a*); cell refinement: *SAINT* (Siemens, 1996*a*); data reduction: *SAINT*; program(s) used to solve structure: *SHELXS*86 (Sheldrick, 1990); program(s) used to refine structure: *SHELXTL* (Siemens, 1996*b*); molecular graphics: *SHELXTL*; software used to prepare material for publication: *SHELXTL*.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: BK1483). Services for accessing these data are described at the back of the journal.

References

Airolidi, C., de Oliveia, S. F., Ruggiero, S. G. & Lechat, J. R. (1990). *Inorg. Chim. Acta*, **174**, 103–108.
Malik, M. A., Motevalli, M., O'Brien, P. & Walsh, J. R. (1997). *Inorg. Chem.* **36**, 1263–1264.
O'Brien, P., John, R. W., Ian, M. W., Majid, M. & Lars, H. (1996). *J. Chem. Soc. Dalton Trans.* pp. 2491–2496.
Sheldrick, G. M. (1990). *Acta Cryst.* A**46**, 467–473.
Sheldrick, G. M. (1996). *SADABS. Siemens Area Detector Absorption Correction Software.* University of Göttingen, Germany.
Siemens (1996*a*). *SMART* and *SAINT*. *Area Detector Control and Integration Software*. Siemens Analytical X-ray Instruments Inc., Madison, Wisconsin, USA.
Siemens (1996*b*). *SHELXTL*. Siemens Analytical X-ray Instruments Inc., Madison, Wisconsin, USA.
Wang, J. & Marshall, W. D. (1974). *Anal. Chem.* **66**, 1658–1663.
Zeng, D., Hampden-Smith, M. J., Alam, T. M. & Rheingold, A. L. (1994). *Polyhedron*, **13**, 2715–2730.

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