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Crystallographic report

(4,4′-Bipyridine)bis[bis(*N*,*N*-diethyldithiocarbamato)zinc(II)]

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The structure of $[Zn(S_2CNEt_2)_2]_2$(4,4′-bipy) shows two independent dimeric molecules, one located about a centre of inversion, the other lying on a two fold axis containing the zinc atoms. Bidentate coordination by the dithiocarbamate ligands and a distorted square pyramidal geometry are found for two of zinc atoms whereas for the third zinc atom, the geometry is intermediate between square pyramidal and trigonal bipyramidal, a result that underscores the flexibility of coordination in these systems. Copyright © 2003 John Wiley & Sons, Ltd.

KEYWORDS: crystal structure; zinc; dithiocarbamate; diimine adduct

COMMENT

The title compound, $[Zn(S_2CNEt_2)_2]_2$(4,4′-bipy) (Fig. 1), crystallizes with two independent molecules in the asymmetric unit, both of which are dimeric. One molecule is centrosymmetric, being centred about the bridging 4,4-bipyridine molecule, and the other is situated about a two fold axis aligned along the Zn···Zn vector. Except for the different symmetry, the obvious difference between the two molecules is seen in the orientation of the pyridine rings. Each of the three independent zinc atoms exists in a five-coordinate geometry defined by an NS_4 donor set. The dithiocarbamate ligands are chelating, but with some asymmetry in their Zn–S bonds; the asymmetry is more pronounced for the Zn(3) atom. The coordination geometry about each of the Zn(1) and Zn(2) atoms more closely resembles a square-pyramidal environment, with the nitrogen atom defining an apical position. By contrast, the Zn(3) atom has a geometry intermediate between square pyramidal and trigonal bipyramidal. The above results show the flexibility in the coordination geometries in these systems. To a first approximation, the structure of the present compound, at least the centrosymmetric molecule, resembles that found for $Zn(S_2CN^iPr_2)_2$(4,4′-bipy).[1]

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EXPERIMENTAL

Pale-yellow crystals were isolated from a 2/1 dichloromethane/toluene solution containing equimolar amounts of $Zn(S_2CNEt_2)_2$[2] and 4,4-bipyridine (Aldrich). IR (KBr): ν(C–S) 995 and ν(C–N) 1425 and 1491 cm^{-1}. Intensity data were collected at 223 K on a Bruker AXS SMART CCD diffractometer for a yellow plate 0.13 × 0.18 × 0.55 mm^3. $C_{30}H_{48}N_6S_8Zn_2$, $M = 879.96$, orthorhombic, *Pbcn*, $a = 22.0721(9)$, $b = 21.4511(9)$, $c = 17.3009(7)$ Å, $V = 8191.5(6)$ $Å^3$, $Z = 8$, 12 007 unique data (θ_{max} 30.1°), $R = 0.090$ (all data), $wR = 0.125$ (all data). Programs used: teXsan, DIRDIF, SHELXL, and ORTEP. CCDC deposition number: 200068.

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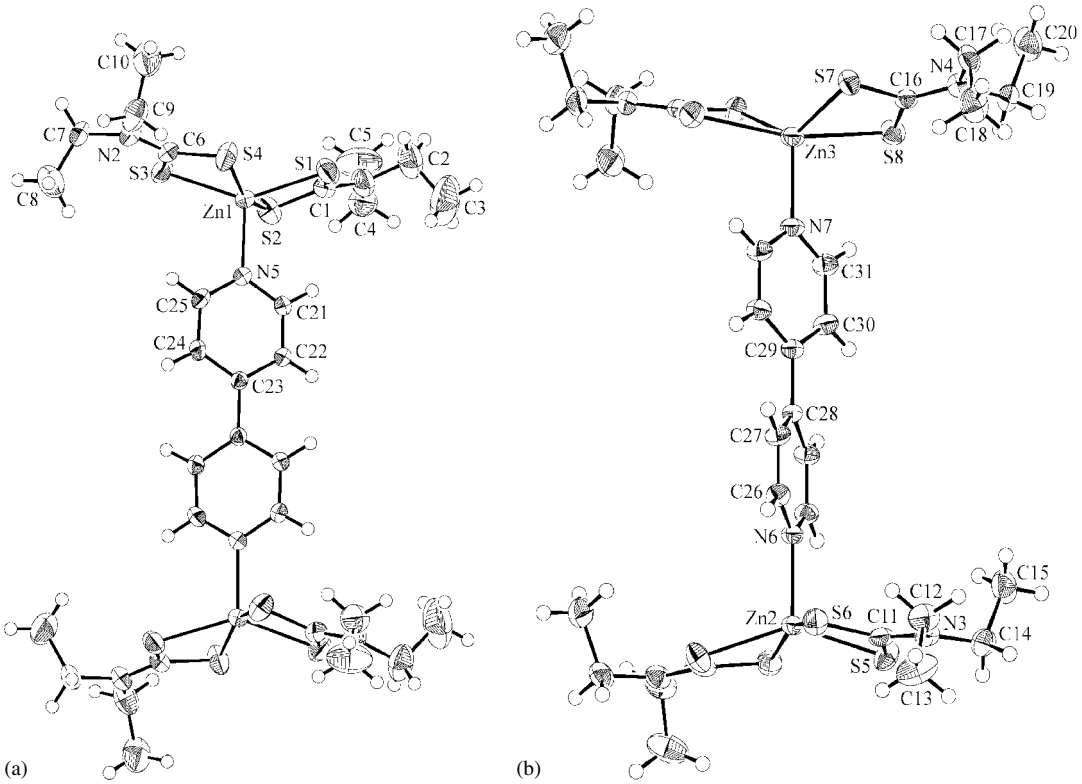

Figure 1. Dimeric structure of $[Zn(S_2CNEt_2)_2]_2$(4,4′-bipy). Key geometric parameters: Zn(1)–S(1) 2.3622(9), Zn(1)–S(2) 2.5350(10), Zn(1)–S(3) 2.3577(8), Zn(1)–S(4) 2.5583(9), Zn(1)–N(5) 2.086(2), S(1)–C(1) 1.725(3), S(2)–C(1) 1.709(3), S(3)–C(6) 1.726(3), S(4)–C(6) 1.716(3), C(1)–N(1) 1.328(4), C(6)–N(2) 1.323(4), Zn(2)–S(5) 2.3524(7), Zn(2)–S(6) 2.5238(7), Zn(2)–N(6) 2.095(3), S(5)–C(11) 1.726(3), S(6)–C(11) 1.714(3), C(11)–N(3) 1.330(3), Zn(3)–S(7) 2.3206(7), Zn(3)–S(8) 2.6254(7), Zn(3)–N(7) 2.082(3), S(7)–C(16) 1.731(3), S(8)–C(16) 1.714(3), C(16)–N(4) 1.328(3) Å; S(1)–Zn(1)–S(2) 73.21(3), S(1)–Zn(1)–S(3) 143.28(3), S(1)–Zn(1)–S(4) 97.38(3), S(1)–Zn(1)–N(5) 110.57(6), S(2)–Zn(1)–S(3) 103.89(3), S(2)–Zn(1)–S(4) 160.55(3), S(2)–Zn(1)–N(5) 97.34(7), S(3)–Zn(1)–S(4) 73.21(3), S(3)–Zn(1)–N(5) 106.12(6), S(4)–Zn(1)–N(5) 101.95(7); S(5)–Zn(2)–S(6) 74.04(3), S(5)–Zn–N(6) 108.05(2), S(5)–Zn(2)–S(5)^i 143.89(4), S(5)–Zn(2)–S(6)^i 100.31(3), S(6)–Zn(2)–N(6) 98.90(2), S(6)–Zn(2)–S(6)^i 162.20(4), S(7)–Zn(3)–S(8) 72.86(2), S(7)–Zn(3)–N(7) 114.00(2), S(7)–Zn(3)–S(7)^i 132.00(4), S(7)–Zn(3)–S(8)^i 101.34(2), S(8)–Zn(3)–N(7) 96.933(19), S(8)–Zn(3)–S(8)^i 166.13(4)°. Symmetry operation *i*: $-x$, y, $0.5 - z$.