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(4,7-Dimethyl-1,10-phenanthroline)-bis(*O*-isopropropyldithiocarbonato)zinc(II)

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An N_2S_2-donor set defines the approximately tetrahedral coordination environment about the zinc centre in the monomeric title compound, $[Zn(S_2CO^iPr)_2(4,7\text{-}Me_2phen)]$ or $[Zn(C_4H_7OS_2)_2(C_{14}H_{12}N_2)]$, which has crystallographically imposed twofold rotation symmetry.

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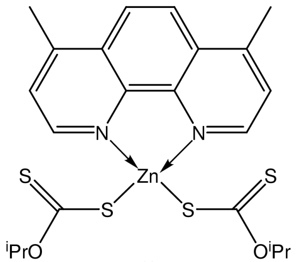
Key indicators

Single-crystal X-ray study
T = 183 K
Mean σ(C–C) = 0.002 Å
R factor = 0.027
wR factor = 0.076
Data-to-parameter ratio = 24.8

For details of how these key indicators were automatically derived from the article, see http://journals.iucr.org/e.

Comment

Amongst the zinc-triad 1,1-thiolates (*e.g.* compounds containing $^-S_2CNR_2$, dithiocarbamate; ^-S_2COR, xanthate; $^-S_2P(OR)_2$ dithiophosphate ligands), two zinc xanthates adopt an unprecedented tetrameric motif (Cox & Tiekink, 1997). Thus, the structures of $Zn(S_2COR)_2$, where $R = {}^iPr$ (Ito, 1972) and $R = {}^nBu$ (as a benzene solvate: Cox & Tiekink, 1999), feature a square of Zn atoms, with each edge bridged by a bidentate xanthate ligand. The distorted tetrahedral geometry about each Zn atom is completed by a chelating xanthate ligand. As is well established in the literature for related systems, the addition of Lewis base(s) disrupts this motif to generate new structural motifs. In the case of $Zn(S_2CO^iPr)_2$, both mononuclear and binuclear adducts have been characterized. In this way, 1,10-phenanthroline mononuclear species are found in the two polymorphs (see below) that have been characterized crystallographically (Klevtsova *et al.*, 2001). By contrast, with the bidentate ligand 4,4′-bipyridine (as a dichloromethane solvate: Klevtsova *et al.*, 2000), a dinuclear species with five-coordinated zinc centres has been found. A similar result occurs when bis(diphenylphosphino)ethane (Beer *et al.*, 2002) is used as the lewis base. In the present study, the X-ray crystal structure of a new mononuclear adduct involving the 4,7-dimethyl-substituted 1,10-phenanthroline ligand, *viz.* $Zn(S_2CO^iPr)_2(4,7\text{-}Me_2phen)$ (I), is reported.



(I)

The structure of (I) has crystallographically imposed twofold rotation symmetry and features a chelating diimine and monodentate xanthate ligands (Fig. 1 and Table 1). The Zn—N1 distances are equal, due to symmetry, at 2.103 (1) Å. The Zn—S1 distance of 2.2920 (3) Å is approximately 0.9 Å shorter than the Zn···S2 separation of 3.1988 (4) Å, indicat-

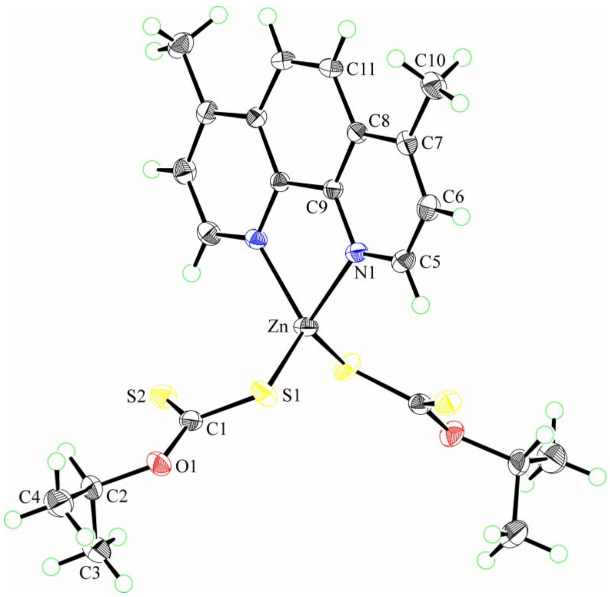


Figure 1
The molecular structure and crystallographic numbering scheme for (I). Displacement ellipsoids are shown at the 50% probability level (Johnson, 1976).

ing the assignment of an exclusively monodentate coordination mode for the xanthate ligands in (I). Furthermore, the pattern in associated C—S bond distances shows that the C═S2 bond has significant thione character (Table 1), again consistent with the above conclusion. Other parameters defining the xanthate ligand follow expected trends. The coordination geometry is therefore best described as distorted tetrahedral, defined by an N_2S_2-donor set. The subtended angles at Zn range from acute for the chelate angle of 78.59 (5)° to 124.15 (2)° for the angle defined by the two S-donor atoms. The structure is essentially molecular, there being no significant intermolecular contacts of note operating in the crystal structure. Thus, the closest interaction that may be construed as a $\pi\cdots\pi$ contact is greater than 4.3 Å. Likewise, a possible C—H$\cdots\pi$ interaction with a C10—H10*b*$\cdots$*Cg*$^{\rm i}$ [*Cg* is ring centroid of the N1-pyridine ring; symmetry code: (i) $-x$, $1 - y$, $-z$] separation of 2.86 Å can not be regarded as particularly significant, given that the angle subtended at H10*b* is 122°. In this regard, it is appropriate to compare the situation in (I) with the aforementioned polymorphs of the unsubstituted 1,10-phenanthroline adducts of $Zn(S_2CO^iPr)_2$ (Klevtsova *et al.*, 2001). In the latter, the difference in the crystal-packing arrangements appears to have a profound influence on the mode of coordination of the xanthate ligand.

In one of the polymorphs of $Zn(S_2CO^iPr)_2$(phen), labelled here as form α, there is a considerable discrepancy in the Zn—N bond distances [*viz*. 2.102 (5) and 2.199 (4) Å]. Even more remarkable is the observation that one of the xanthate ligands is effectively chelating [Zn—S 2.436 (2) and 2.527 (2) Å], whilst the other is clearly monodentate [Zn—S 2.321 (2) and 3.404 (2) Å]. In form β, the Zn—N bond distances of 2.149 (3) and 2.174 (2) Å are closer to each other than in form α. The two sets of Zn—S bond distances, *viz*. 2.507 (1) and 2.528 (1) Å, and 2.425 (1) and 2.697 (1) Å, indicate that, at least to a first approximation, the xanthate ligands are chelating. The authors of this work (Klevtsova *et al.*, 2001) highlighted the different crystal-packing arrangements operating in their polymorphic structures. In form α, centrosymmetric molecules aggregate *via* π–π interactions to form isolated dimeric units. By contrast, in form β, there are no π–π interactions.

In summary, in the three closely related $Zn(S_2CO^iPr)_2$(diimine) adducts, the coordination mode of the xanthate ligand varies from monodentate to bidentate. Furthermore, the possible combinations of these options are observed in the three structures. Clearly, the subtle interplay between the flexible coordination modes of xanthate ligands in general (Tiekink & Winter, 1992) and the dictates of crystal packing are such as to allow for a diversity of coordination geometries in these systems, as has been discussed for the closely related organotin 1,1-thiolates (Buntine *et al.*, 1998; Tiekink *et al.*, 1999; Mohamed-Ibrahim *et al.*, 2000).

Experimental

Light-brown crystals were obtained from the slow evaporation of an acetone–$CHCl_3$ (1/1) solution of $Zn(S_2CO^iPr)_2(4,7\text{-}Me_2phen)$ that had been prepared by refluxing equimolar amounts of $Zn(S_2CO^iPr)_2$ (Cox & Tiekink, 1999) and 4,7-dimethyl-1,10-phenanthroline (Aldrich) in chloroform solution. Analysis found (calculated) for $C_{22}H_{26}N_2O_2S_4Zn$: C 48.4 (48.6), H 4.6 (4.8)%. From TG analysis, crystals were found to decompose in the range 392 to 458 K, with a weight difference consistent with the loss of the diimine chelate. IR: (KBr) ν(C—S) 1096, 1047 and ν(C—O) 1170, 1191 cm^{-1}. ^{1}H NMR ($CDCl_3$): δ 5.33 (*br*, CH–N), 8.16 (*s*, CH), 7.73 (*m*, CH—C$_{\rm Me}$), 5.33 [*hept*, CH (^{i}Pr), *J* = 4.8 Hz], 2.90 [*s*, Me (phen)], 1.19 p.p.m. [*br*, Me (^{i}Pr)].

Crystal data

$[Zn(C_4H_7OS_2)_2(C_{14}H_{12}N_2)]$
$M_r = 544.06$
Monoclinic, $C2/c$
$a = 19.6834$ (10) Å
$b = 9.8097$ (5) Å
$c = 12.8171$ (7) Å
$\beta = 103.403$ (1)°
$V = 2407.4$ (2) Å^3
$Z = 4$
$D_x = 1.501$ Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 6953 reflections
$\theta = 2.3$–30.1°
$\mu = 1.39$ mm^{-1}
$T = 183$ (2) K
Block, light brown
0.57 × 0.39 × 0.21 mm

Data collection

Bruker AXS SMART CCD diffractometer
ω scans
Absorption correction: multi-scan (*SADABS*; Sheldrick, 1996; Blessing, 1995)
$T_{\min} = 0.509$, $T_{\max} = 0.747$
9944 measured reflections
3524 independent reflections
3322 reflections with $I > 2\sigma(I)$
$R_{\rm int} = 0.019$
$\theta_{\max} = 30.1°$
$h = -27 \rightarrow 20$
$k = -13 \rightarrow 13$
$l = -18 \rightarrow 17$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.027$
$wR(F^2) = 0.076$
$S = 1.05$
3524 reflections
142 parameters
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.046P)^2 + 1.2962P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max} < 0.001$
$\Delta\rho_{\max} = 0.51$ e Å^{-3}
$\Delta\rho_{\min} = -0.29$ e Å^{-3}

Table 1
Selected geometric parameters (Å, °).

Zn—S1	2.2920 (3)	S2—C1	1.6571 (13)
Zn—N1	2.1028 (10)	C1—O1	1.3380 (15)
S1—C1	1.7145 (13)	O1—C2	1.4588 (16)
S1—Zn—N1	101.27 (3)	N1—Zn—N1^{i}	78.59 (5)
S1—Zn—S1^{i}	124.15 (2)	Zn—S1—C1	99.93 (4)
S1—Zn—N1^{i}	121.97 (3)	C1—O1—C2	120.42 (10)

Symmetry code: (i) $-x, y, \frac{1}{2} - z$.

The C-bound H atoms were placed in calculated positions and included in the final refinement in the riding-model approximation.

Data collection: *SMART* (Bruker, 2000); cell refinement: *SAINT* (Bruker, 2000); data reduction: *SHELXTL* (Bruker, 2000); program(s) used to solve structure: *PATTY* in *DIRDIF*92 (Beurskens *et al.*, 1992); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *ORTEP*II (Johnson, 1976); software used to prepare material for publication: *SHELXL*97.

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