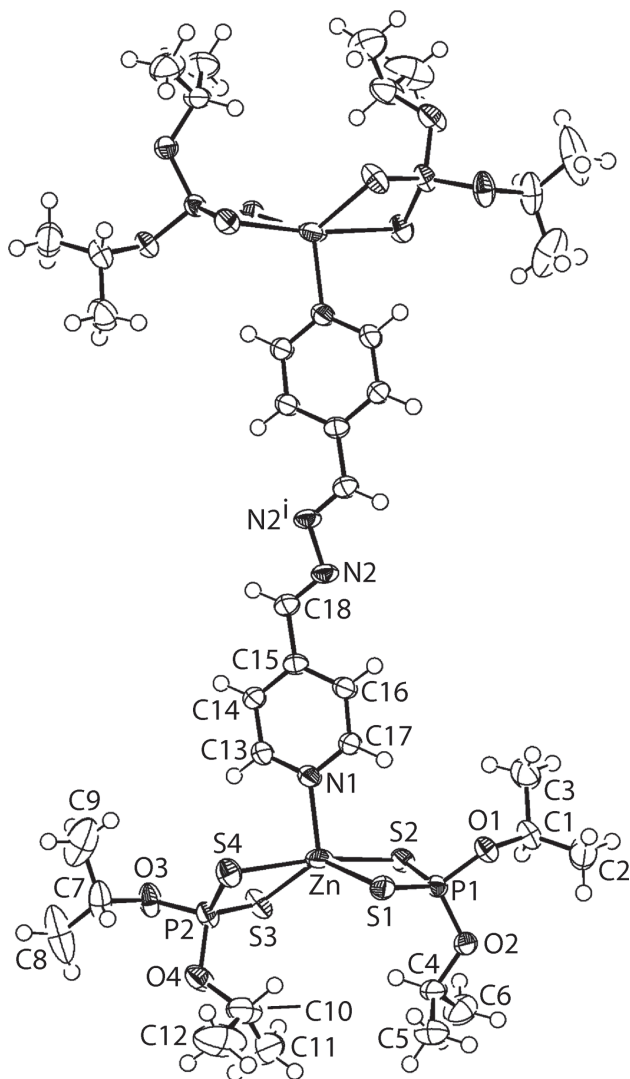


Yee Seng Tan and Edward R.T. Tiekink*

Crystal structure of tetrakis(O,O'-diisopropyldithiophosphato- κ^2S,S')- (μ_2 -1,2-bis(4-pyridylmethylene)hydrazine- $\kappa^2N:N'$)zinc(II),

$C_{36}H_{66}N_4O_8P_4S_8Zn_2$



Abstract

$C_{36}H_{66}N_4O_8P_4S_8Zn_2$, triclinic, $P\bar{1}$ (no. 2), $a = 7.94960(10)$ Å, $b = 11.5638(2)$ Å, $c = 16.5616(2)$ Å, $\alpha = 75.604(1)^\circ$, $\beta = 86.321(1)^\circ$, $\gamma = 83.103(2)^\circ$, $V = 1463.06(4)$ Å³, $Z = 1$, $R_{gt}(F) = 0.0424$, $wR_{ref}(F^2) = 0.1072$, $T = 100(2)$ K.

CCDC no.: 1903609

The molecular structure is shown in the figure. Table 1 contains crystallographic data and Table 2 contains the list of the atoms including atomic coordinates and displacement parameters.

Table 1: Data collection and handling.

Crystal:	Yellow prism
Size:	0.15 × 0.08 × 0.06 mm
Wavelength:	Cu $K\alpha$ radiation (1.54184 Å)
μ :	5.08 mm ⁻¹
Diffractometer, scan mode:	XtaLAB Synergy, ω
θ_{max} , completeness:	67.1°, >99%
$N(hkl)_{measured}$, $N(hkl)_{unique}$, R_{int} :	31791, 5233, 0.029
Criterion for I_{obs} , $N(hkl)_{gt}$:	$I_{obs} > 2 \sigma(I_{obs})$, 4906
$N(param)_{refined}$:	288
Programs:	CrysAlis ^{PRO} [1], SHELX [2, 3], WinGX/ORTEP [4]

Source of material

The $Zn[S_2P(O-i-Pr)_2]_2$ precursor was prepared in high yield from the *in situ* reaction of $Zn(NO_3)_2 \cdot 6 H_2O$ (Alfa Aesar; 14.87 g, 0.05 mol), *i*-PrOH (Merck; 16.05 mL, 0.21 mol), P_2S_5 (Sigma-Aldrich; 11.11 g, 0.05 mol) and 50° w/w NaOH solution (Merck; 8.80 mL, 0.11 mol). The 1,2-bis(4-pyridylmethylene)hydrazine precursor was prepared in high yield by refluxing 4-picolyamine (Aldrich; 2.03 mL, 0.02 mol) and hydrazinium hydroxide (Merck; 0.49 mL, 0.01 mol) in ratio 2:1 in ethanol solution (Merck; 5 mL). The title compound was obtained by mixing the suspension of the $Zn[S_2P(O-i-Pr)_2]_2$ (0.50 g, 1.02 mmol) and 1,2-bis(4-pyridylmethylene)hydrazine (0.22 g, 1.05 mmol) in dimethylformamide (Merck; 5 mL), followed by stirring for 30 min at 373 K. The solution was filtered and the filtrate was collected in a sample vial containing acetonitrile (Merck; 1 mL). Yellow blocks formed after one day. Yield: 0.53 g (87%, based on $Zn[S_2P(O-i-Pr)_2]_2$). M. pt (Biobase Automatic Melting

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Table 2: Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å²).

Atom	x	y	z	<i>U</i> _{iso} */ <i>U</i> _{eq}
Zn	0.13182(6)	0.55581(5)	0.72672(3)	0.04352(17)
S1	0.18842(10)	0.45555(7)	0.86473(5)	0.02501(18)
S2	0.05167(10)	0.34912(7)	0.71701(5)	0.02400(18)
S3	−0.09759(11)	0.67729(8)	0.66614(6)	0.0301(2)
S4	0.18781(11)	0.78110(7)	0.75900(5)	0.02757(19)
P1	0.11108(10)	0.31239(7)	0.83603(5)	0.01980(17)
P2	−0.03636(11)	0.81383(7)	0.70957(5)	0.02375(19)
O1	0.2566(3)	0.20575(19)	0.86011(13)	0.0234(5)
O2	−0.0392(3)	0.2616(2)	0.89677(13)	0.0234(5)
O3	−0.0572(3)	0.9264(2)	0.63286(14)	0.0311(6)
O4	−0.1811(3)	0.8509(2)	0.77127(14)	0.0315(6)
N1	0.3461(3)	0.5574(2)	0.65253(17)	0.0252(6)
N2	0.9280(3)	0.4870(3)	0.52601(16)	0.0239(6)
C1	0.2480(4)	0.0914(3)	0.8367(2)	0.0275(7)
H1	0.137184	0.093784	0.810595	0.033*
C2	0.2605(6)	−0.0073(3)	0.9147(3)	0.0417(9)
H2A	0.161868	0.003355	0.951799	0.062*
H2B	0.364329	−0.004868	0.942861	0.062*
H2C	0.263635	−0.084929	0.900563	0.062*
C3	0.3924(5)	0.0792(4)	0.7734(2)	0.0396(9)
H3A	0.380010	0.147891	0.724837	0.059*
H3B	0.389387	0.004751	0.755662	0.059*
H3C	0.500933	0.077249	0.798918	0.059*
C4	−0.2051(4)	0.3335(3)	0.8941(2)	0.0296(8)
H4	−0.203222	0.407337	0.847456	0.036*
C5	−0.2347(5)	0.3692(4)	0.9763(3)	0.0442(10)
H5A	−0.143956	0.415489	0.983744	0.066*
H5B	−0.235296	0.296800	1.022091	0.066*
H5C	−0.344167	0.418261	0.976205	0.066*
C6	−0.3334(5)	0.2575(4)	0.8776(3)	0.0431(10)
H6A	−0.307127	0.239029	0.823202	0.065*
H6B	−0.446908	0.301287	0.877432	0.065*
H6C	−0.329962	0.182554	0.921280	0.065*
C7	−0.0186(6)	1.0449(3)	0.6386(2)	0.0409(10)
H7	−0.000216	1.043944	0.697978	0.049*
C8	−0.1673(8)	1.1318(4)	0.6072(4)	0.0782(19)
H8A	−0.265614	1.113899	0.645219	0.117*
H8B	−0.192888	1.125126	0.551537	0.117*
H8C	−0.141480	1.213536	0.604165	0.117*
C9	0.1417(8)	1.0740(5)	0.5854(3)	0.0652(15)
H9A	0.233916	1.010575	0.604401	0.098*
H9B	0.173745	1.150991	0.590711	0.098*
H9C	0.120535	1.079290	0.526887	0.098*
C10	−0.2077(5)	0.7719(4)	0.8538(2)	0.0455(11)
H10	−0.113592	0.704982	0.864566	0.055*
C11	−0.3734(6)	0.7213(5)	0.8551(3)	0.0654(14)
H11A	−0.368880	0.675436	0.812451	0.098*
H11B	−0.465169	0.787142	0.843493	0.098*
H11C	−0.394191	0.668442	0.910129	0.098*
C12	−0.2030(6)	0.8484(6)	0.9158(3)	0.0669(16)
H12A	−0.090898	0.876825	0.912507	0.100*
H12B	−0.225396	0.800349	0.972274	0.100*
H12C	−0.289649	0.917442	0.902508	0.100*
C13	0.3663(4)	0.6474(3)	0.5852(2)	0.0288(7)
H13	0.276343	0.709905	0.570767	0.035*

Table 2 (continued)

Atom	x	y	z	<i>U</i> _{iso} */ <i>U</i> _{eq}
C14	0.5130(4)	0.6525(3)	0.5360(2)	0.0262(7)
H14	0.523162	0.717482	0.488494	0.031*
C15	0.6457(4)	0.5622(3)	0.55632(19)	0.0211(6)
C16	0.6239(4)	0.4684(3)	0.6262(2)	0.0243(7)
H16	0.712060	0.404995	0.642084	0.029*
C17	0.4736(4)	0.4688(3)	0.6719(2)	0.0262(7)
H17	0.459137	0.403988	0.719016	0.031*
C18	0.8055(4)	0.5690(3)	0.50667(19)	0.0237(7)
H18	0.817482	0.634892	0.459970	0.028*

Apparatus MP45): 399.75–400.55 K. **IR** (Bruker Vertex 70 V equipped with Platinum ATR from 400 to 80 cm^{−1}): 1104 (m) ν(C–O), 960(s) ν(P–O), 660 (s) ν(P–S)_{asym}, 552 (m) ν(P–S)_{sym} cm^{−1}. **¹H NMR** (Bruker Ascend 400 MHz, d₆-DMSO): δ 8.76 (dd, 4H, 2-aryl-H, ³J_{HH} = 6.04 Hz, ⁴J_{HH} = 2.93 Hz), 8.70 (s, 2H, N=CH), 7.85 (dd, 4H, 3-aryl-H, ³J_{HH} = 6.10 Hz, ⁴J_{HH} = 2.96 Hz), 3.82 (d sept, 8H, OCH, ³J_{PH} = 13.25 Hz, ³J_{HH} = 6.36 Hz), 1.19 (d, 48H, CH₃, ³J_{HH} = 6.23 Hz) ppm. **¹³C{¹H} NMR** (Bruker Ascend 400 MHz, d₆-DMSO): δ 159.5 (C=N), 150.5 (2-C₅H₄N), 140.7 (1-C₅H₄N), 122.2 (3-C₅H₄N), 69.0 (d, OCH, ²J_{PC} = 6.73 Hz), 23.7 (d, CH₃, ³J_{PC} = 4.51 Hz) ppm. **³¹P{¹H} NMR** (Bruker Ascend 400 MHz, d₆-DMSO): δ 106.7 ppm.

Experimental details

The C-bound H atoms were geometrically placed (C–H = 0.95–1.00 Å) and refined as riding with *U*_{iso}(H) = 1.2–1.5*U*_{eq}(C).

Comment

Generally, 1:1 reactions between {Zn[S₂P(OR)₂]₂}_n, which are uniformly self-associated in the condensed phase [5], and potentially bridging bipyridyl donors lead to polymeric chains [6–8]. However, this is not always the case owing to steric effects. For example, when R is the bulky cyclohexyl group, only mononuclear species, with rare monodentate coordination for trans-1,2-bis(2-pyridyl)ethene, is found in Zn[S₂P(OCy)₂]₂(trans-1,2-bis(2-pyridyl)ethene) [7] or binuclear species when 4,4'-bipyridine is employed, i.e. {Zn[S₂P(OCy)₂]₂}(4,4'-bipyridine) [8] are observed. When the distance between the bridging nitrogen atoms is greatly enhanced such effects may be militated so that in the case when the bipyridyl molecule is 1,2-bis(4-pyridylmethylene)hydrazine, a zig-zag coordination polymer, {Zn[S₂P(OCy)₂]₂}(trans-1,2-bis(2-pyridyl)ethene)₂, ensues [9]. In continuation of studies in this area [10], herein the product of the 1:1 reaction between Zn[S₂P(O-i-Pr)₂]₂ and 1,2-bis(4-pyridylmethylene)hydrazine, i.e. the 1:2 species {Zn[S₂P(O-i-Pr)₂]₂}(1,2-bis(4-pyridylmethylene)hydrazine) has been

examined crystallographically, rather than the anticipated 1:1 species.

The full binuclear complex is shown in the figure (70% displacement ellipsoids and symmetry operation $i: 2-x, 1-y, 1-z$) which is located about a centre of inversion. Two distinct coordination modes for the dithiophosphate ligands are noted. The S1-ligand is chelating with disparate Zn–S bond lengths: the Zn–S1 bond [2.3366(9) Å] is 0.25 Å shorter than the Zn–S2 bond [2.5912(10) Å]. An isodentate coordination is found for the S3-dithiophosphate ligand with the Zn–S3 bond length of 2.2858(9) Å being nearly 0.60 Å shorter than the Zn···S4 separation of 2.8762(1) Å. The difference in the modes of coordination of the dithiophosphate ligands correlates with systematic variations in the associated P–S bond lengths. Thus, for the anisodentate ligand the difference between the the P–S bonds is 0.05 Å with the shorter bond length associated with the S4 atom, i.e. the atom forming the weak contact to zinc [P–S3, S4 = 2.0103(12) and 1.9648(12) Å]. For the asymmetrically chelating ligand, the difference in the P–S bonds reduces to 0.02 Å [P–S1, S2 = 2.0044(11) and 1.9859(11) Å], again with the S2 involved in the weaker Zn–S bond forming the shorter of the P–S bonds. The fifth position in the distorted pentacoordinate geometry is occupied by a pyridyl donor of the bridging 1,2-bis(4-pyridylmethylene)hydrazine ligand; Zn–N1 = 2.034(3) Å. The angles subtended by the resultant NS_4 donor set range from a narrow 78.93(3)° for the S3–Zn–S4 chelate angle to a wide 171.53(3)° for the angle formed by the weakly bound sulphur atom of each ligand, i.e. S2–Zn–S4. With a value of $\tau = 0.65$, the five-coordinate geometry is intermediate between the ideal trigonal-bipyramidal [$\tau = 1.0$] and square-pyramidal [$\tau = 0.0$] geometries [11].

In the crystal, the binuclear molecules assemble into columns parallel to the a -axis direction with no directional interactions between them.

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