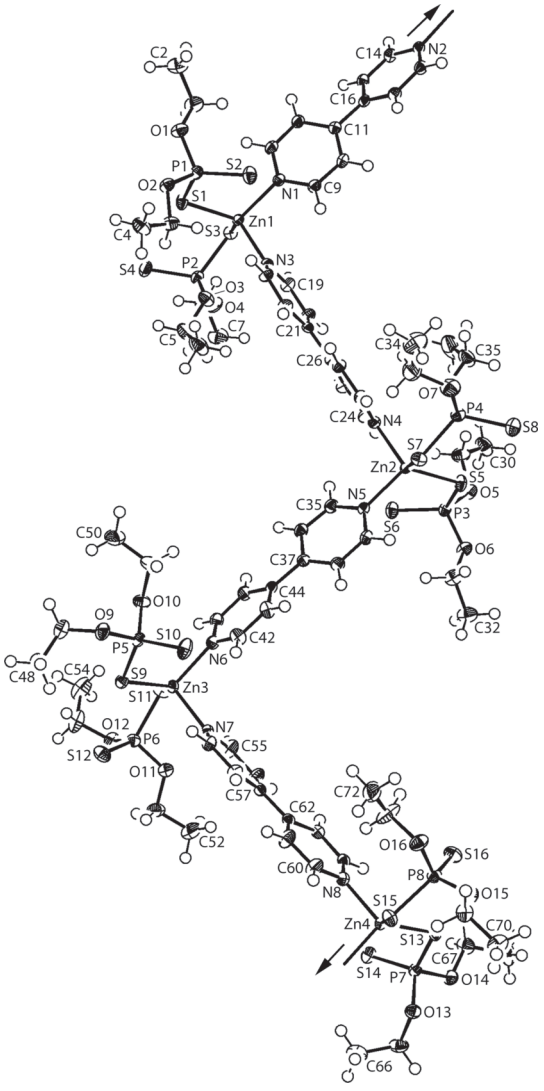
Yee Seng Tan and Edward R.T. Tiekink*

Crystal structure of a low-temperature (100 K) polymorph of *catena*-poly [(μ_2-4,4′-bipyridine-κ^2*N,N′*)-bis(*O,O′*-diethyldithiophosphato-κ^1*S*) zinc(II)], $C_{18}H_{28}N_2O_4P_2S_4Zn$



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Abstract

$C_{18}H_{28}N_2O_4P_2S_4Zn$, triclinic, $P\bar{1}$ (no. 2), $a = 15.2379(1)$ Å, $b = 17.3322(2)$ Å, $c = 21.8829(1)$ Å, $\alpha = 75.919(1)°$, $\beta = 78.050(1)°$, $\gamma = 68.170(1)°$, $V = 5159.97(8)$ Å^3, $Z = 8$, $R_{gt}(F) = 0.0246$, $wR_{ref}(F^2) = 0.0681$, $T = 100$ K.

CCDC no.: 1957379

A part of 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:	Colourless prism
Size:	0.28 × 0.17 × 0.12 mm
Wavelength:	Cu $K\alpha$ radiation (1.54184 Å)
μ:	5.76 mm^{-1}
Diffractometer, scan mode:	XtaLAB Synergy, ω
θ_{max}, completeness:	67.1°, >99%
$N(hkl)_{measured}$, $N(hkl)_{unique}$, R_{int}:	123255, 18426, 0.031
Criterion for I_{obs}, $N(hkl)_{gt}$:	$I_{obs} > 2\,\sigma(I_{obs})$, 17365
$N(param)_{refined}$:	1143
Programs:	CrysAlis^{PRO} [1], SHELX [2, 3], WinGX/ORTEP [4]

Source of material

The $Zn[S_2P(OEt)_2]_2$ 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), EtOH (Merck; 12.25 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 title compound was obtained by mixing a suspension of this precursor (0.50 g, 1.15 mmol) and 4,4′-bipyridine (Merck; 0.18 g, 1.15 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). Colourless blocks formed after one day. Yield: 0.46 g, (67.6%, based on $Zn[S_2P(OEt)_2]_2$). **M.pt** (Stuart SMP 30 Melting point apparatus): 420.2–421.9 K. **IR** (Bruker Vertex 70 V equipped with Platinum ATR from 400 to 80 cm^{-1}): 1057(w) ν(C—O); 940(s) ν(P—O); 667(s) $\nu(P—S)_{asym}$; 521(m) $\nu(P—S)_{sym}$; 294(m) ν(Zn—S); 380(w) ν(Zn—N).

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

Atom	*x*	*y*	*z*	U_{iso}*/U_{eq}
Zn1	1.27642(2)	0.07163(2)	0.07760(2)	0.01050(5)
Zn2	0.72088(2)	0.43395(2)	0.42150(2)	0.01085(5)
Zn3	0.26991(2)	0.02044(2)	0.59357(2)	0.01154(5)
Zn4	−0.25437(2)	0.46831(2)	0.89893(2)	0.01162(5)
S1	1.23935(3)	0.01375(2)	0.00699(2)	0.01662(8)
S2	1.16429(3)	0.22510(3)	−0.04588(2)	0.01933(9)
S3	1.38694(3)	−0.03354(2)	0.14090(2)	0.01434(8)
S4	1.33166(3)	−0.21187(3)	0.16243(2)	0.02243(9)
S5	0.76166(3)	0.49006(2)	0.49145(2)	0.01568(8)
S6	0.82759(3)	0.28049(2)	0.55427(2)	0.01811(9)
S7	0.61060(3)	0.54206(2)	0.35999(2)	0.01528(8)
S8	0.67151(3)	0.71469(3)	0.35391(2)	0.02640(10)
S9	0.19049(3)	−0.00534(2)	0.52636(2)	0.01404(8)
S10	0.13376(3)	0.20121(3)	0.45112(2)	0.02146(9)
S11	0.37827(3)	−0.09027(3)	0.65260(2)	0.01767(9)
S12	0.18010(3)	−0.14169(3)	0.67108(2)	0.02008(9)
S13	−0.20078(3)	0.51391(2)	0.96891(2)	0.01571(8)
S14	−0.13417(3)	0.30750(2)	1.03947(2)	0.01695(8)
S15	−0.35606(3)	0.56966(2)	0.83013(2)	0.01652(8)
S16	−0.16391(3)	0.62632(3)	0.82114(2)	0.02018(9)
P1	1.18693(3)	0.11368(3)	−0.06241(2)	0.01342(8)
P2	1.31363(3)	−0.10984(2)	0.19258(2)	0.01358(8)
P3	0.81163(3)	0.39373(2)	0.56375(2)	0.01319(8)
P4	0.68508(3)	0.62071(3)	0.31560(2)	0.01441(8)
P5	0.19564(3)	0.08202(2)	0.44657(2)	0.01285(8)
P6	0.28871(3)	−0.14872(3)	0.70786(2)	0.01378(8)
P7	−0.20182(3)	0.42504(2)	1.04798(2)	0.01246(8)
P8	−0.28551(3)	0.65366(3)	0.79243(2)	0.01390(8)
O1	1.25043(8)	0.09469(8)	−0.12815(5)	0.0181(2)
O2	1.09596(8)	0.10366(7)	−0.08057(5)	0.0155(2)
O3	1.20573(8)	−0.04811(7)	0.19927(6)	0.0189(2)
O4	1.33449(9)	−0.12861(7)	0.26423(5)	0.0203(3)
O5	0.90597(8)	0.40195(7)	0.57791(5)	0.0165(2)
O6	0.74914(8)	0.41947(7)	0.62839(5)	0.0167(2)
O7	0.65535(9)	0.65838(8)	0.24594(6)	0.0262(3)
O8	0.79198(8)	0.55684(7)	0.30699(6)	0.0199(2)
O9	0.14869(8)	0.06414(7)	0.39520(5)	0.0189(2)
O10	0.30703(8)	0.05658(7)	0.42120(5)	0.0172(2)
O11	0.26206(8)	−0.11112(7)	0.77138(5)	0.0191(2)
O12	0.35364(8)	−0.24311(7)	0.73409(5)	0.0192(2)
O13	−0.31136(8)	0.44580(7)	1.07637(5)	0.0169(2)
O15	−0.35500(8)	0.74447(7)	0.80511(5)	0.0176(2)
O16	−0.28275(9)	0.66834(7)	0.71725(5)	0.0207(3)
N1	1.35491(9)	0.15071(8)	0.04131(6)	0.0118(3)
N2	1.65809(9)	0.39541(8)	−0.06228(6)	0.0130(3)
N3	1.17131(9)	0.13826(8)	0.13849(6)	0.0118(3)
N4	0.82489(9)	0.36448(8)	0.36108(6)	0.0124(3)
N5	0.64200(9)	0.35469(8)	0.45698(6)	0.0123(3)
N6	0.35574(10)	0.09386(8)	0.55467(6)	0.0140(3)
N7	0.16944(9)	0.09730(8)	0.65171(6)	0.0135(3)
N8	−0.15272(9)	0.38416(8)	0.84627(6)	0.0140(3)
C1	1.35002(12)	0.08948(13)	−0.13911(8)	0.0231(4)
H1A	1.3884	0.0382	−0.1122	0.028*
H1B	1.3558	0.1396	−0.1285	0.028*
C2	1.38477(12)	0.08592(13)	−0.20826(8)	0.0249(4)
H2A	1.4524	0.0804	−0.2169	0.037*
H2B	1.3479	0.1379	−0.2344	0.037*
H2C	1.3767	0.0372	−0.2185	0.037*
C3	1.00827(12)	0.11942(11)	−0.03694(8)	0.0198(4)
H3A	0.9887	0.1763	−0.0262	0.024*
H3B	1.0177	0.0769	0.0028	0.024*
C4	0.93287(13)	0.11388(12)	−0.06863(9)	0.0241(4)
H4A	0.8746	0.1188	−0.0385	0.036*
H4B	0.9554	0.0594	−0.0827	0.036*
H4C	0.9194	0.1598	−0.1054	0.036*
C5	1.13063(13)	−0.08271(11)	0.23007(9)	0.0233(4)
H5A	1.1402	−0.1091	0.2748	0.028*
H5B	1.1311	−0.1263	0.2078	0.028*
C6	1.03745(13)	−0.01054(12)	0.22719(11)	0.0312(4)
H6A	0.9851	−0.0315	0.2480	0.047*
H6B	1.0284	0.0145	0.1827	0.047*
H6C	1.0381	0.0324	0.2489	0.047*
C7	1.41502(13)	−0.20013(12)	0.28741(8)	0.0254(4)
H7A	1.4754	−0.1890	0.2699	0.030*
H7B	1.4180	−0.2519	0.2742	0.030*
C8	1.40080(14)	−0.21147(13)	0.35842(9)	0.0293(4)
H8A	1.4538	−0.2596	0.3755	0.044*
H8B	1.3407	−0.2222	0.3752	0.044*
H8C	1.3985	−0.1601	0.3710	0.044*
C9	1.32977(11)	0.22655(10)	0.05775(7)	0.0146(3)
H9	1.2708	0.2465	0.0837	0.018*
C10	1.38646(11)	0.27678(10)	0.03832(7)	0.0147(3)
H10	1.3661	0.3304	0.0506	0.018*
C11	1.47346(11)	0.24839(10)	0.00074(7)	0.0121(3)
C12	1.49854(11)	0.17030(10)	−0.01740(7)	0.0144(3)
H12	1.5568	0.1491	−0.0437	0.017*
C13	1.43775(11)	0.12459(10)	0.00336(7)	0.0151(3)
H13	1.4551	0.0719	−0.0097	0.018*
C14	1.69316(11)	0.31061(10)	−0.04750(7)	0.0138(3)
H14	1.7604	0.2835	−0.0519	0.017*
C15	1.63609(11)	0.26108(10)	−0.02619(7)	0.0138(3)
H15	1.6640	0.2013	−0.0161	0.017*
C16	1.53709(11)	0.29933(10)	−0.01947(7)	0.0122(3)
C17	1.50051(11)	0.38762(10)	−0.03381(7)	0.0142(3)
H17	1.4336	0.4164	−0.0291	0.017*
C18	1.56257(11)	0.43241(10)	−0.05486(7)	0.0149(3)
H18	1.5367	0.4923	−0.0646	0.018*
C19	1.19221(11)	0.13689(10)	0.19559(7)	0.0152(3)
H19	1.2552	0.1057	0.2054	0.018*
C20	1.12601(11)	0.17894(10)	0.24059(7)	0.0150(3)
H20	1.1439	0.1769	0.2802	0.018*
C21	1.03300(11)	0.22428(9)	0.22757(7)	0.0115(3)
C22	1.01116(11)	0.22379(10)	0.16881(7)	0.0150(3)
H22	0.9480	0.2524	0.1585	0.018*
C23	1.08134(11)	0.18166(10)	0.12582(7)	0.0146(3)
H23	1.0656	0.1833	0.0856	0.018*
C24	0.90555(11)	0.30354(10)	0.37904(8)	0.0161(3)
H24	0.9160	0.2923	0.4221	0.019*
C25	0.97360(12)	0.25674(11)	0.33757(8)	0.0168(3)
H25	1.0290	0.2136	0.3524	0.020*
C26	0.96097(11)	0.27286(10)	0.27370(7)	0.0120(3)

Table 2 (continued)

Atom	x	y	z	U_{iso}*/U_{eq}
C27	0.87777(11)	0.33656(10)	0.25522(7)	0.0136(3)
H27	0.8663	0.3500	0.2122	0.016*
C28	0.81219(11)	0.37998(10)	0.29962(7)	0.0140(3)
H28	0.7556	0.4227	0.2862	0.017*
C29	0.99217(12)	0.37729(12)	0.53321(8)	0.0223(4)
H29A	0.9835	0.4160	0.4917	0.027*
H29B	1.0058	0.3192	0.5267	0.027*
C30	1.07310(13)	0.38117(12)	0.55961(10)	0.0285(4)
H30A	1.1309	0.3677	0.5289	0.043*
H30B	1.0837	0.3402	0.5994	0.043*
H30C	1.0577	0.4382	0.5678	0.043*
C31	0.64853(12)	0.42862(12)	0.63842(8)	0.0209(4)
H31A	0.6401	0.3811	0.6256	0.025*
H31B	0.6120	0.4821	0.6126	0.025*
C32	0.61331(13)	0.42894(13)	0.70800(8)	0.0251(4)
H32A	0.5449	0.4378	0.7156	0.038*
H32B	0.6246	0.4746	0.7206	0.038*
H32C	0.6475	0.3746	0.7330	0.038*
C33	0.66389(15)	0.60428(13)	0.20259(9)	0.0302(4)
H33A	0.6199	0.5717	0.2192	0.036*
H33B	0.7298	0.5639	0.1977	0.036*
C34	0.63928(16)	0.65927(15)	0.13969(9)	0.0365(5)
H34A	0.6484	0.6237	0.1087	0.055*
H34B	0.6808	0.6936	0.1248	0.055*
H34C	0.5726	0.6964	0.1445	0.055*
C35	0.87014(13)	0.58892(12)	0.28151(10)	0.0253(4)
H35A	0.8652	0.6341	0.3037	0.030*
H35B	0.8682	0.6128	0.2357	0.030*
C36	0.96164(14)	0.51656(14)	0.29137(13)	0.0410(5)
H36A	1.0157	0.5368	0.2753	0.061*
H36B	0.9665	0.4728	0.2684	0.061*
H36C	0.9624	0.4928	0.3368	0.061*
C37	0.68047(11)	0.27094(10)	0.45769(7)	0.0154(3)
H37	0.7473	0.2472	0.4460	0.018*
C38	0.62713(12)	0.21808(10)	0.47464(7)	0.0156(3)
H38	0.6568	0.1595	0.4735	0.019*
C39	0.52927(11)	0.25119(10)	0.49348(7)	0.0120(3)
C40	0.48985(12)	0.33749(10)	0.49479(8)	0.0163(3)
H40	0.4239	0.3624	0.5087	0.020*
C41	0.54790(12)	0.38616(10)	0.47569(8)	0.0164(3)
H41	0.5199	0.4451	0.4758	0.020*
C42	0.31778(12)	0.17713(11)	0.53288(8)	0.0177(3)
H42	0.2508	0.2011	0.5323	0.021*
C43	0.37162(12)	0.22940(10)	0.51135(8)	0.0171(3)
H43	0.3418	0.2879	0.4959	0.021*
C44	0.46981(11)	0.19633(10)	0.51232(7)	0.0121(3)
C45	0.50950(11)	0.10943(10)	0.53377(8)	0.0155(3)
H45	0.5764	0.0836	0.5342	0.019*
C46	0.45090(12)	0.06141(10)	0.55424(8)	0.0164(3)
H46	0.4791	0.0024	0.5688	0.020*
C47	0.16451(13)	−0.01967(11)	0.38450(9)	0.0231(4)
H47A	0.2152	−0.0620	0.4090	0.028*
H47B	0.1857	−0.0221	0.3389	0.028*
C48	0.07433(15)	−0.03968(13)	0.40481(10)	0.0307(4)
H48A	0.0843	−0.0950	0.3953	0.046*
H48B	0.0236	0.0037	0.3818	0.046*

Table 2 (continued)

Atom	x	y	z	U_{iso}*/U_{eq}
H48C	0.0559	−0.0409	0.4506	0.046*
C49	0.33982(13)	0.10112(12)	0.36037(8)	0.0223(4)
H49A	0.3884	0.1231	0.3661	0.027*
H49B	0.2857	0.1496	0.3437	0.027*
C50	0.38220(15)	0.04084(14)	0.31406(9)	0.0313(4)
H50A	0.4005	0.0713	0.2723	0.047*
H50B	0.3350	0.0168	0.3105	0.047*
H50C	0.4387	−0.0047	0.3293	0.047*
C51	0.19425(13)	−0.13683(11)	0.82225(8)	0.0223(4)
H51A	0.2178	−0.1989	0.8364	0.027*
H51B	0.1318	−0.1204	0.8070	0.027*
C52	0.18396(18)	−0.09344(15)	0.87613(10)	0.0398(5)
H52A	0.1377	−0.1087	0.9108	0.060*
H52B	0.1616	−0.0321	0.8614	0.060*
H52C	0.2458	−0.1112	0.8915	0.060*
C53	0.38761(14)	−0.30803(12)	0.69567(9)	0.0293(4)
H53A	0.3541	−0.2876	0.6576	0.035*
H53B	0.3731	−0.3589	0.7203	0.035*
C54	0.49179(16)	−0.33073(14)	0.67573(10)	0.0380(5)
H54A	0.5133	−0.3757	0.6506	0.057*
H54B	0.5250	−0.3505	0.7134	0.057*
H54C	0.5059	−0.2810	0.6499	0.057*
C55	0.18965(12)	0.09915(11)	0.70812(8)	0.0204(4)
H55	0.2488	0.0615	0.7215	0.025*
C56	0.12845(12)	0.15330(11)	0.74754(8)	0.0209(4)
H56	0.1455	0.1522	0.7872	0.025*
C57	0.04136(11)	0.20968(10)	0.72896(7)	0.0126(3)
C58	0.01973(12)	0.20584(10)	0.67108(7)	0.0152(3)
H58	−0.0395	0.2419	0.6570	0.018*
C59	0.08450(11)	0.14955(10)	0.63419(7)	0.0149(3)
H59	0.0683	0.1478	0.5950	0.018*
C60	−0.17993(12)	0.36935(11)	0.79679(8)	0.0212(4)
H60	−0.2438	0.3986	0.7881	0.025*
C61	−0.11993(12)	0.31394(11)	0.75812(8)	0.0205(4)
H61	−0.1427	0.3052	0.7240	0.025*
C62	−0.02559(11)	0.27071(10)	0.76937(7)	0.0126(3)
C63	0.00256(11)	0.28630(10)	0.82059(7)	0.0131(3)
H63	0.0662	0.2585	0.8300	0.016*
C64	−0.06221(11)	0.34229(10)	0.85774(7)	0.0134(3)
H64	−0.0418	0.3514	0.8927	0.016*
C65	−0.34049(13)	0.39258(12)	1.13352(8)	0.0214(4)
H65A	−0.3909	0.4284	1.1613	0.026*
H65B	−0.2854	0.3600	1.1573	0.026*
C66	−0.37756(13)	0.33272(12)	1.11585(9)	0.0258(4)
H66A	−0.3968	0.2970	1.1545	0.039*
H66B	−0.3274	0.2970	1.0887	0.039*
H66C	−0.4327	0.3651	1.0929	0.039*
O14[a]	−0.16418(8)	0.45149(8)	1.10007(5)	0.0177(2)
C67[a]	−0.06684(12)	0.45251(12)	1.08937(8)	0.0222(4)
H67A[a]	−0.0465	0.4669	1.0433	0.027*
H67B[a]	−0.0227	0.3962	1.1062	0.027*
C68[a]	−0.0654(4)	0.5181(3)	1.1234(3)	0.0296(11)
H68A[a]	−0.1076	0.5739	1.1053	0.044*
H68B[a]	−0.0003	0.5188	1.1181	0.044*
H68C[a]	−0.0876	0.5041	1.1687	0.044*
O14′[a]	−0.16418(8)	0.45149(8)	1.10007(5)	0.0177(2)

Table 2 (continued)

Atom	x	y	z	U_{iso}*/U_{eq}
C67′[a]	−0.06684(12)	0.45251(12)	1.08937(8)	0.0222(4)
H67C[a]	−0.0347	0.4362	1.0479	0.027*
H67D[a]	−0.0305	0.4115	1.1231	0.027*
C68′[a]	−0.0699(4)	0.5382(4)	1.0899(3)	0.0354(12)
H68D[a]	−0.1015	0.5778	1.0543	0.053*
H68E[a]	−0.0048	0.5386	1.0858	0.053*
H68F[a]	−0.1054	0.5554	1.1299	0.053*
C69	−0.45037(12)	0.77971(11)	0.78591(8)	0.0196(3)
H69A	−0.4768	0.7340	0.7907	0.023*
H69B	−0.4475	0.8080	0.7408	0.023*
C70	−0.51284(13)	0.84238(12)	0.82716(8)	0.0240(4)
H70A	−0.5745	0.8722	0.8111	0.036*
H70B	−0.4820	0.8832	0.8265	0.036*
H70C	−0.5228	0.8126	0.8708	0.036*
C71	−0.21623(15)	0.60301(13)	0.68298(9)	0.0331(5)
H71A	−0.2202	0.5470	0.7049	0.040*
H71B	−0.1502	0.6015	0.6814	0.040*
C72	−0.24125(17)	0.62239(13)	0.61747(9)	0.0331(5)
H72A	−0.1944	0.5810	0.5929	0.050*
H72B	−0.2410	0.6793	0.5970	0.050*
H72C	−0.3048	0.6196	0.6193	0.050*

[a]Occupancy: 0.5.

Experimental details

The C-bound H atoms were geometrically placed (C—H = 0.95–0.99 Å) and refined as riding with U_{iso}(H) = 1.2–1.5U_{eq}(C). The methyl-C68 atom was found, from refinement, to be statistically disordered over two positions with 50:50% site occupancy. Each position was modelled with independent anisotropic displacement parameters. Owing to poor agreement, one reflection, i.e. (7 0 2), was omitted from the final cycles of refinement. Translational pseudosymmetry is observed (<90%) but after careful analysis the refinement was carried out using the given unit cell.

Comment

The neutral, usually bidentate bridging ligand, 4,4′-bipyridine (4,4′-bipy), has proven to be a mainstay in coordination chemistry for the construction of coordination polymers, up to and including three-dimensional metal-organic framework architectures. An early aspiration of complexing zinc-triad 1,1-dithiolates, such as dithiophosphates [$^-S_2P(OR)_2$], with 4,4′-bipy was the expectation that the aggregated precursor structures, through the agency of M···S bridging [5], would be assembled into higher-dimensional architectures *via* links provided by the 4,4′-bipy molecules. While complexation by 4,4′-bipy did occur, this was at the expense of M···S bridging so that, usually, only one-dimensional coordination polymers eventuated [6]. In the case of zinc dithiophosphates, {Zn[$S_2P(OR)_2$]$_2$(4,4′-bipy)}$_n$, one-dimensional, zig-zag polymers are formed when R = [7], Et [8] and iPr [9]. However, when the R group is bulky, such as when R = cyclohexyl (Cy), only zero-dimensional, binuclear molecules could be isolated, i.e. {Zn[$S_2P(OCy)_2$]$_2$}$_2$(4,4′-bipy) [10]. Such steric control over supramolecular association in the zinc-triad dithiophosphate adducts of bipyridyl-type molecules is well established [6, 10–12]. In continuation of studies in this area, a low temperature (100 K) form of {Zn[$S_2P(OEt)_2$]$_2$(4,4′bipy)}$_n$, (I), was characterised crystallographically and compared with the previously reported room-temperature form [8].

The asymmetric unit of (I) is shown in the figure (70% probability displacement ellipsoids; only one position for the statistically disordered C68 atom is shown) and comprises four independent Zn[$S_2P(OEt)_2$]$_2$(4,4′-bipy) repeat units linked to form part of a one-dimensional coordination polymer with a zig-zag topology. The coordination environment for each zinc centre is approximately the same whereby each is coordinated by two sulphur atoms derived from two monodentate dithiophosphate ligands and two pyridyl-nitrogen atoms. The Zn—S(coordinating) bond lengths lie in the experimentally distinct range 2.2854(4) Å, for Zn4—S13, to 2.3519(4) Å, for Zn1—S3. Similarly, the Zn—N bond lengths span a range of over 0.045 Å, i.e. 2.0405(13) Å, for Zn1—N3, to 2.0879(13) Å, for Zn4—N2^i (symmetry operation (i): $-2 + x, y, 1 + z$). Evidence that the dithiophosphate ligands are coordinating in a monodentate mode is seen in the non-bonding separations. For each repeat unit, one dithiophosphate ligand is orientated to place a thione-sulphur atom in close proximity to the zinc centre, whereas the other directs one of the ethoxy-oxygen atoms towards the zinc atom. An interesting trend is noted in the non-bonding-Zn···S, O separations in that the zinc atom forming the shortest Zn···S separation, forms the longest Zn···O separation, i.e. Zn4···S16 = 3.4445(5) Å and Zn4—O13 = 3.7553(11) Å, and vice versa, i.e. Zn2···S6 = 3.6248(4) Å and Zn2—O8 3.1598(12) Å; the other zinc centres follow the same trend but, with intermediate separations Zn3···S12 = 3.4964(5) Å and Zn3···O10 = 3.6291(11) Å, and Zn1···S2 = 3.5116(4) Å and Zn1···O3 = 3.2159(12) Å. The P—S bond lengths also exhibit definitive trends with those involving the coordinating sulphur atom being systematically longer (range 2.0190(5) Å, for P7—S13, to 2.0417(6) Å, for P8—S15) than those formed by the formally thione-sulphur atoms [range 1.9331(6) Å, for P8—S16, to 1.9470(6) Å, for P7—S14]. Interestingly, the shortest and longest P—S(thione) bonds involve atoms forming weak Zn···S and no Zn···S interactions, respectively, indicating no trend in the nature of the sulphur atom and the magnitude of the P=S bond. The coordination geometries for the zinc atoms are based on P_2S_2 donor sets which define approximate tetrahedra. By

contrast to the bond lengths, systematic trends are lacking in the bond angles about the zinc atom. Thus, the bonds subtended by the coordinating sulphur atoms span a range of ca 10°, i.e. S5—Zn2—S7 = 109.371(16)° to S9—Zn3—S11 = 120.758(17)°, and those by the pyridyl-nitrogen atoms, ca 5°, i.e. N8—Zn4—$N2^{i}$ = 97.50(5)° to N1—Zn1—N3 = 102.09(5)°. However, despite these variations, the range of tetrahedral angles about the individual zinc atoms is narrow, being about 21° for the Zn4 atom [S15—Zn4—$N2^{i}$ = 97.15(4)° to S13—Zn4—S15 = 117.883(16)°] and about 23° for the Zn1 atom [S3—Zn1—N1 = 97.80(4)° to S1—Zn1—N3 = 120.32(4)°]. The twists between the pyridyl rings of the 4,4′-bipy molecules also differentiate the four repeat units with the dihedral angles between the N1-/N2-pyridyl [35.06(7)°], N3-/N4-pyridyl [17.40(8)°], N5-/N6-pyridyl [22.25(8)°] and N7-/N8-pyridyl [13.00(8)°] rings varying by over 20°.

In the crystal, the zig-zag chains run parallel to [2 0 −1]. The connections between the chains to consolidate the three-dimensional architecture are of the type C—H···O, C—H···S and C—H···π. Of each of these, the shortest and most directional interactions are pyridyl-C—H···O(ethoxy), pyridyl-C—H···S(coordinating) and methyl-C—H···π(pyridyl) [C56—H56···$O1^{ii}$: H56···$O1^{ii}$ = 2.47 Å, C56···$O1^{ii}$ = 3.351(2) Å with angle at H56 = 153°, C38—H38···$S9^{iii}$: H38···$S9^{iii}$ = 2.82 Å, C38···$S9^{iii}$ = 3.7031(17) Å with angle at H38 = 156° and C6—H6a···Cg(N7, C55—C59)^{iv}: H6a···Cg(N7, C55—C59)^{iv} = 2.85 Å, C6···Cg(N7, C55—C59)^{iv} = 3.776(2) Å with angle at H6a = 158° for symmetry operations (ii) $-1+x$, y, $1+z$, (iii) $1-x$, $-y$, $1-z$ and (iv) $1-x$, $-y$, $1-z$].

The crystal of the room temperature (296 K) polymorph of (I) is also triclinic $P\bar{1}$, with two independent repeat units of $Zn[S_2P(OEt)_2]_2$(4,4′-bipy) in the asymmetric unit [8]. Similar coordination modes for the dithiophosphate ligands about each zinc atom, as described above, are apparent in the room-temperature form. The pitch in the zig-zag chains in (I) range from 16.2 to 17.5 Å, and match those in the literature precedent, i.e. 16.4 to 17.5 Å [8].

Finally, in an accompanying report, a low temperature (100 K) polymorph for $\{Cd[S_2P(OEt)_2]_2(4,4'bipy)\}_n$ was described [13]. This, as was the room temperature (293 K) form [14], is a linear coordination polymer with a trans-N_2S_4 coordination geometry for the cadmium(II) centre. The obvious difference between the room- and low-temperature forms is in the number of $Cd[S_2P(OEt)_2]_2$(4,4′-bipy) repeating units. In the former, the repeat unit lies on a centre of inversion, whereas in the latter, there are four independent repeat units, two in general positions and two with the cadmium atom lying on a centre of inversion.

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