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Key indicators

Single-crystal X-ray study
 T = 293 K
 Mean $\sigma(C-C) = 0.012 \text{ \AA}$
 H-atom completeness 86%
 Disorder in main residue
 R factor = 0.051
 wR factor = 0.135
 Data-to-parameter ratio = 18.5

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

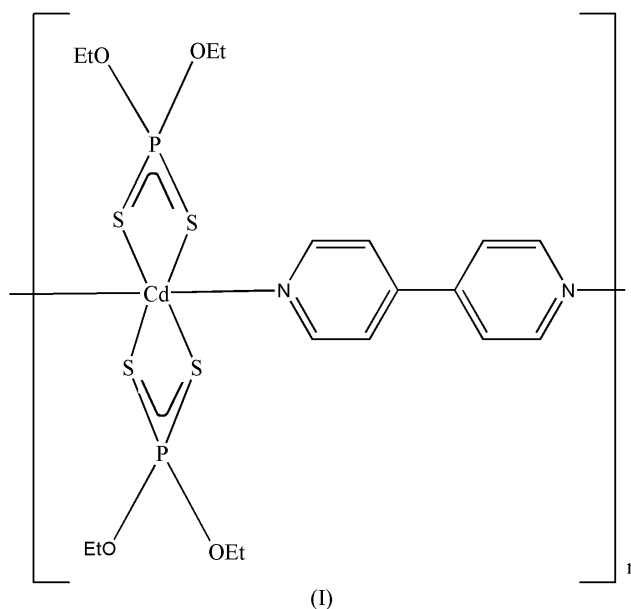
catena-Poly[[bis(O,O'-diethyl dithiophosphato- κ^2S,S')cadmium(II)]- μ -4,4'-bipyridine-N:N']

The title compound, $[Cd(C_4H_{10}O_2PS_2)_2(C_{10}H_8N_2)]_n$, contains linear chains linked through the bipyridine groups. The Cd atom, lying on a center of symmetry, exhibits a slightly distorted octahedral coordination environment, consisting of four S atoms of the chelating diethyl dithiophosphate ligands and two N atoms of the bridging 4,4'-bipyridine ligand.

Comment

Tremendous interest has been attracted to organodithio derivatives of phosphorus because of their versatile coordination modes to metals (Ito, 1972; Shety & Quintus, 1970; McCleverty *et al.*, 1982; Zheng *et al.*, 1999) and their extensive commercial application, for example, in lubrication engineering and the plastics industry (So *et al.*, 1993; Mikhailov *et al.*, 1970; Lawton *et al.*, 1972). There is a great deal of literature available detailing the synthesis, chemistry and structural studies of complexes of dithiophosphate ligands. Metal-dialkyl dithiophosphate complexes have also been found to be useful (Livingstone & Mihkelson, 1970; Harrison & Kikabhai, 1987). The amines in lubrication oil are critical for the properties of the metal-dialkyl dithiophosphate additives (Shiomi *et al.*, 1989). Thus, we are interested in synthesizing other similar types of adducts. We report here the synthesis and crystal structure of a new compound, (I).

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In (I), the crystal structure consists of $Cd(dtp)_2$ units (dtp is O,O'-diethyl dithiophosphate) and each Cd atom lies on a center of symmetry. Two dtp ligands are coordinated to the

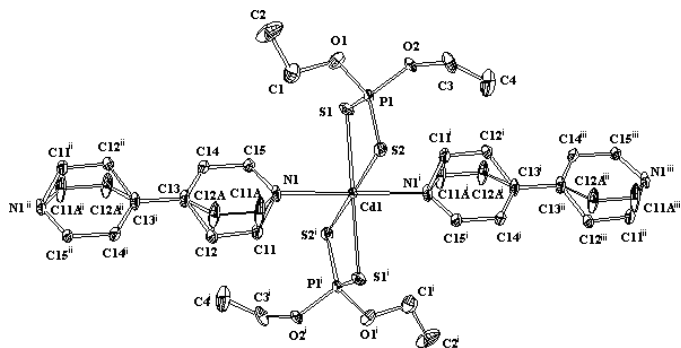


Figure 1

A section of the crystal structure of the title compound. Displacement ellipsoids are drawn at the 30% probability level. Both disorder components are shown for the bipyridine rings. H atoms have been omitted for clarity. [Symmetry codes: (i) $-1-x, 1-y, 1-z$; (ii) $-x, 1-y, 2-z$; (iii) $-2-x, 1-y, -z$.]

central metal atom through their two S atoms, resulting in a four-membered chelate ring in the equatorial plane. $\text{Cd}(\text{dtp})_2$ units are linked by the N atoms of the 4,4'-bipyridine ligands to form a linear chain (Fig. 1). Thus, the Cd atom exists in a slightly distorted octahedral configuration. A packing diagram is presented in Fig. 2.

The Cd–N bond length is in good agreement with the values in $[\text{Cd}(\text{S}_2\text{COEt})_2(\text{bpy})]$ [2.457 (6) and 2.478 (6) Å; Brendan *et al.*, 1990]. However, it is slightly longer than that in $[[\text{Cd}(\text{SC}(\text{O})\text{Ph})_2(\mu\text{-bpy})_n]$ [2.333 (2) Å; Vittal *et al.*, 2003].

The Cd–S distances are close to those found in $[\text{Cd}(\text{Et-dtp})_2(\text{hex})_2]$ [Et-dtp is diethyl dithiophosphate; 2.682 (1) and 2.704 (1) Å; Shimoi *et al.*, 1982] and $[\text{Cd}(\text{C}_3\text{H}_5\text{OS}_2)_2(\text{C}_{15}\text{H}_{16}\text{N}_2\text{O}_2\text{S})]$ [2.606 (2) and 2.710 (2) Å; Sun *et al.*, 1994], basically consistent with six-coordinated Cd complexes. Although some C atoms of the bipy ring exhibit disorder, this has no serious effect on the structure. However, the Cd–S bonds are longer than those in tetrahedral $[\text{Cd}(\text{S}_2\text{P}(\text{OCH}_3)_2)_2]$ [2.565 (2) and 2.571 (2) Å; Ito & Otake, 1996] and $[\text{Cd}(\text{S}_2\text{P}^t\text{Bu}_2)_2]$ (Byrom *et al.*, 2000). The S–P distances are close to the typical double bond length (1.94 Å).

The S1–Cd–S2 and S1–P1–S2 angles [76.86 (5) and 115.21 (8)°] are comparable with those in the complex $(\text{NMe}_4)[\text{Cd}\{\text{S}_2\text{P}(\text{OPr}^t)_2\}_3]$ [74.95 (4) and 113.36 (8)°; McCleverty *et al.*, 1982]. The four-membered ring formed by atoms Cd1, S1, S2 and P1 is almost planar and the mean deviation from the least-squares plane is 0.0036 Å.

Experimental

$\text{Cd}(\text{dtp})_2$ (0.241 g, 0.5 mmol) and 4,4'-bipyridine (0.078 g, 0.5 mmol) were dissolved in CH_2Cl_2 (10 ml). The mixture was stirred for 15 min and filtered. The filtrate was added to CH_3CN (10 ml) and allowed to stand in air at room temperature. After a few days, colorless block-shaped crystals of (I) were obtained in 60% yield. Analysis found: C 33.7, H 4.37, N 4.38%; calculated for $\text{C}_{18}\text{H}_{28}\text{CdN}_2\text{O}_4\text{P}_2\text{S}_4$: C 33.8, H 4.42, N 4.38%. IR (KBr pellet, cm^{-1}): 2983 (s), 2898 (s), 1600 (w), 1533 (s), 1533 (s), 1439 (m), 1384 (m), 1410 (m), 1218 (m), 1014 (w), 943 (w), 807 (m), 788 (m), 758 (m), 678 (s), 623 (m), 660 (m), 526 (m), 490 (s).

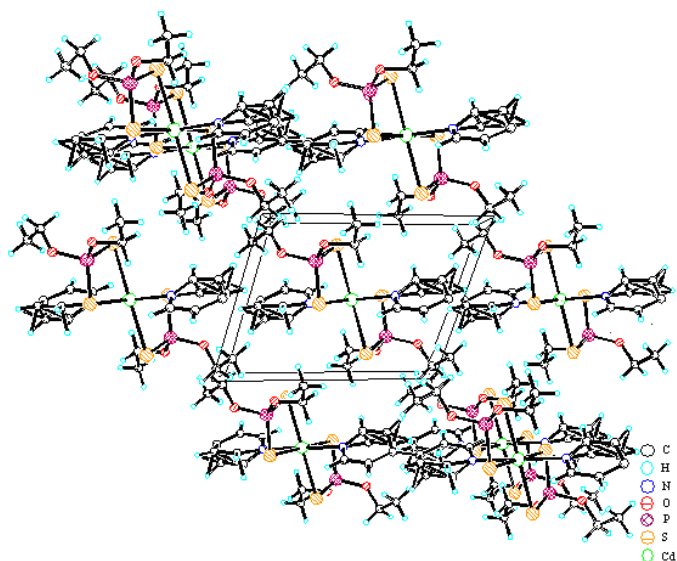


Figure 2

Packing diagram of (I).

Crystal data

$[\text{Cd}(\text{C}_4\text{H}_{10}\text{O}_2\text{PS}_2)_2(\text{C}_{10}\text{H}_8\text{N}_2)]$
 $M_r = 639.00$
 Triclinic, $P\bar{1}$
 $a = 8.819$ (6) Å
 $b = 8.852$ (5) Å
 $c = 10.404$ (6) Å
 $\alpha = 98.71$ (3)°
 $\beta = 103.96$ (4)°
 $\gamma = 118.818$ (16)°
 $V = 655.5$ (7) Å³

$Z = 1$
 $D_x = 1.619$ Mg m⁻³
 Mo $K\alpha$ radiation
 Cell parameters from 2089 reflections
 $\theta = 2.1$ – 27.5 °
 $\mu = 1.30$ mm⁻¹
 $T = 293$ (2) K
 Block, colorless
 $0.30 \times 0.15 \times 0.08$ mm

Data collection

Rigaku Mercury 70 diffractometer
 ω scans
 Absorption correction: multi-scan
 (CrystalClear; Rigaku, 2000)
 $T_{\min} = 0.791$, $T_{\max} = 0.901$
 5084 measured reflections
 2975 independent reflections

2687 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.020$
 $\theta_{\max} = 27.5$ °
 $h = -9 \rightarrow 11$
 $k = -11 \rightarrow 10$
 $l = -13 \rightarrow 12$

Refinement

Refinement on F^2
 $R[F^2 > 2\sigma(F^2)] = 0.051$
 $wR(F^2) = 0.135$
 $S = 1.04$
 2975 reflections
 161 parameters
 H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.0768P)^2 + 2.5033P]$
 where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\max} < 0.001$
 $\Delta\rho_{\max} = 2.37$ e Å⁻³
 $\Delta\rho_{\min} = -0.85$ e Å⁻³

Table 1

Selected geometric parameters (Å, °).

Cd1–N1	2.422 (4)	P1–S1	1.990 (2)
Cd1–S1	2.696 (2)	P1–S2	1.983 (2)
Cd1–S2	2.701 (2)		
N1 ⁱ –Cd1–S1	89.48 (12)	N1–Cd1–S2	92.97 (11)
N1–Cd1–S1	90.52 (12)	S1–Cd1–S2	76.86 (5)
N1 ⁱ –Cd1–S2	87.03 (11)	S1–P1–S2	115.20 (8)

Symmetry code: (i) $-1-x, 1-y, 1-z$.

In (I), two disordered atoms (C11 and C12) of the 4,4'-bipyridine ligand were split into two parts for refinement. The occupancies of these disordered components were assumed to be 0.53 and 0.47 for each of C11 and C12. Although the rings are not strongly constrained,

the C–C bond lengths involving the disordered C atoms were all reasonable. H atoms belonging to the disordered C atoms were not included. Other H atoms were placed at calculated positions (C–H = 0.93–0.97 Å), riding on their parent atoms, with $U_{\text{iso}}(\text{H}) = 1.2$ or 1.5 times $U_{\text{eq}}(\text{C})$. The highest electron-density peak is 1.04 Å from the Cd center.

Data collection: *CrystalClear* (Rigaku, 2000); cell refinement: *CrystalClear*; data reduction: *CrystalClear*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 1990); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *SHELXTL* (Bruker, 1997); software used to prepare material for publication: *SHELXTL*.

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