metal-organic papers

[μ-1,1′-Bis(diphenylphosphino)ferrocene-P,P′]bis-[bis(N,N-diethyldithiocarbamato-S,S′)cadmium(II)]

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The trinuclear title compound, (μ_2-dppf){Cd(S_2CNEt_2)_2}_2 or [Cd_2Fe(C_3H_{10}NS_2)_4(C_{21}H_{14}P)_2], is disposed about a crystallographic centre of inversion and features five-coordinate Cd atoms that exist in distorted square-pyramidal geometries defined by a PS_4 donor set.

Comment

A remarkable feature of the structural chemistry of the zinc-triad 1,1-dithiolates, *e.g.* dithiocarbamates ($^-$S_2CNR_2), xanthates ($^-$S_2COR) and dithiophosphinates ($^-$S_2PR_2), is the appearance of a wide variety of structural motifs (Cox & Tiekink, 1997). These motifs range from isolated monomeric, dimeric and tetrameric structures to two- and three-dimensional arrays. Although it is well known that the addition of a Lewis base disrupts the structure of the parent aggregate and leads to the formation of different structural types, these investigations have been largely restricted to the study of nitrogeneous bases while the chemistry with phosphine ligands is relatively unexplored, in particular for bidentate phosphine ligands.

(I)
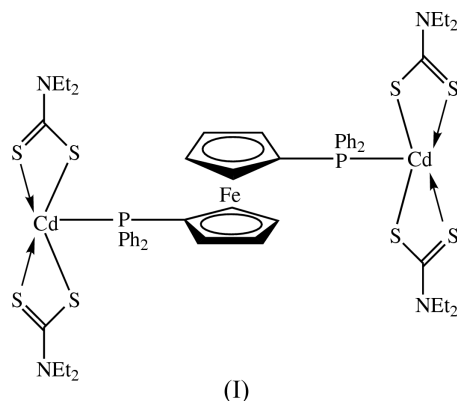
For the cadmium 1,1-dithiolates, the dimeric motif found for Cd(S_2CNEt_2)_2 (Domenicano *et al.*, 1968; Shugam & Agre, 1968; Dee & Tiekink, 2002) and Cd[S_2P(c–C_6H_{11})_2]_2 (Casas *et al.*, 1995) is disrupted upon the coordination of an equimolar amount of PEt_3 (Zeng, Hampden-Smith, Alam & Rheingold, 1994) and P(^{n}Bu)_3 (Casas *et al.*, 1995), respectively, to form monomeric structures. In the same way, the layer structure of Cd(S_2CO^{i}Pr)_2 (Iimura, 1973; Tomlin *et al.*, 1999; Tiekink, 2000) is destroyed upon adduct formation with PPh_3 to yield a five-coordinate structure (Abrahams *et al.*, 1986). In the present report, the structure of the 1:1 adduct formed between dinuclear [Cd(S_2CNEt_2)_2]_2 and bis(diphenylphosphino)-ferrocene (dppf), *i.e.* (μ-dppf){Cd(S_2CNEt_2)_2}_2, (I), is reported (Fig. 1 and Table 1).
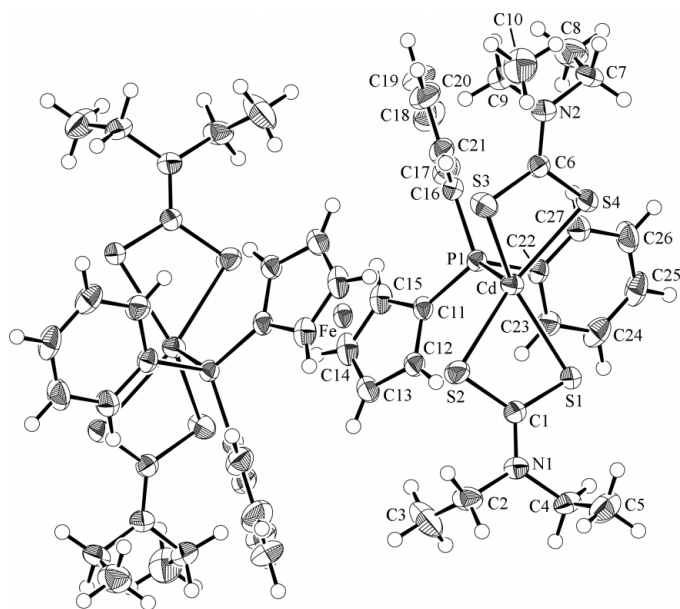
Figure 1
The molecular structure and crystallographic numbering scheme for (I). Displacement ellipsoids are shown at the 50% probability level (Johnson, 1976).

The trinuclear structure of (I) is centrosymmetric, with the Fe atom situated on a crystallographic centre of inversion. The dppf ligand bridges two $Cd(S_2CNEt_2)_2$ entities with, as implied from symmetry, the dppf adopting an open-bridge mode of coordination and an antiperiplanar staggered conformation (Bandoli & Dolmella, 2000). The Cd atom exists in a five-coordinate geometry defined by two chelating dithiocarbamate ligands and the P atom of the phosphine. The dithiocarbamate ligands chelate in an almost symmetric mode, forming a relatively narrow range of Cd—S distances of 2.6029 (5) to 2.6273 (5) Å, with an average Cd—S distance of 2.6139 (3) Å. The coordination geometry is best described as being based on a square-pyramidal geometry with the S1—S4 atoms lying, respectively, −0.1294 (5), 0.1342 (5), −0.1341 (6) and 0.1293 (5) Å out of the least-squares plane through them, so that the Cd atom is 0.6570 (1) Å above this plane in the direction of the P atom (Spek, 2000). The dihedral angle between the two CdS_2C chelate rings is 34.07 (4)°. The Cd—P bond distance of 2.6539 (5) Å is longer than the Cd—S bond distances. The most relevant structure available for comparison is the aforementioned $Cd(S_2CNEt_2)_2PEt_3$ compound [(II); Zeng, Hampden-Smith & Alam, 1994] in which the Cd atom is also five-coordinate. The influence of the nature of the phosphine is apparent in the two structures. Thus, in (II), the Cd—P distance of 2.575 (3) Å is significantly shorter than that in (I) and this impacts upon the coordination mode of the dithiocarbamate ligands, which now form asymmetric Cd—S bond distances [i.e. 2.575 (3)/2.715(2) Å and 2.557 (2)/2.723(2) Å] compared with the situation in (I). Reflecting this difference, the coordination geometry in (II) is intermediate between square pyramidal and trigonal bipyramidal. Finally, it is worth mentioning that a closely related zinc structure, viz.

$(\mu_2\text{-depe})\{Zn(S_2CNEt_2)_2\}_2$, where depe is bis(diethylphosphino)ethane, is also available in the literature (Zeng, Hampden-Smith & Larson, 1994). This structure is centrosymmetric and features a five-coordinate Zn atom that exists in a distorted trigonal-bipyramidal geometry.

Experimental

A $CHCl_3$ (50 ml) mixture of $Cd(S_2CNEt_2)_2$ (200 mg; Cox & Tiekink, 1999) and an hemimolar amount of dppf (Aldrich) was refluxed for 1 h. The solvent was removed in vacuo and the residue recrystallized from a $CHCl_3/CH_3CN$ (3:1) solution to yield yellow blocks; m.p. (decomposition) 463 K. IR (KBr) 1488 ν(C—N) and 991 ν(C—S) cm^{-1}. ^{1}H NMR ($CDCl_3$): δ 7.37–7.26 (m, 10H, phenyl H), 4.35 (m, 4H, cyclopentadienyl H), 4.00 (q, 8H, CH_2, J = 7.2 Hz) and 1.33 (t, 12H, CH_3, J = 7.2 Hz). ^{13}C NMR ($CDCl_3$): δ 203.0 (CS_2), 137.4–128.0 (phenyl C), 74.0–72.8 (cyclopentadienyl C), 50.6 (CH_2) and 12.0 (CH_3).

Crystal data

$C_{54}H_{68}Cd_2FeN_4P_2S_8$	D_x = 1.510 Mg m^{-3}
M_r = 1372.19	Mo $K\alpha$ radiation
Monoclinic, $C2/c$	Cell parameters from 24873
a = 16.6641 (6) Å	reflections
b = 13.1396 (5) Å	θ = 1.5–30.1°
c = 27.8664 (11) Å	μ = 1.30 mm^{-1}
β = 98.482 (1)°	T = 223 (2) K
V = 6034.9 (4) Å^3	Block, pale yellow
Z = 4	0.42 × 0.23 × 0.23 mm

Data collection

Bruker AXS SMART CCD diffractometer	8787 independent reflections
ω scans	7066 reflections with $I > 2\sigma(I)$
Absorption correction: multi-scan	R_{int} = 0.031
(SADABS; Bruker, 2000)	θ_{max} = 30.1°
T_{min} = 0.573, T_{max} = 0.741	$h = -23 \rightarrow 14$
24873 measured reflections	$k = -17 \rightarrow 18$
	$l = -37 \rightarrow 39$

Refinement

Refinement on F^2	H-atom parameters constrained
$R[F^2 > 2\sigma(F^2)]$ = 0.031	$w = 1/[\sigma^2(F_o^2) + (0.0404P)^2]$
$wR(F^2)$ = 0.074	where $P = (F_o^2 + 2F_c^2)/3$
S = 0.95	$(\Delta/\sigma)_{max}$ = 0.001
8787 reflections	$\Delta\rho_{max}$ = 0.71 e Å^{-3}
323 parameters	$\Delta\rho_{min}$ = −0.32 e Å^{-3}

Table 1
Selected geometric parameters (Å, °).

Cd—S1	2.6079 (5)	S3—C6	1.7310 (19)
Cd—S2	2.6175 (5)	S4—C6	1.7257 (19)
Cd—S3	2.6029 (5)	P1—C11	1.8006 (19)
Cd—S4	2.6273 (5)	P1—C16	1.8144 (19)
Cd—P1	2.6539 (5)	P1—C22	1.8212 (18)
S1—C1	1.7269 (19)	N1—C1	1.328 (2)
S2—C1	1.7196 (19)	N2—C6	1.322 (2)
S1—Cd—S2	69.213 (16)	Cd—S1—C1	86.03 (6)
S1—Cd—S3	144.657 (19)	Cd—S2—C1	85.87 (6)
S1—Cd—S4	105.851 (16)	Cd—S3—C6	85.31 (6)
S2—Cd—S3	101.051 (17)	Cd—S4—C6	84.65 (6)
S2—Cd—S4	156.76 (2)	S1—C1—S2	118.88 (11)
S3—Cd—S4	69.328 (16)	S1—C1—N1	120.77 (14)
S1—Cd—P1	102.541 (17)	S2—C1—N1	120.35 (14)
S2—Cd—P1	110.979 (18)	S3—C6—S4	118.76 (11)
S3—Cd—P1	112.501 (18)	S3—C6—N2	120.86 (15)
S4—Cd—P1	92.246 (17)	S4—C6—N2	120.38 (15)

metal-organic papers

The C-bound H atoms were placed in their geometrically calculated positions and included in the final refinement in the riding model approximation with overall isotropic displacement parameters U_{iso}: $U_{eq}(C)$ for Hsp^2, $1.25U_{eq}(C)$ for methylene H, and $1.5U_{eq}(C)$ for methyl H atoms.

Data collection: *SMART* (Bruker, 2000); cell refinement: *SAINT* (Bruker, 2000); data reduction: *SHELXTL* (Bruker, 2000); program(s) used to solve structure: *DIRDIF*92 *PATTY* (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.

References

Abrahams, B. F., Corbett, M., Dakternieks, D., Gable, R. W., Hoskins, B. F., Tiekink, E. R. T. & Winter, G. (1986). *Aust. J. Chem.* **39**, 1993–2001.
Bandoli, G. & Dolmella, A. (2000). *Coord. Chem. Rev.* **209**, 161–196.
Beurskens, P. T., Admiraal, G., Beurskens, G., Bosman, W. P., Garcia-Granda, S., Gould, R. O., Smits, J. M. M. & Smykalla, C. (1992). *The DIRDIF Program System*. Technical Report. Crystallography Laboratory, University of Nijmegen, The Netherlands.
Bruker (2000). *SMART, SAINT* and *SHELXTL* (Versions V5.6) and *SADABS* (Version 2.01). Bruker AXS Inc., Madison, Wisconsin, USA.
Casas, J. S., García-Tasende, M. S., Sánchez, A., Sordo, J., Vázquez-López, E. M., Castellano, E. E. & Zukerman-Schpector, J. (1995). *Inorg. Chim. Acta*, **239**, 87–91.
Cox, M. J. & Tiekink, E. R. T. (1997). *Rev. Inorg. Chem.* **17**, 1–23.
Cox, M. J. & Tiekink, E. R. T. (1999). *Z. Kristallogr.* **214**, 670–676.
Dee, C. M. & Tiekink, E. R. T. (2002). *Z. Kristallogr. New Cryst. Struct.* **217**, 91–93.
Domenicano, A., Torelli, L., Vaciago, A. & Zambonelli, L. (1968). *J. Chem. Soc. A*, pp. 1351–1361.
Iimura, Y. (1973). *Sci. Pap. Inst. P. C. R. (Jpn)*, **67**, 43–46.
Johnson, C. K. (1976). *ORTEP*II. Report ORNL-5138. Oak Ridge National Laboratory, Tennessee, USA.
Sheldrick, G. M. (1997). *SHELXL*97. University of Göttingen, Germany.
Shugam, E. A. & Agre, V. M. (1968). *Kristallografiya*, **13**, 253–257.
Spek, T. (2000). *PLATON*. Utrecht University, The Netherlands.
Tiekink, E. R. T. (2000). *Acta Cryst.* C**56**, 1176.
Tomlin, D. W., Cooper, T. M., Zelmon, D. E., Gebeyehu, Z. & Hughes, J. M. (1999). *Acta Cryst.* C**55**, 717–719.
Zeng, D., Hampden-Smith, M. J., Alam, T. M. & Rheingold, A. L. (1994). *Polyhedron*, **13**, 2715–2730.
Zeng, D.; Hampden-Smith, M. J. & Larson, E. M. (1994). *Acta Cryst.* C**50**, 1000–1002.