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Synthesis, crystal structure and spectroscopic properties of bis(diphenyldithiophosphinato)cadmium(II)

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Abstract

Reacting cadmium(II) perchlorate with the ammonium salt of diphenyldithiophosphinic acid in ethanol yielded the title compound, which crystallized in the triclinic space group $P\bar{1}$ with $a=9.273(1)$, $b=10.426(1)$, $c=13.845(3)$ Å, $\alpha=94.38(1)$, $\beta=103.16(1)$, $\gamma=104.63(1)°$ and $Z=2$. The crystal contains dimeric complexes in which two cadmium atoms and two bridging ligands form an eight-membered ring, the coordination of each metallic centre being made up to four by an additional S,S-dentate chelating diphenyldithiophosphinate ligand. Solid state vibrational spectra (IR and Raman) and multinuclear NMR spectra in DMSO solution (^{13}C, ^{31}P and ^{113}Cd) are discussed and compared with those of aliphatic cadmium(II) dithiophosphinates.

Key words: Crystal structures; Cadmium complexes; Bidentate ligand complexes; Chelate complexes

Introduction

The structures of cadmium(II) dithiophosphinates have barely been explored in the solid state by X-ray diffraction. As far as we are aware, only the structure of $[Cd(S_2PEt_2)_2]$ has been reported [1]. During investigation of the residual Lewis acidity exhibited by some aliphatic cadmium dithiophosphinates [2], we incidentally observed that $[Cd(S_2PPh_2)_2]$ showed certain physical differences from the alkyl derivatives (e.g. very poor solubility in solvents of low dielectric constant, and high conductivity in DMSO). This prompted us to study this compound in detail, to which end we have grown monocrystals whose structure we have solved by X-ray analysis. Despite the above mentioned dissimilar behaviour in solution, the crystal structure of the phenyl derivative is similar to that of $[Cd(S_2PEt_2)_2]$ [1]. The differences between the two structures and the spectroscopic properties of $[Cd(S_2PPh_2)_2]$ are discussed below.

Experimental

Ammonium diphenyldithiophosphinate was prepared as described previously [3] and $Cd(ClO_4)_2\cdot 6H_2O$ (Merck) (**Caution**) was used as received. Elemental analysis was performed with a Carlo Erba 1108 microanalyser. Mass spectra were recorded on a Kratos MS50TC spectrometer connected to a DS90 data system and operating under EI conditions (direct insertion probe, 70 eV, 250 °C). All the ions were identified using the DS90 software. IR spectra were recorded in KBr pellets on a Perkin Elmer 1330 spectrometer. The Raman spectrum was obtained with a Dilor Omars 89 spectrometer (argon ion laser, 5145 Å). ^{13}C (62.83 MHz), ^{31}P (101.26 MHz) and ^{113}Cd (55.84 MHz) NMR spectra were recorded in DMSO-d_6 (in 10 mm o.d. tubes at room temperature) on a Bruker WM-250 spectrometer and were referred to the solvent signal, 85% H_3PO_4 and 0.1 M $Cd(ClO_4)_2$, respectively. Conductivity measurements were made with a WTW conductivity meter.

Preparation of $[Cd(S_2PPh_2)_2]$

A solution of $Cd(ClO_4)_2\cdot 6H_2O$ (0.55 g, 1.3 mmol) in ethanol (5 ml) was slowly added, with stirring, to

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$NH_4S_2PPh_2$ (0.70 g, 2.6 mmol) dissolved in ethanol (10 ml). The white solid formed after stirring was filtered out, washed with ethanol and dried under vacuum. M.p. 170 °C (decomposition). *Anal.* Found: C, 47.2; H, 3.5; S, 22.5. Calc. for $C_{24}H_{20}P_2S_4Cd$: C, 47.2; H, 3.3; S, 22.0%. Molar conductivity: 23.4 S cm^2 mol^{-1} (10^{-3} M in DMSO). The base peak and the main metallated ion in the mass spectrum (based on the isotope ^{114}Cd) were at *m/z* (%) 217 (Ph_2PS, 100) and 612 (*M*, 11.5). Monocrystals suitable for X-ray diffraction studies were grown by recrystallization from DMSO.

Crystal structure determination of [Cd(S₂PPh₂)₂]

Crystal data

$C_{24}H_{20}P_2S_4Cd$, $M=611.03$, triclinic, $a=9.273(1)$, $b=10.426(1)$, $c=13.845(3)$ Å, $\alpha=94.38(1)$, $\beta=103.16(1)$, $\gamma=104.63(1)°$, $U=1248.3(7)$ Å^3 (by least-squares refinement on diffractometer angles for 25 automatically centred reflections, $13<\theta<22°$; $\lambda=0.71073$ Å), space group $P\bar{1}$, $Z=2$, $D_c=1.625$ g cm^{-3}, μ(Mo Kα)$=13.30$ mm^{-1}.

Data collection and processing

An irregular crystal of maximum and minimum linear dimensions 0.50 and 0.25 mm was examined at room temperature on a CAD4 diffractometer, using $\omega/2\theta$ mode with ω scan width$=0.8+0.35\tan\theta$ and graphite monochromated Mo Kα radiation. Of the 4576 reflections measured ($0<\theta<25°$, $-11<h<10$, $12<k<12$, $0<l<16$), 4267 were unique (merging $R=0.014$), of which 3878 with $I>3\sigma(I)$ were used in refinement after correction for Lorentz and polarization effects. Absorption corrections were applied at a later stage in the refinement [4] (max. and min. correction factors 1.13 and 0.77). The intensity of one standard reflection was essentially constant throughout the experiment.

Structure analysis and refinement

The structure was solved by standard direct methods followed by normal difference Fourier techniques. Full-matrix least-squares refinement enabled all the non-H atoms in the structure to be located. These were assigned anisotropic thermal parameters. H atoms were not included in the model. The function minimized, $\Sigma w(|F_o|-|F_c|)^2$ with the weighting $w=1/[\sigma^2(F_o)+0.0003{*}F_o{}^2]$, gave final R $(=\Sigma(|F_o|-|F_c|)/\Sigma|F_o|)$ and R' $(=[\Sigma w(|F_o|-|F_c|)^2/\Sigma wF_o{}^2]^{1/2})$ values of 0.036 and 0.041, respectively. Refinement of data used scattering factors for non-H atoms from Cromer and Mann [5] with corrections for anomalous dispersion from Cromer and Liberman [6]. Calculations were performed on a VAX 6420 computer using the programs SHELX76 [7], SCHAKAL and ORTEP [8]. Atomic positions are listed in Table 1.

TABLE 1. Fractional atomic coordinates and equivalent isotropic temperature factors (Å^2)

Atom	*x/a*	*y/b*	*z/c*	B_{iso}^{a}
Cd	0.4508(1)	0.1156(1)	0.3987(1)	3.121(9)
P(1)	0.4358(1)	0.1570(1)	0.6583(1)	2.55(2)
P(2)	0.2354(1)	0.2275(1)	0.2409(1)	2.66(2)
S(11)	0.5993(1)	0.1831(1)	0.5799(1)	2.81(2)
S(12)	0.3538(1)	−0.0340(1)	0.6770(1)	3.65(3)
S(21)	0.4507(1)	0.3338(1)	0.3135(1)	3.26(3)
S(22)	0.1725(1)	0.0553(1)	0.2988(1)	3.41(3)
C(111)	0.2800(4)	0.2228(4)	0.5981(3)	2.9(1)
C(112)	0.3160(5)	0.3429(4)	0.5576(3)	3.5(1)
C(113)	0.1962(7)	0.3940(6)	0.5116(4)	4.7(1)
C(114)	0.0447(6)	0.3242(6)	0.5070(4)	5.1(2)
C(115)	0.0113(6)	0.2067(6)	0.5468(5)	5.1(2)
C(116)	0.1285(5)	0.1530(5)	0.5936(4)	4.0(1)
C(121)	0.5297(5)	0.2573(4)	0.7786(3)	3.1(1)
C(122)	0.4894(5)	0.3708(4)	0.8078(3)	3.4(1)
C(123)	0.5707(7)	0.4492(5)	0.8998(4)	4.9(1)
C(124)	0.6857(8)	0.4095(7)	0.9628(4)	6.4(2)
C(125)	0.7223(7)	0.2936(8)	0.9352(4)	6.7(2)
C(126)	0.6471(6)	0.2192(6)	0.8419(4)	5.2(2)
C(211)	0.0980(5)	0.3236(4)	0.2449(3)	3.0(1)
C(212)	−0.0549(5)	0.2569(5)	0.2345(4)	4.0(1)
C(213)	−0.1604(6)	0.3336(6)	0.2359(4)	4.7(1)
C(214)	−0.1113(6)	0.4703(6)	0.2469(4)	4.5(1)
C(215)	0.0438(6)	0.5365(5)	0.2572(4)	4.8(2)
C(216)	0.1481(5)	0.4631(4)	0.2568(4)	3.7(1)
C(221)	0.2243(5)	0.1876(4)	0.1095(3)	3.2(1)
C(222)	0.3327(7)	0.1335(7)	0.0803(5)	6.1(2)
C(223)	0.3257(8)	0.1026(8)	−0.0201(5)	7.0(2)
C(224)	0.2119(7)	0.1203(6)	−0.0922(4)	5.6(2)
C(225)	0.1026(8)	0.1739(9)	−0.0656(5)	7.6(2)
C(226)	0.1065(7)	0.2071(8)	0.0352(4)	6.6(2)

$^aB_{iso}=\frac{4}{3}\Sigma_{ij}B_{ij}\mathbf{a}_i\mathbf{a}_j$.

Results and discussion

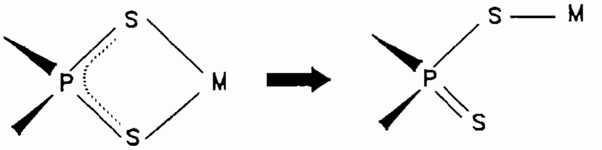
Description of the structure

The lattice is formed by discrete centrosymmetric dimers (Fig. 1) similar to those observed in $[Cd(S_2PEt_2)_2]$ [1] and $[Zn(S_2PPr_2)_2]$ [9]. Each cadmium atom is coordinated to two bridging ligands and one chelating ligand, giving rise to a distorted tetrahedral kernel with S–Cd–S angles ranging from 79.85 (imposed by the ligand bite) to 137.35° (Table 2). The chelating ligand is slightly more anisobidentate in the phenyl derivative, and the two Cd–S bridging distances are more unequal in this compound (see Table 3, where the values of the chief structural parameters of the three above-mentioned dithiophosphinates are listed for comparison). The P–S distances (Tables 2 and 3) reflect these differences in the metal–sulfur bonds, longer Cd–S distances accompanying shorter phosphorus–sulfur bonds in $[Cd(S_2PPh_2)_2]$ as the π charge on the PS_2 group evolves towards the distribution indicated in the following.

TABLE 2. Significant interatomic distances (Å) and angles (°) with e.s.d.s in parentheses[a]

Cd–S(11)	2.520(1)	P(1)–C(111)	1.815(4)
Cd–S(21)	2.641(1)	P(1)–C(121)	1.800(4)
Cd–S(22)	2.528(1)	P(2)–S(21)	2.006(2)
Cd–S(12)^{i}	2.572(1)	P(2)–S(22)	2.027(2)
Cd–S(11)^{i}	3.078(1)	P(2)–C(211)	1.816(5)
P(1)–S(11)	2.034(2)	P(2)–C(221)	1.808(5)
P(1)–S(12)	2.004(2)		
S(11)–Cd–S(21)	108.87(4)	S(11)–P(1)–C(111)	109.9(1)
S(11)–Cd–S(22)	137.35(4)	S(11)–P(1)–C(121)	105.4(1)
S(11)–Cd–S(12)^{i}	101.08(4)	S(12)–P(1)–C(111)	110.6(1)
S(21)–Cd–S(22)	79.85(4)	S(12)–P(1)–C(121)	109.5(2)
S(21)–Cd–S(12)^{i}	99.75(4)	C(111)–P(1)–C(121)	107.9(2)
S(22)–Cd–S(12)^{i}	118.93(4)	S(21)–P(2)–S(22)	110.75(7)
Cd–S(11)–P(1)	105.00(5)	S(21)–P(2)–C(211)	111.6(1)
P(1)–S(12)–Cd^{i}	94.03(6)	S(21)–P(2)–C(221)	109.7(2)
Cd–S(21)–P(2)	82.97(5)	S(22)–P(2)–C(211)	109.9(1)
Cd–S(22)–P(2)	85.54(5)	S(22)–P(2)–C(221)	109.2(2)
S(11)–P(1)–S(12)	113.25(7)	C(211)–P(2)–C(221)	105.5(2)

[a]Symmetry operation: $^{i}-1-x,\ -y,\ 1-z$.



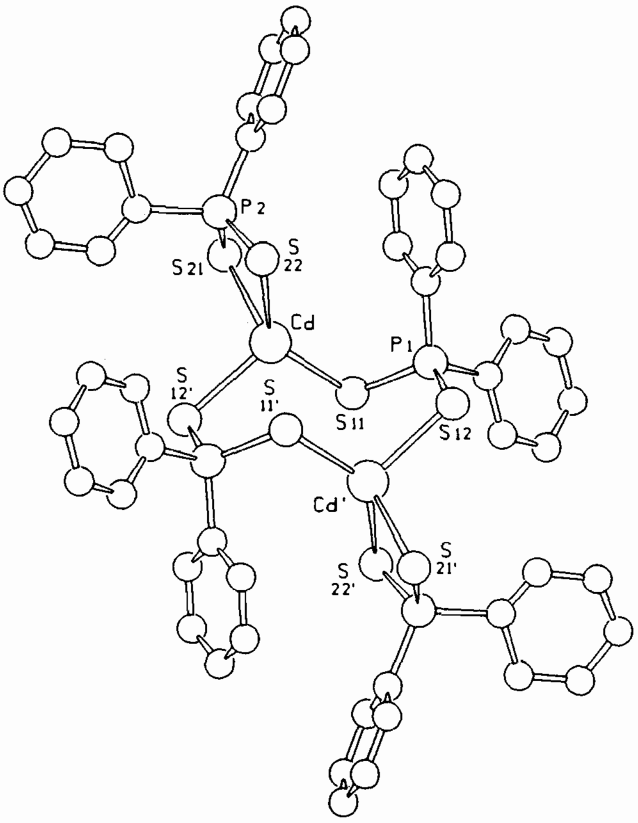


Fig. 1. The structure of $[Cd(S_2PPh_2)_2]$, with the atom-numbering scheme.

All these bond differences mean that in $[Cd(S_2PPh_2)_2]$ the twisted chair-shaped eight-membered (P–S–Cd–S)$_2$ ring is more distorted than in $[Cd(S_2PEt_2)_2]$. Weak Cd...S(11′) and Cd′...S(11) interactions form across the ring (interatomic distance 3.078 Å; sum of the van der Waals radii 3.40 Å [10]), suggesting, as with the ethyl derivative, the presence of some residual Lewis acidity on the metal. There is no evidence for significant interdimeric covalent interactions (Fig. 2). In order to account for the differences in physico-chemical behaviour between the two compounds, one is tempted to argue that the distortion in the eight-membered ring may increase some local electrostatic packing forces in the lattice, even though the dimer units remain non-polar overall due to the permanence of a centre of symmetry.

IR and Raman solid state spectra

The vibrational spectra of the complex $[Cd(S_2PPh_2)_2]$ show ν_{asym}(P–S) as a strong broad IR band at 635 cm^{-1} and ν_{sym}(P–S) as a strong Raman band at 561 cm^{-1} (strong IR band at 555 cm^{-1}). The parameter $\Delta\nu = \nu_{asym}(PS) - \nu_{sym}(PS)$ has been used [11, 12] as indicative of the coordination mode of the ligand: its value for $[Cd(S_2PPh_2)_2]$, ≈80 cm^{-1}, is in the middle of the range 70–90 cm^{-1} reported for anisobidentate bicoordination. Although solid-state effects cannot be ruled out, the bridging ligand shown by the X-ray study may be responsible for the broadness of the bands; in fact, ν_{sym}(PS) was split in the IR spectrum recorded using crystals instead of powder.

Behaviour in solution

Unlike the diethyl- and dicyclohexyldithiophosphinates of cadmium(II) [2], $[Cd(S_2PPh_2)_2]$ is not soluble

TABLE 3. Some structural parameters of dimeric zinc(II) and cadmium(II) dithiophosphinates

Compound	Chelating ligand			Bridging ligand			M···S[a]	Reference
	M–S	S–P	S–P–S	M–S	S–P	S–P–S		
$[Zn(S_2PPr_2)_2]$	2.344	2.011		2.306	2.005			
	2.447[b]	1.987[b]	86.3[b]	2.321	2.002	118.2		9
$[Cd(S_2PEt_2)_2]$	2.543(2)	2.031(3)		2.557(2)	2.028(3)			
	2.653(3)	1.991(3)	110.5(1)	2.544(2)	2.030(3)	113.8(1)	3.1[c]	1(b)
$[Cd(S_2PPh_2)_2]$	2.641(1)	2.006(2)		2.520(1)	2.034(2)			
	2.528(1)	2.027(2)	110.75(7)	2.572(1)	2.004(2)	113.25(2)	3.078(1)	this work

[a] Weak intramolecular interactions. [b] Average values. [c] Values calculated using published parameters.

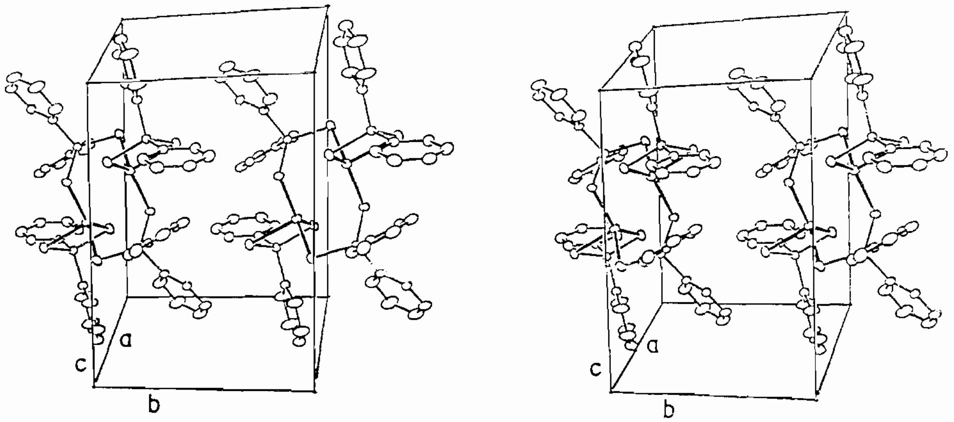


Fig. 2. ORTEP stereoscopic view of the packing in the lattice of $[Cd(S_2PPh_2)_2]$.

in organic solvents of low dielectric constant, such as $CHCl_3$ or CH_2Cl_2. However, it readily dissolves in DMSO, in which its electrical conductivity (23.4 S cm^2 mol^{-1} at 10^{-3} M) is lower than that of ammonium diphenyldithiophosphinate (31.7 S cm^2 mol^{-1}) but clearly higher than the values reported for $[Cd(S_2PR_2)_2]$ (R = Et, Cy), 7.3 and 4.1 S cm^2 mol^{-1} [2]. Thus the solution of $[Cd(S_2PPh_2)_2]$ in DMSO must involve a fairly ionogeneous equilibrium, possibly involving partial displacement of the ligand by the solvent. Note that total dissociation of $S_2PPh_2^-$ from the cadmium(II) coordination sphere would give a higher conductivity corresponding to a 2:1 electrolyte.

The occurrence of partial dissociation is supported by the differences between the chief NMR parameters of $[Cd(S_2PPh_2)_2]$ and those of $NH_4S_2PPh_2$ (see Table 4, which also lists data for $[HgMe(S_2PPh_2)]$). Like those of dialkyldithiophosphinates of cadmium(II) [2], the ^{31}P spectrum of $[Cd(S_2PPh_2)_2]$ consists of a single resonance. In this case, this behaviour may be attributed not only to a possible intrinsic lability leading to a time-averaged signal encompassing both the bridging and the chelating ligands, but also to the influence of the dissociation equilibrium induced by the solvent. In both the cadmium and the methylmercury(II) complexes [13], ^{31}P is only slightly less shielded than in the ammonium salt. Complexation seems to shift the *ipso* carbon signal of the phenyl groups toward lower frequencies, and to increase the C_i–P coupling constant slightly. The most significant spectroscopic difference between the diethyl- [2] and diphenyldithiophosphinates of cadmium(II) concerns the ^{113}Cd signal, which shifts from 231.3 ppm in the former to 159.2 ppm in the phenyl derivative, in keeping with the more ionic character of the latter solution.

TABLE 4. Significant NMR parameters[a]

Compound	$\delta(^{13}C)C_i$	$^1J(^{13}C-^{31}P)$	$\delta(^{31}P)$
$NH_4S_2PPh_2$	145.75	77.0	63.0
$[Cd(S_2PPh_2)_2]$	140.06	79.5	65.9
$[HgMe(S_2PPh_2)]$	139.65	81.5	64.6

[a] DMSO-d$_6$ as solvent.

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