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THE X-RAY CRYSTAL STRUCTURE OF BIS(DICYCLOHEXYLDITHIOPHOSPHATO)CADMIUM(II)

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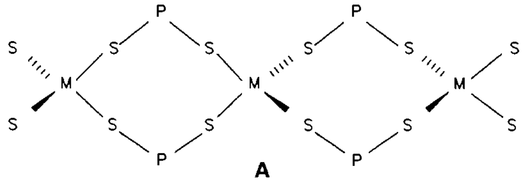
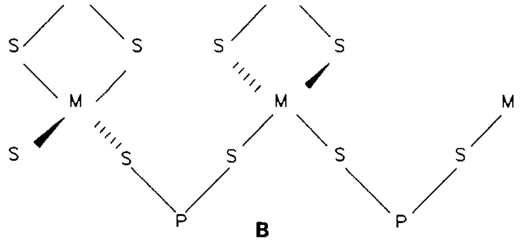
Abstract—The compound bis(dicyclohexyldithiophosphato)cadmium(II), $[Cd\{S_2P(OCy)_2\}_2]$, has been obtained by reacting cadmium(II) perchlorate with the sodium salt of dicyclohexyldithiophosphoric acid in ethanol. Its structure was solved by X-ray diffraction. The structure consists of dimers in which each metal centre is coordinated by a chelating ligand and two bridging ligands, giving a coordination number of 4. The two bridging ligands and the two cadmium atoms form an eight-membered ring with a twisted chair conformation.

Previous papers on complexes formed between Group 12 elements and dithiophosphorus ligands, $[M(S_2PX_2)_2]$ [M = Zn, Cd, Hg; X = R (dithiophosphinates), OR (dithiophosphates)], have mentioned three solid state structural arrangements.[1] In the first, **A**, bridging ligands give rise to polymeric structures, as in $[Hg\{S_2P(OEt)_2\}_2]$:[2]



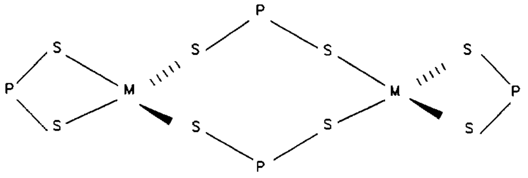
A

The second, **B**, found in $[Zn\{S_2P(OEt)_2\}_2]$ and $[Hg\{S_2P(O^iPr)_2\}_2]$,[3] is also polymeric, but contains both chelating and bridging ligands:



B

The third, **C**, found in several Zn^{II} and Cd^{II} dithiophosphates and dithiophosphinates,[4] likewise contains both chelating and bridging ligands, but since the latter form pairs linking the same two metal centres, crystals consist of dimers instead of polymers.



C

In case **C**, the central eight-membered ring of the dimer has a twisted chair conformation in centrosymmetric dimers and a saddle conformation in dimers with a two-fold axis or no symmetry at all.[1] The above arrangements probably differ very little in energy, allowing changes in ligand substituents to induce changes in the type of structure adopted. $[Zn\{S_2P(OEt)_2\}_2]$, for example, crystallizes with a type **B** structure,[3] and $[Zn\{S_2P(O^iPr)_2\}_2]$ with a type **C** structure[4] (*cf.* also the dithiophosphates of mercury(II) referred to above). Nevertheless, all cadmium(II) derivatives studied by X-ray diffraction have been found to have type **C** structures, with twisted chair conformations in the case of dithiophosphinates and saddle conformations[4] in the case of isopropyldithiophosphates.

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We report here the synthesis and spectroscopic and structural properties of $[Cd\{S_2P(OCy)_2\}_2]$ (for an alternative synthetic route see ref. 5). Its structure, solved by X-ray diffraction, consists of the usual dimers, but unlike those of the isopropyl derivative,[4] they have a twisted chair conformation. The influence of this conformational change on the Cd-ligand bonds is discussed.

EXPERIMENTAL

$Cd(ClO_4)_2 \cdot 6H_2O$ (Merck) was used as received. Sodium dicyclohexyldithiophosphate was obtained by addition of sodium carbonate to dicyclohexyldithiophosphoric acid, prepared by published methods.[6,7] Elemental analysis was performed with a Carlo Erba 1108 Microanalyser. IR spectra were recorded in KBr pellets on a Mattson Cygnus 100 FT-IR spectrometer. Proton decoupled ^{13}C (62.83 MHz), ^{31}P (101.26 MHz) and ^{113}Cd (55.84 MHz) NMR spectra were recorded in $CDCl_3$ (in 5 or 10 mm o.d. tubes at room temperature) on a Bruker WM-250 spectrometer and were referred to TMS, 85% H_3PO_4 and 0.1 M $Cd(ClO_4)_2$, respectively.

Synthesis of $[Cd\{S_2P(OCy)_2\}_2]$

$Cd(ClO_4)_2 \cdot 6H_2O$ (0.46 g, 1.10 mmol) dissolved in ethanol (10 cm^3) was added to sodium dicyclohexyldithiophosphate (0.70 g, 2.21 mmol) dissolved in the same solvent (20 cm^3). The mixture was stirred overnight and the resulting solution was slowly concentrated until a white solid appeared. M.p. 180°C. Found, C 41.1, H 6.8, S 18.2; Calc. for $C_{24}H_{44}O_4P_2S_4Cd$, C 41.2, H 6.3, S 18.3%. IR: 1036s, 976vs $\nu(O—R)$, 829s, 789s $\nu(PO_2)$, 658s, 638s $\nu(PS_2)_{asym}$, 573m $\nu(PS_2)_{sym}$. ^{13}C NMR: δ(ppm) 79.1d, C_i, $^2J(^{13}C—^{31}P)$ 7.7 Hz; ^{31}P NMR: δ 98.6; ^{113}Cd NMR: δ 386.4s.

Recrystallization of this solid in chloroform yielded crystals suitable for X-ray studies.

Crystal structure of $[Cd\{s_2P(OCy)_2\}_2]$

X-Ray data collection and reduction. A colourless prismatic crystal of approximate dimensions $0.16 \times 0.08 \times 0.08$ mm^3 was obtained by recrystallization from chloroform and used in X-ray analysis.

Crystallographic data: $C_{24}H_{44}O_4P_2S_4Cd$, m_r = 699.2, monoclinic, space group $P2_1/n$ (No. 14), $Z = 4$, $a = 10.266(2)$, $b = 20.255(2)$, $c = 16.105(5)$ Å, $\beta = 107.252°$, $V = 3198.1(1)$ Å^3, $D_{calc} = 1.452$ g cm^{-3} and $\mu(Mo\text{-}K_\alpha) = 10.556$ cm^{-1}.

Data for structure determination were collected at room temperature with a CAD-4 Enraf–Nonius automatic diffractometer with graphite monochromated Mo-K_α radiation ($\lambda = 0.70930$ Å). The $\omega/2\theta$ scan technique was used. Of the 9126 reflections collected in the range 3–29°, 1836 with $I > 3\sigma(I)$ were used for refinement. Absorption corrections were applied[8] (max. correction factor 1.250, min. 0.512).

Structure solution and refinement. The structure was solved using direct methods and subsequent Fourier difference maps. Cadmium, sulphur, phosphorus and oxygen were refined with anisotropic displacement parameters. All carbon atoms were refined with isotropic displacement parameters, except those of the cyclohexyl ring bound to O(12), which were given their own individual isotropic temperature factors and fixed positional parameters. The positions of all H atoms were calculated geometrically (C—H = 0.95 Å) and included in structure factor calculations with $B_{iso} = 4.0$ Å^2 fixed, but were not refined. The secondary extinction coefficient was 1.0618×10^{-8}. Final R and R_w values were 0.086 and 0.089 for 179 parameters, and the maximum height in the final ΔF map was 0.787 eÅ^{-3} around the Cd atom. Most calculations were performed on a DEC MicroVAXII computer with the programs SHELXS86,[9] VAXSDP[10] and SCHAKAL.[11]

RESULTS AND DISCUSSION

Table 1 lists selected bond distances and angles and Fig. 1 shows the atom numbering scheme used.

Cadmium(II) bis-dicyclohexyldithiophosphate crystallizes as centrosymmetric dimers in which an eight-membered centrosymmetric ring in twisted chair conformation is formed by two dithiophosphate ligands bridging between two cadmium atoms (Fig. 1). Additionally, each cadmium atom is coordinated to the two sulphur atoms of a chelating ligand, which complete a distorted tetrahedral coordination polyhedron with minimum and maximum S—Cd—S angles of 78.3(2) (imposed by the ligand bite) and 131.4(2)° respectively.

The structure is similar to those found in other dithiophosphorus (dithiophosphate and dithiophosphinate) compounds of main group elements ($[M^{II}(S_2PR_2)_2]$: M = Zn, R = Pr^{4c} or OPr_{iso};[4a] M = Cd, R = Et,[4d,4e] Ph[4f] or OPr_{iso};[4a] M = Pb, R = OPh[12]). The major difference between the cyclohexyl and isopropyl cadmium derivatives concerns the conformation of the eight-membered ring, which is a twisted chair in the former and a saddle in the latter. This is in keeping with the suggestion[4a] that the R group determines the final symmetry of the dimer in the crystalline state, possibly due to packing considerations. This difference in con-

Table 1. Selected bond lengths (Å) and angles (°) for [Cd{$S_2P(OCy)_2$}$_2$]

Cd—S(11)	2.526(8)	S(21)—P(2)	1.988(9)
Cd—S(12)	2.660(8)	S(22)—P(2)^i	1.962(9)
Cd—S(21)	2.517(5)	P(1)—O(11)	1.57(2)
Cd—S(22)	2.544(6)	P(1)—O(12)	1.71(2)
S(11)—P(1)	1.96(1)	P(2)—O(21)	1.58(2)
S(12)—P(1)	1.97(1)	P(2)—O(22)	1.54(1)
S(11)—Cd—S(12)	78.3(2)	S(11)—P(1)—O(11)	110.7(8)
S(11)—Cd—S(21)	131.4(2)	S(11)—P(1)—O(12)	112.9(9)
S(11)—Cd—S(22)	111.9(2)	S(12)—P(1)—O(11)	112.3(9)
S(12)—Cd—S(21)	107.0(2)	S(12)—P(1)—O(12)	110.0(9)
S(12)—Cd—S(22)	99.0(2)	O(11)—P(1)—O(12)	98(1)
S(21)—Cd—S(22)	114.7(2)	S(21—P(2)—S(22)^i	114.2(4)
Cd—S(11)—P(1)	86.1(4)	S(21)—P(2)—O(21)	112.6(8)
Cd—S(12)—P(1)	82.5(3)	S(21)—P(2)—O(22)	105.8(6)
Cd—S(21)—P(2)	103.1(3)	S(22)—P(2)^i—O(21)^i	103.2(7)
Cd—S(22)—P(2)^i	93.9(3)	S(22)—P(2)^i—O(22)^i	112.9(6)
S(11)—P(1)—S(12)	113.0(4)	O(21)—P(2)—O(22)	108.3(9)

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

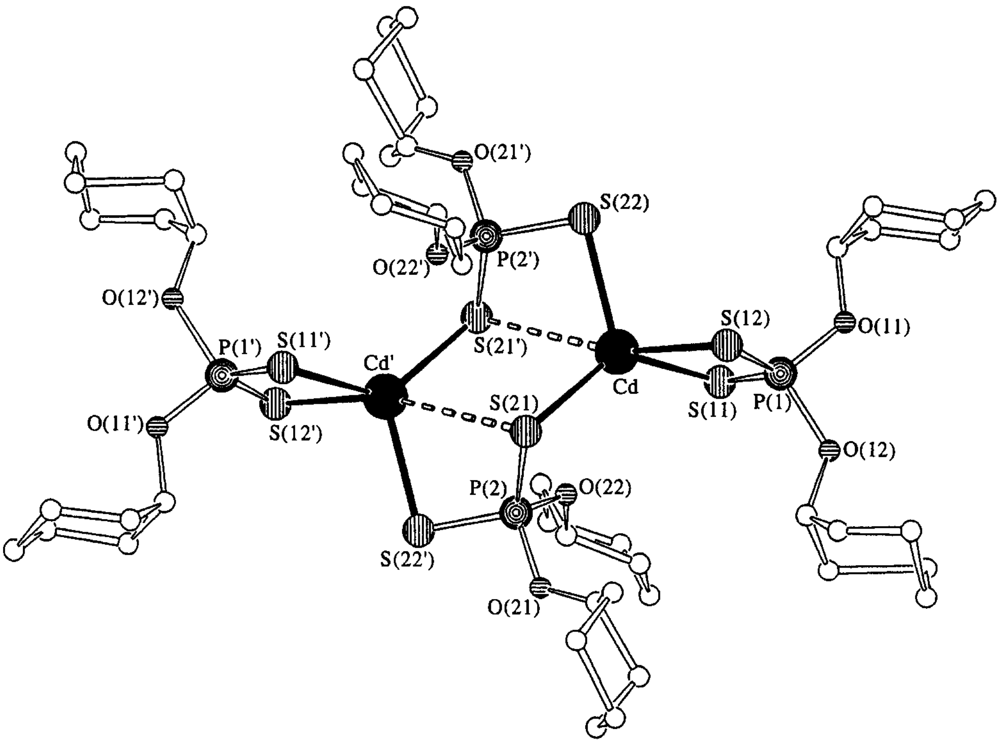

Fig. 1. Structure of [Cd{$S_2P(OCy)_2$}$_2$], with the atom-numbering scheme.

Table 2. Bond distances (Å) and bond angles (°) in dimeric cadmium dithiophosphates and dithiophosphinates

Compound	Ring conformation[a]	Chelating ligand			Bridging ligand			Cd···S	Ref.
		Cd—S	S—P	S—P—S	Cd—S	S—P	S—P—S		
$[Cd(S_2PEt_2)_2]$	TC	2.543(2) 2.653(2)	2.031(3) 1.991(3)	110.5(1)	2.557(2) 2.544(2)	2.028(3) 2.030(3)	113.8(1)	3.1	4e
$[Cd(S_2PPh_2)_2]$	TC	2.641(1) 2.528(1)	2.006(2) 2.027(2)	110.75(7)	2.520(1) 2.572(1)	2.034(2) 2.004(2)	113.25(2)	3.078(1)	4f
$[Cd\{S_2P(OPr)_2\}_2]$	S	2.552(7) 2.590(8)	1.974(2) 1.972(2)	112.2(5)	2.486(7) 2.499(7)	1.957(11) 1.962(9)	116.0(5)	3.194(8)	4a
$[Cd\{S_2P(OCy)_2\}_2]$	TC	2.526(8) 2.660(8)	1.96(1) 1.97(1)	113.0(4)	2.517(5) 2.544(6)	1.988(9) 1.962(9)	114.2(4)	3.34	This work

[a] S = saddle, TC = twisted chair.

formation is probably responsible for other minor differences (see Table 2): the chelating ligand is slightly more anisobidentate in the cyclohexyl derivative, and the two Cd—S bridging distances are also longer and more unequal in this compound. This, in turn, could explain the larger Cd—S transannular distance [Cd—S(21)^i = 3.34Å; $i = -x, -y, 1-z$], which is slightly shorter than the sum of the Van der Waals radii (3.40Å).[13] The Cd—S distances in this dithiophosphate are in fact more similar to those found in cadmium dithiophosphinates ($[Cd(S_2PR_2)_2]$; R = Et or Ph[4d–f]), although the dimer ring is more open in the dithiophosphate derivative (Table 2). The P—S distances of $[Cd\{S_2P(OCy)_2\}_2]$ lie in the range found in other dithiophosphate complexes with bridging or chelating ligands.

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