Polymeric Structure and Solid NMR Spectra of Cadmuim (II) Dialkyldithiophosphates (Alkyl = Propyl, Butyl, Isopropyl and Isobutyl)

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By dropwise adding thio ligands to concentrated aqueous solutions of $Cd(ClO_4)_2 \cdot 6H_2O$, polymeric complexes, Cd(II) *O*, *O'*-dipropyldithiophosphate (1), *O*, *O'*-dibutyl-dithiophosphate (2), *O*, *O'*-diisopropyl-dithiophosphate (3) and *O*, *O'*-diisobutyl-dithiophosphate (4) were obtained. The structure of 4 was determined by X-ray diffraction analysis, showing that the metal ion sits in distorted tetrahedral sulphur coordination sphere and that the eight-membered bimetallic rings take the twist chair and boat conformations, alternately. Based on facts that the S(1)—Cd bond length [0.25099(12) nm] is shorter than the other S—Cd bond length [0.25399(12)—0.25701(18) nm] and that the S(1)-involving angles [113.45(4)°—118.43(5)°] are systematically larger than the normal angles of a tetrahedron, the ligands are hypothesized to be erratically functionalized to Cd(II). To certify the steric nonequivalence of ligands, the compounds were investigated by solid ^{13}C, ^{31}P and ^{113}Cd NMR spectroscopy.

Keywords dialkyldithiophosphate, cadmium complex, crystal structure, solid NMR

Introduction

It has been well reviewed by Haiduc *et al.*[1] that the dithiophosphates are good building blocks for molecular architecture owing to their changeable dentation and particular affinity toward metal ions. Complexes prepared from such ligands and a metal ion can exist in different structures. For example relevant to this work, the IIB transition metal complexes crystallographically defined so far have provided the samples in Fig. 1.[2-16]

Amongst the schemed structures, the **e** type was first and only exemplified by $[Hg\{S_2P(OEt)_2\}_2]$.[11,17] More recently, a Cd(II) complex in **c** form was reported by Byrom.[6] It was afforded by reaction of $CdSO_4$ hydrate and diisobutyldithiophosphate in molar ratio 1:2 and found to contain chair-formed bimetallic rings in it. Attempt to reprepare the compound and analogues by dropwise adding ligands to metal solutions in the same ratio resulted in the formation of polymeric compounds. Their structures were exemplified by that of **4**. Here the contribution intends to note the preparation, the structure and NMR spectral features of the polymeric complexes.

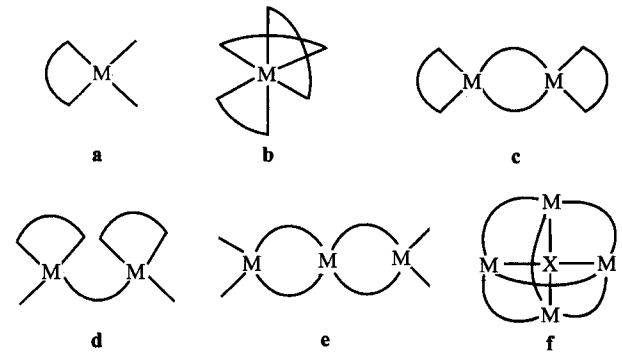

Fig. 1 Frameworks of IIB metal complexes of dialkyldithiophosphates (X = S, O).

Experimental

Chemicals

Potassium *O*, *O'*-dialkyldithiophosphates were obtained as 49%—51% aqueous solutions from kind donation of Cheminova Company (Denmark). $Cd(ClO_4)_2 \cdot 6H_2O$ was a crystalline product of G. Frederick Smith Company. They were used as received without further treatment.

Physical measurements

IR spectra were recorded on a Perkin-Elmer 2000 FT-IR spectrometer (KBr disks). Microanalyses were performed on a CHNS (LEGO) analyzer. NMR determinations were carried out on a Varian CMX and CMX Infinity NMR Spectrometer System. Especially, the ^1H NMR spectra were obtained in $CDCl_3$ using TMS and liquid ^{31}P NMR in $CDCl_3$ using 85%

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H_3PO_4 as standards. Solid NMR determinations were run in proton-decoupling scheme. ^{13}C NMR spectra were plotted with reference to adamantane (CH_2 δ 38.56, CH δ 29.57) and ^{31}P to 85% H_3PO_4 and ^{113}Cd to $Cd(NO_3)_2$ (δ −100). More specifics of solid NMR are given in text.

Syntheses of the complexes

The procedure for preparing complexes **1**—**4** can be generalized as follows. To a solution of $Cd(ClO_4)_2 \cdot 6H_2O$ (0.50 mmol in 5 mL of Milli-Q water) was added dropwise the dialkyldithiophosphate (1.00 mmol in 25 mL) under vigorous stirring. The addition was lasted for 20 min. After the period, white precipitates were collected and washed by water several times. The solid was dried *in vacuo* and then redissolved in methanol to recrystallize. Three days or so later, needle crystals were harvested in yield of no less than 70% for all complexes.

$[Cd(S_2P(OCH_2CH_2CH_3)_2)_2]_n$(**1**) ^1H NMR ($CDCl_3$, TMS) δ: 4.13 (dt, $J_{H\text{-}H}$ = 6.5 Hz, $J_{P\text{-}H}$ = 9.0 Hz, CH_2, 2H), 1.75 (sext., $J \approx 7.2$ Hz, 2H, CH_2), 0.97 (t, J = 7.2 Hz, 3H, CH_3); IR (KBr) ν: 2965 (v), 2877 (v), 1464 (m), 1388 (m), 1278 (w), 1255 (w), 1147 (w), 1127 (w), 1057 (s), 992 (v, broad), 902 (w), 851 (m), 827 (m), 731 (m, P=S), 675 (s), 645 (v), 568 (s, S-Cd) cm^{-1}. Anal. calcd for $C_{12n}H_{28n}Cd_nO_{4n}P_{2n}S_{4n}$: C 26.75, H 5.20; found C 26.54, H 5.38.

$[Cd(S_2P(OCH_2CH_2CH_2CH_3)_2)_2]_n$(**2**) ^1H NMR ($CDCl_3$, TMS) δ: 4.14 (dt, $J_{H\text{-}H}$ = 7.2 Hz, $J_{H\text{-}P}$ = 7.8 Hz, 2H, CH_2), 1.70 (quint., $J \approx 6.8$ Hz, 2H, CH_2), 1.43 (sext., $J \approx 7.3$ Hz, 2H, CH_2), 0.90 (t, J = 6.3 Hz, 3H, CH_3); IR (KBr) ν: 2959 (v), 2870 (v), 1430 (s), 1382 (s), 1300 (w), 1259 (w), 1232 (m), 1146 (m), 1122 (w), 1060 (m), 951 (v, broad), 899 (s), 835 (s), 800 (s), 724 (m, P=S), 899 (s), 835 (s), 800 (s), 724 (m), 675 (v), 643 (v), 570 (s, S-Cd) cm^{-1}. Anal. calcd for $C_{16n}H_{36n}Cd_nO_{4n}P_{2n}S_{4n}$: C 32.30, H 6.06; found C 31.74, H 6.22.

$[Cd(S_2P(OCH(CH_3)_2)_2)_2]_n$(**3**) ^1H NMR ($CDCl_3$, TMS) δ: 4.90—5.00 (m, CH, 1H), 1.77 (d, J = 6.2 Hz, 6H, CH_3); IR (KBr) ν: 2980 (v), 2933 (v), 1465 (s), 1451 (s), 1386 (v), 1374 (v), 1347 (m), 1180 (s), 1142 (m), 1103 (m), 956 (v, broad), 886 (s), 752 (v, P=S), 643 (v), 530 (v, S—Cd) cm^{-1}. Anal. calcd for $C_{12n}H_{28n}Cd_nO_{4n}P_{2n}S_{4n}$: C 26.75, H 5.20; found C 26.21, H 5.03.

$[Cd(S_2P(OCH_2CH(CH_3)_2)_2)_2]_n$(**4**) ^1H NMR ($CDCl_3$, TMS) δ: 3.94 (dd, $J_{H\text{-}H} \approx J_{H\text{-}P}$ = 7.50 Hz, 2H, CH_2), 1.95—2.10 (m, CH, 1H), 0.97 (d, J = 7.2 Hz, CH_3, 6H); IR (KBr) ν: 2960 (v), 2874 (s), 1469 (v), 1391 (v), 1368 (v), 1344 (w), 1301 (m), 1273 (m), 1180 (m), 1163 (m), 1131 (s), 952 (v, broad), 861 (m), 824 (m), 671 (v, P=S), 647 (v), 568 (s, S—Cd) cm^{-1}. Anal. calcd for $C_{16n}H_{36n}Cd_nO_{4n}P_{2n}S_{4n}$: C 32.30, H 6.06; found C 30.96, H 6.15.

Results and discussion

Preparation of complexes **1**—**4**

The titled compounds were prepared by reactions of ligands with $Cd(ClO_4)_2$ in molar ratio of 2:1. They were obtained as colorless crystals. In comparison of the procedure for preparing $[Cd\{S_2P(OBu\text{-}i)_2\}]$,[6] the only alteration made in this effort is that the ligands were added dropwise instead mixed directly to the Cd(II) salt solution. Consequently, it resulted in the formation of the polymers. The fact strongly recommends that the instantaneous ratio of ligand to metal is a decisive factor of the structures of the complexes.

Description of the structure of **4**

The single crystal suitable for X-ray diffraction analysis was obtained from recrystallization of the obtained precipitates in CH_3OH. It is colorless and block shaped and in size of 0.3 mm × 0.4 mm × 0.4 mm. Cell symmetry belongs to monoclinic and lattice type is centrosymmetric C. Cell parameters are a = 3.0033(5) nm, b = 1.0319(2) nm, c = 1.9222(3) nm; β = 111.570(11)°; V = 5.539755 nm^3; Z = 8.

Fig. 2 is a perspective view of a metal centered unit of **4**. It shows that the metal ion sits in a tetrahedral coordination sphere with vertexes occupied by 4 sulfur atoms. By the P—S bond lengths [0.19714(22)—0.19904(17) nm] (Table 1), the thiophosphate groups are all isobidentate.[1] However, the Cd—S distances suggest that the ligands are not equally functionalized to Cd(II). For instance, the Cd—S(1) distance [0.25099(12) nm] is markedly shorter than the Cd—S(2) distance [0.25695(15) nm], Cd—S(3) distance [0.25701(18) nm] and Cd—S(4) distance [0.25399(12) nm]. Consequently, the S(1)-involving angles, S(1)-Cd-S(2) [114.98(5)°], S(1)-Cd-S(3) [118.43(5)°] and S(1)-Cd-S(4) [113.45(4)°] are systematically larger than normal angles of a tetrahedron in contrast to S(2)-Cd-S(3) [91.13 (4)°], S(3)-Cd-S(4) [100.67(5)°]. Herewith, we assume that the ligands diversely react to metal ions. Again, it can be seen from Fig. 2 that the two S(1)P(2)S(3) planes, like those in $Zn_2[(i\text{-}C_4H_9O)PS_2]_4$,[6] intersect each other, but two S(2)P(1)S(4) planes, like those in $Cd_2[(i\text{-}C_4H_9O)PS_2]_4$, parallel to each other. The observation indicates that two coterminous 8-membered rings are one in twist-chair and the other in twist-boat configuration.

NMR *spectroscopy* of **1**—**4**

If the ligands are crystallographically unequal, the differences among ligands should be NMR recognizable. In strategy of exposing the diversity of ligands, the complexes were investigated by liquid and solid NMR techniques.

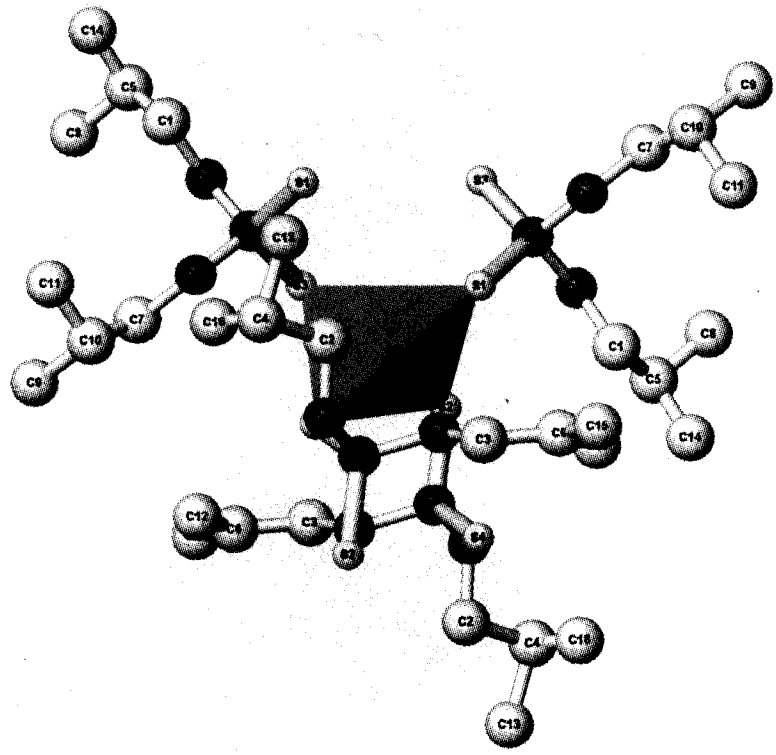

Fig. 2 Perspective view of a metal centered unit of **4**.

Table 1 Selected bond lengths (nm) and bond angles (°) of complex **4**

Bond angles (nm)			
Cd—S(1)	0.25099(12)		
Cd—S(2)	0.25695(15)		
Cd—S(3)	0.25701(18)		
Cd—S(4)	0.25399(12)		
S(1)—P(2)	0.19904(17)		
S(2)—P(1)	0.19875(16)		
S(3)—P(2)	0.19714(22)		
S(4)—P(1)	0.19825(19)		
P(1)—O(1)	0.15844(36)		
P(1)—O(2)	0.15714(40)		
P(2)—O(3)	0.15815(51)		
P(2)—O(4)	0.15729(37)		
Bond lengths (°)			
S(1)-Cd-S(2)	114.98(5)	S(2)-P(1)-S(4)	114.29(7)
S(1)-Cd-S(3)	118.43(5)	S(1)-P(2)-O(3)	112.81(15)
S(1)-Cd-S(4)	113.45(4)	S(1)-P(2)-O(4)	102.35(16)
S(2)-Cd-S(3)	91.13(5)	S(2)-P(1)-O(1)	113.45(17)
S(2)-Cd-S(4)	115.63(4)	S(2)-P(1)-O(2)	103.23(13)
S(3)-Cd-S(4)	100.67(5)	O(1)-P(1)-O(2)	106.16(18)
Cd-S(1)-P(2)	100.42(6)	O(3)-P(2)-O(4)	106.93(24)
Cd-S(2)-P(1)	99.29(6)	O(1)-P(1)-S(4)	107.59(13)
Cd-S(3)-P(2)	104.27(7)	O(2)-P(1)-S(4)	111.86(18)
Cd-S(4)-P(1)	111.59(6)	O(3)-P(2)-S(3)	101.73(18)
S(1)-P(2)-S(3)	119.77(9)	O(4)-P(2)-S(3)	112.94(18)

As expected, the ^{1}H NMR spectra of the complexes in $CDCl_3$ (360 MHz) show the peak regions corresponding to the proton categories. The multiplicities of the signals of all protons except those on carbons attached to oxygen atoms are interpretable by proton-proton couplings. In contrast, the signal of the protons on carbons near to oxygen suggest a heteronuclear coupling to phosphorus. Seen from Fig. 3, the signals of **1**—**4** are viewed, respectively, as quartet, quartet, heptet and triplet. By the regularity of the signals, the constants, $^3J_{P\text{-}H}$, are known to be approximately equal to $^3J_{H\text{-}H}$. Interestingly, **3** shows the signals at an unusual low field, indicating the proton is more efficiently deshielded than other alkyl protons.

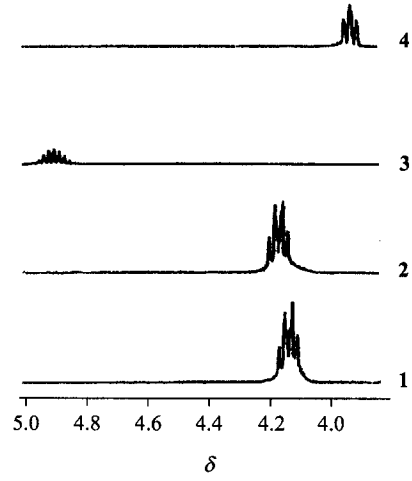

Fig. 3 Peaks of the protons on carbon bound to oxygen of **1**—**4**.

The ^{31}P NMR spectra of **1**—**4** in $CDCl_3$ (Fig. 4) confirms the heteronuclear coupling and the electronic effect. In the figure, the signals of phosphorus nuclei are simply split by the nearby protons. The constants $^3J_{P\text{-}H}$ (~ 7—10 Hz) are agreeable with these expressed by ^1H NMR. Here is noticed that the signal of **3** is more upfield placed. It implies that the P atoms in **3** are more heavily shielded, which further asserts that isopropyl group is better electron donating.

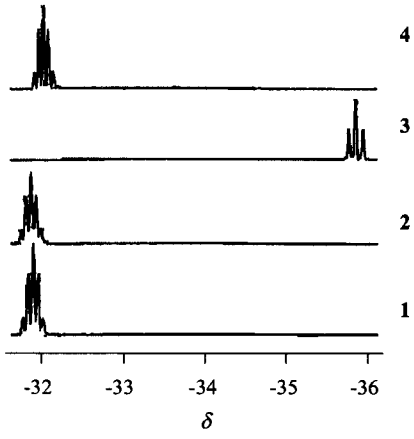

Fig. 4 ^{31}P NMR spectra of **1**—**4** in $CDCl_3$.

Based on the liquid ^1H and ^{31}P NMR spectra evidences, it is concluded that, in solution, the ligands in each complex are equivalent. Obviously, the conclusion conflicts to the crystal facts. An explanation to the happening is that the diversities among ligands are averaged by the fast molecular tumbling.

To freeze up the orientation of molecules, solid samples were used to the further NMR studies on half spin nuclei, ^{31}P, ^{13}C and ^{113}Cd. Meanwhile, to clarify and intensify the spectra, a second frequency channel was used to decouple the noises of protons.

Fig. 5 displays the central peaks of $^{31}P\{H\}$ spectra of **1**—**4** (145 MHz), in which the complexes, **1**, **2** and **4** exhibit two clean peaks. The peak separations of complexes **1**, **2** and **4** are 310.3, 384.3 and 659.8 Hz, respectively. Under the circumstances that the protons have been decoupled and the abundance of magnetic active isotope ^{13}C is very low, the couplings of ^{31}P to ^1H and ^{13}C should not be typically observed.[18] In addition, the ^{113}Cd spectra of **1**, **2** and **4** (79.9 MHz) give singlets respectively at δ 503.92, 507.65 and 529.5, indicative of no ^{31}P-^{113}Cd coupling. Hence, the peak separations are preferably ascribed to the diversity of ligands. If the ascription holds up, the finding means that the P atoms in **1**, **2** and **4** exist in two different situations. Dissimilarly, the ^{113}Cd NMR signal of **3** exhibits an ambiguous multiplet at an extremely high field (δ 424.80) (Fig. 6). The upfield location is understandable in term of the stronger electron-donation of isopropyl groups as mentioned before. But, the peak pattern is somewhat inexplicable.

Fig. 7 exhibits the full $^{13}C\{H\}$ spectra of **1**—**4** (90.52

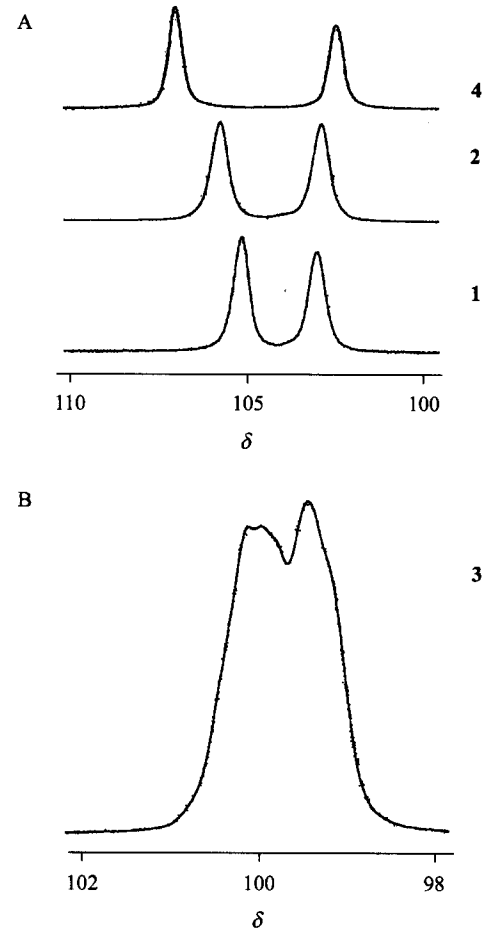

Fig. 5 Solid ^{31}P spectra of **1**, **2**, **4** (A) and **3** (B).

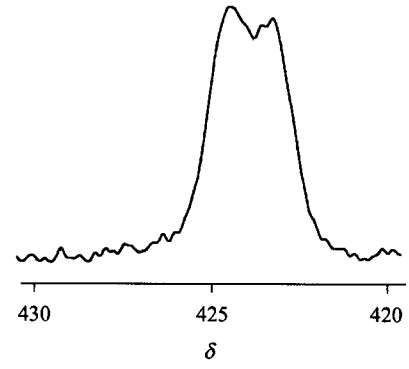

Fig. 6 Solid ^{113}Cd spectrum of **3**.

MHz). It lays out the peaks in the range of δ 0—80. The number of peak groups of each compound is accordant with the carbon types. However, the peak patterns are very sophisticated and so, we do not intend to allot the individuals to their originations. However, in case of the magnetic isotope unenriched, the intercarbon coupling and long-range heteronuclear coupling are ignorable.[14] The methyl carbons, especially, of **2**, should give a singlet in which the provided nuclei are magnetically equivalent. Clearly this is not true. Therefore, the gashes of signals are proposed to arise from nonequivalence of magnetic orientations of alkyl groups.

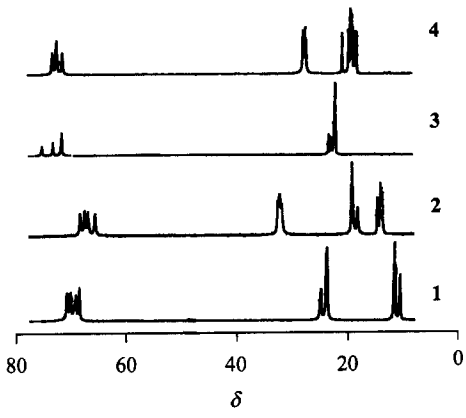

Fig. 7 Solid ^{13}C NMR spectra of **1**—**4**.

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