

## Polymeric Structure and Solid $^{31}\text{P}$ , $^{113}\text{Cd}$ NMR Spectra of Cadmium(II) Dialkyldithiophosphate (Alkyl = *n*-butyl and *i*-butyl)

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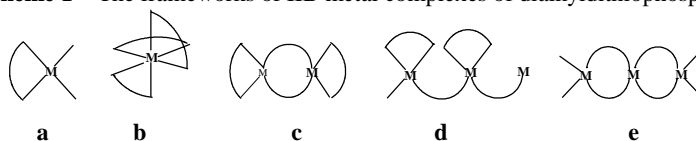
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**Abstract:** Two polymeric complexes,  $[\text{Cd}(\text{BTP})_2]_n$  **1** and  $[\text{Cd}(i\text{-BTP})_2]_n$  **2**, were prepared and investigated by solid  $^{31}\text{P}$  and  $^{113}\text{Cd}$  NMR spectroscopies. The crystal structure of **2** was determined by X-ray diffraction.

**Keywords:** Cadmium(II) complex, dialkyldithiophosphate, crystal structure, solid NMR.

Owing to the particular affinity toward metal ion and changeable dentation, dialkyldithiophosphates are commonly used ligands in preparation of the transition metal complexes with variable structures<sup>1</sup>. For instances relevant to this work, the IIB metal complexes defined crystallographically so far have provided the examples as follows<sup>2-12</sup> (**Scheme 1**).

**Scheme 1** The frameworks of IIB metal complexes of dialkyldithiophosphate



More recently, a **c** type  $\text{Cd}_2(i\text{-BTP})_4$  was reported by Byrom, *et al.*<sup>5</sup>. It was afforded by reaction of  $\text{Cd}(\text{SO}_4)_2 \cdot 8\text{H}_2\text{O}$  and diisobutyldithiophosphate in molar ratio of 1:2. An attempt to reprepare the compound and analogue by adding the ligand (Danafloat145 and 245) dropwise into concentrated solution of  $\text{Cd}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$  (G. Frederick Smith Co.) in the same ratio of metal:ligand resulted in the formation of polymers,  $[\text{Cd}(\text{BTP})_2]$  and  $[\text{Cd}(i\text{-BTP})_2]$  in yield of no less than 70%. The complexes were identified by IR ( $570\text{ cm}^{-1}$  ( $\nu_{\text{S-Cd}}$ ),  $643\text{ cm}^{-1}$  ( $\nu_{\text{C-S}}$ ) for **1** and  $568\text{ cm}^{-1}$  ( $\nu_{\text{S-Cd}}$ ),  $647\text{ cm}^{-1}$  ( $\nu_{\text{C-S}}$ ) for **2**) and NMR spectroscopies. The structure of **2** was determined by X-ray diffraction<sup>13</sup>.

**Figure 1** shows a metal-centered unit of **2**. The metal ion lies in a tetrahedron with

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4 sulfur atoms occupying the vertexes. By the P-S distances (1.9714(22)-1.9904(17)Å) (see **Figure** note), the ligands are known to be isobidentate<sup>1</sup>. However, it is seen from the bond parameters that the 4 Cd-S bonds are not equivalent each other, of which the Cd-S1 (2.5099(12)Å) is markedly shorter than Cd-S2 (2.5695(15)Å), Cd-S3 (2.5701(18)Å) and Cd-S4 (2.5399(12)Å). In contrast to S2-Cd-S3 (91.13(4)°) and S3-Cd-S4 (100.67(5)°), the S1-involving angles, S1-Cd-S2 (114.98(5)°), S1-Cd-S3 (118.43(5)°) and S1-Cd-S4 (113.45(4)°) are systematically larger than the normal angle of tetrahedron (109.5°). Hereby, the ligands are assumed to be crystallographically unequal. In the meantime, it is also seen that the thiophosphate groups are not equally functionalized to Cd(II). Two S1P2S3 plans, like the bridgings in Zn<sub>2</sub>[(*i*-C<sub>4</sub>H<sub>9</sub>O)PS<sub>2</sub>]<sub>4</sub> [5], intersect each other, whereas the S2P1S4 plans, like bridgings in Cd<sub>2</sub>[(*i*-C<sub>4</sub>H<sub>9</sub>O)PS<sub>2</sub>]<sub>4</sub>, parallel each other. This fact means that the two adjacent 8-membered rings exist in 'boat' and 'chair' conformations, respectively.

**Figure 1** The perspective view of a metal centered unit of **2** with hydrogen atoms omitted



**Selected bond lengths (Å) and angles (°)** Cd-S1 2.5099(12), Cd-S2 2.5695(15), Cd-S3 2.5701(18), Cd-S4 2.5399(12), S1-P2 1.9904(17), S2-P1 1.9875(16), S3-P2 1.9714(22), S4-P1 1.9825(19), P1-O1 1.5844(36), P1-O2 1.5714(40), P2-O3 1.5815(51), P2-O4 1.5729(37), S1-Cd-S2 114.98(5), S1-Cd-S3 118.43(5), S1-Cd-S4 113.45(4), S2-Cd-S3 91.13(5), S2-Cd-S4 115.63(4), S3-Cd-S4 100.67(5), Cd-S1-P2 100.42(6), Cd-S2-P1 99.29(6), Cd-S3-P2 104.27(7), Cd-S4-P1 111.59(6), S1-P2-S3 119.77(9), S2-P1-S4 114.29(7), S1-P2-O3 112.81(15), S1-P2-O4 102.35(16), S2-P1-O1 113.45(17), S2-P1-O2 103.23(13), O1-P1-O2 106.16(18), O3-P2-O4 106.93(24), O1-P1-S4 107.59(13), O2-P1-S4 111.86(18), O3-P2-S3 101.73(18), O4-P2-S3 112.94(18).

To show the diversity of the ligands, the complexes were investigated by <sup>1</sup>HNMR on a Varian CMX-400 Infinity NMR Spectrometer in CDCl<sub>3</sub>. The spectrum of **1** exhibits 4 groups of peaks for the *n*-butyl protons at δ 4.14(q), δ 1.70(quin.), δ 1.42(quin) and δ 0.91(t). The one located at lowest field is assigned to the protons on -CH<sub>2</sub>- linked to oxygen. It is quartetly splitted, suggesting a *J*<sub>H-P</sub> coupling. Its symmetry (1:3:3:1) implies that the constant <sup>3</sup>*J*<sub>H-P</sub> is approximately equal to <sup>3</sup>*J*<sub>H-H</sub> (~8Hz). Correspondingly, **2** gives 3 sets of peaks for the isobutyl protons at δ3.95(t), δ2.03(m) and 0.98(d). The splitting pattern of the -CH(O) proton confirms the heteronuclear coupling.

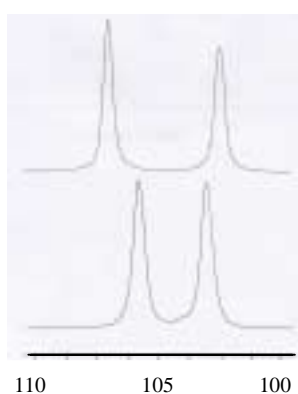
By the <sup>1</sup>HNMR signal region number and signal multiplicity of **1** and **2**, it is recognized that the chemically equivalent protons in different ligands are also magnetically identical in solution. The deduction is conflicting to the crystallographic facts. The happening is most likely due to the fast interconversion among conformers in liquid.

To freeze up the structure, solid <sup>31</sup>P MAS NMR determinations with proton-

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decoupling were carried out. The frequency of channel 1 is 145MHz. **Figure 2** shows the spectra of **1** and **2**. It can be seen that the two compounds display two peaks, individually. The peak gaps are *ca* 405Hz and 667Hz, respectively for **1** and **2**. Since the spectra were recorded in a proton-decoupling scheme and the abundance of  $^{13}\text{C}$  and  $^{113}\text{Cd}$  are very low, the heteronuclear coupling should not be typically observed and, therefore, the separations are attributed to the inequality of the phosphorus atoms.

**Figure 2** Solid  $^{31}\text{P}$  NMR spectra of **1** (lower) and **2** (upper)



The  $^{113}\text{Cd}$  NMR spectra of **1** and **2** give the central peaks at  $\delta$  507.7 and  $\delta$  529.5, respectively. The chemical shift of **2** is manifestly down-field shifted from that of **1**. It suggests that the Cd(II) in **1** is more heavily shielded than that in **2**.

### Acknowledgment

Thank for the financial support of Chinese Scholarship Council.

### References and Notes

1. I. Haiduc, D. B. Sowerby, S. Lu, *Polyhedron*, **1995**, *14*, 3389.
2. J. A. McCleverty, R. S. Z. Kowalski, N. A. Bailey, *et al.*, *J. Chem. Soc. Dalton Trans.*, **1981**, *6*, 64.
3. T. Ito, T. Igarashi, H. Hagihara, *Acta Cryst.*, **1969**, *B25*, 2303.
4. S. L. Lawton, G. T. Kokotailo, *Inorg. Chem.*, **1969**, *8*, 2410.
5. C. Byrom, M. A. Malik, P. O'Brien, *et al.*, *Polyhedron* **2000**, *19*, 211.
6. H. Wunderlich, *Acta Cryst.* **1982**, *B38*, 614.
7. G. Svensson, J. Albertsson, *Acta Chem. Scand.*, **1991**, *45*, 820.
8. J. S. Casas, A. Castineiras, M. S. Garcia-Tasende, *et al.*, *Polyhedron*, **1995**, *14*, 2055.
9. J. A. McCleverty, S. Gill, R. S. Z. Kowalski, *et al.*, *J. Chem. Soc. Dalton Trans.*, **1982**, 493.
10. Y. Watanabe, *Sci. Pap. Phys. Chem. Res.*, **1980**, *74*, 150.
11. S. L. Lawton, *Inorg. Chem.*, **1971**, *10*, 328.
12. Y. Watanabe, H. Hagihara, *Acta Cryst.*, **1972**, *A28*, S89.
13. The single crystal suitable for X-ray diffraction was obtained from recrystallization of the formed precipitates in  $\text{CH}_3\text{OH}$ . Crystal habits: colorless and block shaped. Crystal size:  $0.3 \times 0.4 \times 0.4 \text{ mm}^3$ . Cell parameters:  $a = 30.033(5) \text{ \AA}$ ,  $b = 10.319(2) \text{ \AA}$ ,  $c = 19.222(3) \text{ \AA}$ ;  $\beta = 111.570(11)^\circ$ ;  $V = 5539.755 \text{ \AA}^3$ .  $Z = 8$ . Cell symmetry: monoclinic. Lattice type: centrosymmetric C. More details of the crystal and instrumentation are available from Dr. Dan Boström.

Received 8 April, 2002