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Syntheses and structural characterization of new dithiophosphinato cadmium complexes

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Abstract. New cadmium complexes of 4-methoxyphenyl dithiophosphinic acids, H_3CO-C_6H_4-(R)PS_2H were prepared. The five dithiophosphinato ligands (L) involved were of the general structure H_3CO-C_6H_4-(R)PS_2^- with R= 3-methylbutyl, (L1); n-butyl, (L2); 2-methylpropyl, (L3); 1-methylpropyl, (L4) and 2-propyl, (L5). To the best of our knowledge, this is the first report on the preparation and characterization of the n-butyl-derivative. The acid forms of the ligands were obtained by treatment of the Lawesson reagent, (LR) [2,4-bis(4-methoxyphenyl)-1,3,2,4-dithiadiphosphetane-2,4-disulfide] with the corresponding Grignard reagent in dry diethylether. The acids formed were transformed into easily crystallizable ammonium salts (NH_4L) for purification. These salts were treated with $CdCl_2$ in ethanol at room temperature to produce the bis-dithiophosphinato cadmium complexes ($[Cd(L)_2]_2$) exclusively. The structures of the complexes were elucidated by elemental analysis, MS, FTIR and Raman spectroscopy techniques as well as ^{1}H-, ^{13}C- and ^{31}P- NMR. The crystal structures of $[Cd(L1)_2]_2$ and $[Cd(L2)_2]_2$ were also studied as examples. X-ray studies confirmed the nonplanar, four-coordination geometry of the complexes and indicate that electron delocalization prevails in the PS_2^- moiety of the dithiophosphinato groups.

Keywords. Cadmium dithiophosphinato complexes; Thio-Phosphorus Complexes; Dithiophosphinic acid; Phosphinodithioic acid; X-ray Structure.

1. Introduction

Dithiophosphoric acids, $(OR)_2P(S)SH$; dithiophosphonic acids, (OR)(R)P(S)SH and dithiophosphinic acids, $(R)_2P(S)SH$, as well as their metal complexes are in current use in rubber vulcanization,[1] lubricating oils[2] and pesticides.[3] Tin and antimony complexes of some dithiophosphinic acids (DTPA) are also of potentially useful as chemotherapy agents in the treatment of some cancers.[4] In addition, some DTPA-^{99}Tc complexes have been introduced as brain imaging agents in radiography[5] and cephalosporin-type chemicals containing DTPA moieties have been suggested as antibiotics in clinical medicine.[6] The commercial sequestering agent CYANEX 301, (bis(2,4,4-trimethylpentyl)dithiophosphinic acid) is in current use for the extraction metals from ores.[7] The same agent is also employed in heavy metal removal from industrial wastes.[8]

The synthesis of DTPA-type compounds is relatively more tedious compared to the synthesis of other dithiophosphorus acids.[9] Coupled with their disagreeable odour and the difficulty in obtaining the starting reagents, these compounds have attracted comparatively less attention in the past.[10] Various routes have been developed for the DTPA synthesis,[11] the most general one being the addition reaction of Grignard reagents with perthiophosphonic acid anhydrides such as Lawesson reagent, (LR). The DTPAs formed were further reacted with ammonia to form the easily crystallizable ammonium salts, facilitating a quick refinement of the DTPA. The ammonium salt is stable and can easily be converted to complexes when desired.[12]

Depending on the identity of the metal cation, the coordination number of the DTPA complex changes. Most of the complexes generally display a four- or

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six-coordination.[13] The nickel(II) complexes are exclusively mono-nuclear and generally of a square-planar topology as is the case with other soft ligands; whereas, DTPA complexes of manganese(II), cobalt(II), Zinc(II) and cadmium(II) are known to display four coordinated, dimeric structures.[14] In the case of the latter complexes, S atoms of the PS_2^- group are known to act as singly-bonded and also as bridging ligands.

X-ray crystallographic studies on the crystal structures ditihophosphinato complexes of group 12 metals, namely, zinc (II), cadmium (II) and mercury (II), are scarce. These dimeric complexes display a chair conformation although some complexes are known to display a boat conformation.[14c, 15]

2. Experimental

2.1 *Materials and Methods*

Analytical-grade LR, 3-methylbutyl bromide, n-butyl bromide, 2-methylpropyl bromide, 1-methylpropyl bromide and 2-propyl bromide were purchased from Merck and used without further purification. Benzene, chloroform, ethanol, diethyl ether, $CdCl_2$ were purchased from Merck. Benzene and diethyl ether were distilled and dried before use. NH_4L1, NH_4L2, NH_4L3, NH_4L4 and NH_4L5 were prepared according to the literature.[12a, 16, 17]

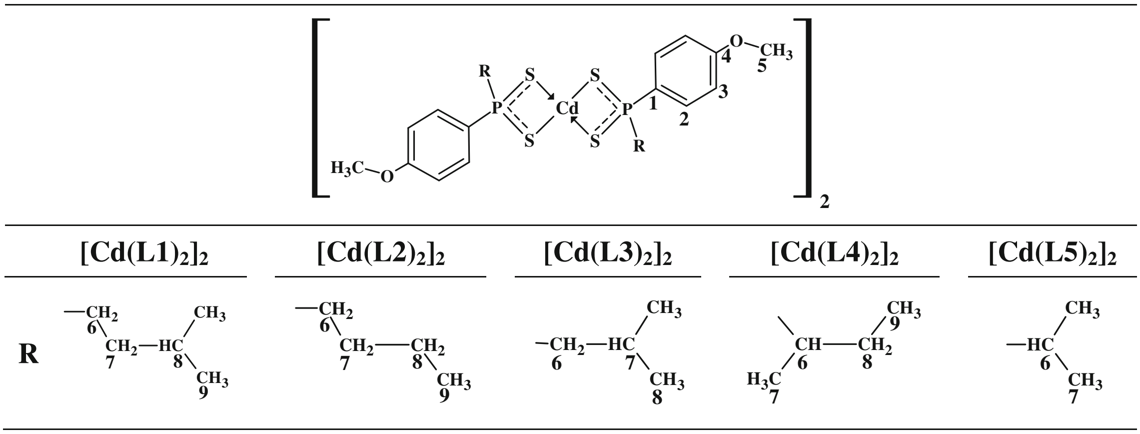
The LC/MS spectra were recorded with a Waters Micromass ZQ connected with Waters Alliance HPLC, using ESI(+) ionization and C-18 column. Melting points were measured with a Gallenkamp apparatus using a capillary tube. ^1H-, $^{13}C\{^1H\}$ - and $^{31}P\{^1H\}$ - spectra were recorded with a Varian Mercury (Agilent) 400 MHz FT spectrometer in $CDCl_3$ $SiMe_4$ (^1H, ^{13}C) and 85% H_3PO_4 (^{31}P) were used as standards. IR spectra were recorded on a Perkin Elmer Spectrum 400 FTIR spectrophotometer (200–4000 cm^{-1}) and are reported in cm^{-1} units. All Raman spectra were measured in the range of 4000–100 cm^{-1}, at room temperature, using a Renishaw in-Via Raman microscope, equipped with Peltier-cooled CCD detectors (−70°C). For Raman microscopy, a 50X objective was usually used and all the spectra were excited by the 785 line of a diode laser. Microanalyses were performed using a LECO CHNS-932 C elemental analyzer.

2.2 *Preparation and structural data*

2.2.1 *Ammonium n-butyl(4-methoxyphenyl)dithiophosphinate, NH_4L2:* The method of preparation was the same as described in the literature.[16]: Yield: 1.52 g (55%). White colour. M.P. 179–180°C. NMR spectroscopic data and mass data are as follows: ^1H NMR (in D_2O): $\delta = 0.66$ (t, $^3J_{HH} = 7.29$ Hz, 6H, -C9$\underline{H}$); 1.14 (m, 2H, -C7$\underline{H}$); 1.27 (m, 2H, -C8$\underline{H}$); 2.06 (m, 2H, -C6$\underline{H}$); 3.70 (s, 3H, $OC\underline{H}_3$); 6.89 (A-part of AA'MM'X, $^4J_{PH} = 2.13$ Hz (J_{AX}), $N = J_{AM} + J_{AM'} = 8.90$ Hz, 2H, *m*-H); 7.80 (M-part of AA'MM'X, $^3J_{PH} = 12.60$ Hz (J_{MX}), $N = 8.90$ Hz, 2H, *o*-H). ^{13}C-NMR (ppm, in D_2O): $\delta = 12.9$ (s, -$\underline{C}$9); 22.8 (d, $^2J_{P-C} = 17.86$ Hz, $\underline{C}$7); 25.9 (d, $^3J_{P-C} = 4.1$ Hz, $\underline{C}$8); 43.6 (d, $J_{P-C} = 56.1$ Hz, P-$\underline{C}$6); 55.4 (s, O-C5H_3); 113.5 (d, $^3J_{P-C} = 13.3$ Hz, Ar-C_{meta}); 131.8 (d, $J_{P-C} = 80.5$ Hz, P-C_{arom}); 131.7 (d, $^2J_{P-C} = 13.3$ Hz, Ar-C_{ortho}); 163.5 (d, $^4J_{P-C} = 3.0$ Hz, CH_3O-$\underline{C}$). ^{31}P-NMR (in D_2O): $\delta = 63.4$. LC/MS MS: m/z 261.2 ($[L2]^+$, 100%), 227.2 ($[(L2\text{-}(n\text{-}C_4H_9)+Na]^+$, 49%), 205.3 ($[L2\text{-}(n\text{-}C_4H_9)]^+$, 11%). Anal. Calcd. for $C_{11}H_{20}NOPS_2$ (277.4 $g.mol^{-1}$): C, 47.6; H, 7.3; N, 5.1; S, 23.1; found: C, 47.8; H, 7.3; N, 5.2; S, 23.4%.

2.2.2 *Preparation of the complexes, $[Cd(L)_2]_2$:* A solution of $CdCl_2$, (0.1 g, 0.55 mmol) in ethanol (10 mL) was added to an ethanolic solution (10 mL) of 1.09 mmol ligand (0.32 g, for NH_4L1; 0.30 g, for NH_4L2; 0.30 g, for NH_4L3 and NH_4L4; 0.29 g, for NH_4L5). The mixture was stirred overnight at room temperature. The resulting solution was left to stand overnight. The complexes were of colourless, fine crystallic appearance. The crystals were filtered off and recrystallized from chloroform. The numbering scheme for compounds is given in figure 1. The structural data for the complexes were as follows.

Bis-{bis-[4-methoxyphenyl(3-methylbutyl)dithiophosphinato]cadmium(II)}, $[Cd(L1)_2]_2$ [Yield: 0.59 g, 73%]. Colourless. M.p. 209–210°C. ^1H NMR (ppm, in $CDCl_3$): $\delta = 0.84$ (d, $^3J_{HH} = 6.5$ Hz, 24H, -C9H); 1.44 (m, 8H, -C8H); 1.54 (m, 8H, -C7H); 2.28 (m, 8H, -C6H); 3.84 (s, 12H, OCH_3); 6.88 (A-part of AA'MM'X, $^4J_{PH} = 2.4$ Hz (J_{AX}), $N = J_{AM} + J_{AM'} = 8.7$ Hz, 8H, *m*-H); 7.89 (M-part of AA'MM'X, $^3J_{PH} = 13.4$ Hz (J_{MX}), $N = 8.7$ Hz, 8H, *o*-H). ^{13}C-NMR (ppm, in $CDCl_3$): $\delta = 22.2$ (s, -C9); 32.5 (d, $^3J_{P-C} = 4.3$ Hz, C8); 28.6 (d, $^2J_{P-C} = 17.5$ Hz, C7); 41.2 (d, $J_{P-C} = 52.5$ Hz, P-C6); 55.3 (s, O-C5H_3); 113.7 (d, $^3J_{P-C} = 14.1$ Hz, Ar-C_{meta}); 126.9 (d, $J_{P-C} = 80.2$ Hz, P-C1); 132.6 (d, $^2J_{P-C} = 13.0$ Hz, Ar-C_{ortho}); 161.9 (d, $^4J_{P-C} = 3.0$ Hz, CH_3O-C4). ^{31}P-NMR (ppm, in $CDCl_3$): $\delta = 71.9$. Analysis: Calculated for $C_{48}H_{72}Cd_2O_8P_4S_8$ (1318.3 $g.mol^{-1}$): C, 43.7; H, 5.5; S, 19.5. Found: C, 43.8; H, 5.7; S, 19.6%. LC/MS: *m/z* 243.0 ($[L1\text{-}(CH_3O\text{-})]^+$, 100%), 1045.3 ($[Cd_2(L1)_3]^+$, 14%).



s: singlet; d: doublet; t: triplet; dd: doublet of doublets; m: multiplet.

Figure 1. Numbering scheme for compound.

Bis-{bis-[n-butyl(4-methoxyphenyl)dithiophosphinato] cadmium(II)}, [Cd(L2)$_2$]$_2$ [Yield: 0.58 g, 84%]. Colourless. M.p. 144–145°C. ^{1}H NMR (ppm, in CDCl$_3$): δ = 0.84 (d, ^{3}J$_{HH}$ = 7.3 Hz, 12H, -C9H); 1.32 (m, 8H, -C8H); 1.53 (m, 8H, -C7H); 2.28 (m, 8H, -C6H); 3.83 (s, 12H, OCH$_3$); 6.93 (A-part of AA'MM'X, ^{4}J$_{PH}$ = 2.4 Hz (J$_{AX}$), N= J$_{AM}$+ J$_{AM'}$ = 8.8 Hz, 8H, m-H); 7.89 (M-part of AA'MM'X, ^{3}J$_{PH}$ = 13.4 Hz (J$_{MX}$), N =8.8 Hz, 8H, o-H). ^{13}C-NMR (ppm, in CDCl$_3$): δ = 13.6 (s, -C9); 25.9 (d, ^{3}J$_{P-C}$ = 4.2 Hz, C8); 23.3 (d, ^{2}J$_{P-C}$ = 18.6 Hz, C7); 42.9 (d, J$_{P-C}$ = 52.3 Hz, P-C6); 55.4 (s, O-C5H$_3$); 113.7 (d, ^{3}J$_{P-C}$ = 14.1 Hz, Ar-C$_{meta}$); 127.0 (d, J$_{P-C}$ = 80.3 Hz, P-C1); 132.6 (d, ^{2}J$_{P-C}$ = 13.0 Hz, Ar-C$_{ortho}$); 162.0 (d, ^{4}J$_{P-C}$ = 2.9 Hz, CH$_3$O-C4). ^{31}P-NMR (ppm, in CDCl$_3$): δ = 71.5. Analysis: Calculated for $C_{44}H_{64}Cd_2O_4P_4S_8$ (1262.2 g mol^{-1}): C,41.9; H, 5.1; S, 20.3. Found: C, 42.0; H, 5.3; S, 20.3%. LC/MS: m/z 228.9 ([L2-(CH$_3$O-)]$^+$, 100%), 632.9 ([Cd(L2)$_2$]$^+$, 7%), 1002.9 ([Cd$_2$(L2)$_3$]$^+$, 6%), 1265.4 ([Cd$_2$(L2)$_4$]$^+$, 4 %).

Bis-{bis-[4-methoxyphenyl(2-methylpropyl)dithiophosphinato]cadmium(II)}, [Cd(L3)$_2$]$_2$ [Yield: 0.55 g, 79%] Colourless. M.p. 199–200°C. ^{1}H NMR (ppm, in CDCl$_3$): δ = 0.88 (d, $^3J_{HH}$ = 6.7 Hz, 24H, -C8H); 2.11 (m, 4H, -C7H); 2.28 (dd, $^3J_{HH}$ = 6.1 Hz, $^2J_{P-H}$ = 11.9 Hz, 8H, -C6H); 3.84 (s, 12H, OCH$_3$); 6.92 (A-part of AA'MM'X, $^4J_{PH}$ = 2.5 Hz (J_{AX}), N = J$_{AM}$+ J$_{AM'}$ = 8.8 Hz, 8H, *m*-H); 7.91 (M-part of AA'MM'X, $^3J_{PH}$ = 13.4 Hz (J_{MX}), N =8.8 Hz, 8H, *o*-H). ^{13}C-NMR (ppm, in CDCl$_3$): δ = 25.5 (d, $^3J_{P-C}$ = 3.9 Hz, C8); 24.3 (d, $^2J_{P-C}$ = 10.0 Hz, C7); 42.9 (d, J_{P-C} = 51.4 Hz, P-C6); 55.4 (s, O-C5H$_3$); 113.7 (d, $^3J_{P-C}$ = 14.1 Hz, Ar-C$_{meta}$); 127.8 (d, J_{P-C} = 80.3 Hz, P-C1); 132.6 (d, $^2J_{P-C}$ = 13.1 Hz, Ar-C$_{ortho}$); 161.9 (d, $^4J_{P-C}$ = 2.9 Hz, CH$_3$O-C4). ^{31}P-NMR (ppm, in CDCl$_3$): δ = 70.1. Analysis: Calculated for $C_{44}H_{64}Cd_2O_4P_4S_8$ (1262.2 g mol^{-1}): C,41.9; H, 5.1; S, 20.3%. Found: C, 42.0; H, 5.4; S, 20.4%. LC/MS: m/z 325.1 ([((C$_6$H$_5$)PS$_2$)Cd+CH$_3$CN]$^+$, 100%), 413.9 ([Cd(L3)+CH$_3$CN]$^+$, 8%).

Bis-{bis-[4-methoxyphenyl(1-methylpropyl)dithiophosphinato]cadmium(II)}, [Cd(L4)$_2$]$_2$ [Yield: 0.56 g, 81%] Colourless. M.p. 247-248°C. ^{1}H NMR (ppm, in CDCl$_3$): δ = 0.89 (t, ^{3}J$_{HH}$ = 7.3 Hz, 12H, -C9H); 1.96 (m, 8H, -C8H); 1.16 (m, ^{3}J$_{HH}$ = 6.86 Hz, ^{2}J$_{P-H}$ = 21.94 Hz, 16H, C6-H and C7-H adjacent); 1.16 (m, 16H, C6-H and C7-H adjacent); 3.84 (s, 12H, OCH$_3$); 6.92 (A-part of AA'MM'X, ^{4}J$_{PH}$ = 2.4 Hz (J$_{AX}$), N= J$_{AM}$+ J$_{AM'}$ = 8.9 Hz, 8H, m-H); 7.87 (M-part of AA'MM'X, ^{3}J$_{PH}$ = 12.7 Hz (J$_{MX}$), N =8.9 Hz, 8H, o-H). ^{13}C-NMR (ppm, in CDCl$_3$): δ = 12.3 (s, -C9); 23.2 (s, C8); 12.3 (d, ^{2}J$_{P-C}$ = 16.8 Hz, C7); 45.3 (d, J$_{P-C}$ = 50.3 Hz, P-C6); 55.3 (s, O-C5H$_3$); 113.4 (d, ^{3}J$_{P-C}$ = 13.7 Hz, Ar-C$_{meta}$); 126.6 (d, J$_{P-C}$ = 77.3 Hz, P-C1); 133.4 (d, ^{2}J$_{P-C}$ = 13.7 Hz, Ar-C$_{ortho}$); 161.9 (d, ^{4}J$_{P-C}$ = 2.9 Hz, CH$_3$O-C4). ^{31}P-NMR (ppm, in CDCl$_3$): δ = 82.5. Analysis: Calculated for $C_{44}H_{64}Cd_2O_4P_4S_8$ (1262.2 g mol^{-1}): C,41.9; H, 5.1; S, 20.3%. Found: C, 42.1; H, 5.2; S, 20.5%. LC/MS: m/z 391.1 ([Cd$_2$P$_2$S$_2$+CH$_3$CN]$^+$, 100 %), 413.1 ([Cd$_2$P$_2$S$_4$+H]$^+$, 77%), 1001.0 ([Cd$_2$(L4)$_3$]$^+$, 4%), 1265.3 ([Cd$_2$(L4)$_4$]$^+$, 11%).

Bis-{bis[iso-propyl(4-methoxyphenyl)dithiophosphinato]cadmium(II)} [Cd(L5)$_2$]$_2$ [Yield: 0.62 g, 94%] Colourless. M.p. 129–130°C. ^{1}H NMR (ppm, in CDCl$_3$): δ = 1.12 (t, $^3J_{PH}$ = 21.2 Hz, 24H, -C7H); 2.25 (m, 4H, -C7H); 3.84 (s, 12H, OCH$_3$); 6.92 (A-part of AA'MM'X, $^4J_{PH}$ = 2.4 Hz (J_{AX}), N = J$_{AM}$+ J$_{AM'}$ = 8.9 Hz, 8H, *m*-H); 7.9 (M-part of AA'MM'X,

$^{3}J_{PH}$ = 12.8 Hz (J_{MX}), N =8.8 Hz, 8H, *o*-H). ^{13}C-NMR (ppm, in CDCl$_3$): δ = 16.7 (d, $^{2}J_{P-C}$ = 1.2 Hz, C7); 38.8 (d, J_{P-C} = 51.3 Hz, P-C6); 55.4 (s, O-C5H$_3$); 113.4 (d, $^{3}J_{P-C}$ = 13.7 Hz, Ar-C$_{meta}$); 125.4 (d, J_{P-C} = 77.6 Hz, P-C1); 133.4 (d, $^{2}J_{P-C}$ = 12.3 Hz, Ar-C$_{ortho}$); 161.9 (d, $^{4}J_{P-C}$ = 3.0 Hz, CH$_3$O-C4). ^{31}P-NMR (ppm, in CDCl$_3$): δ = 83.6. Analysis: Calculated for $C_{40}H_{56}Cd_2O_4P_4S_8$ (1206,1 g mol^{-1}): C, 39.83; H, 4.68; S, 21.52%. Found: C, 39.61; H, 4.53; S, 21.52 %. LC/MS: m/z 391.2 ([(L5)$_2$CdS]$^+$, 100%); 602.1 ([Cd(L5)$_2$+Na]$^+$, 12%); 959.8 ([Cd$_2$(L5)$_3$]$^+$, 16%); 1205.6 ([Cd$_2$(L5)$_4$]$^+$, 4%).

2.3 *X-ray crystallography*

Single-crystal X-ray diffraction analyses of [Cd(L1)$_2$]$_2$ and [Cd(L2)$_2$]$_2$ were performed on a Bruker Kappa APEXII CCD area-detector diffractometer using Mo K$_\alpha$ (λ = 0.71073 Å) (for [Cd(L1)$_2$]$_2$) and Cu K$_\alpha$ (λ = 1.5418 Å) (for [Cd(L2)$_2$]$_2$) radiations at a temperature of 100 K. Structures were solved by direct methods[18] and refined by full-matrix least squares against F^2 using all data.[18] All non-H atoms were refined anisotropically. H atoms were positioned geometrically at distances of 0.93 Å (aromatic CH), 0.97 Å (CH$_2$) and 0.96 Å (CH$_3$) (for [Cd(L1)$_2$]$_2$) and 0.95 Å (aromatic CH), 0.99 Å (CH$_2$) and 0.98 Å (CH$_3$) (for [Cd(L2)$_2$]$_2$) from the parent C atoms; a riding model was used during the refinement proceses and the U$_{iso}$ (H) values were constrained to be xU$_{eq}$ (carrier atom), where x = 1.2 for CH and CH$_2$, and x = 1.5 for CH$_3$. Experimental data are given in table 1.

3. Results and Discussion

3.1 *Synthesis and characterization*

In this work, five novel cadmium-DTPA complexes and one new dithiophosphinato ligand (NH$_4$L2) were synthesized. LR was reacted with five different Grignard reagents to obtain dithiophosphinic acids. As the dithiophosphinic acids are viscous liquids and difficult

Table 1. Experimental details for [Cd(L1)$_2$]$_2$ and [Cd(L2)$_2$]$_2$.

Compound	[Cd(L1)$_2$]$_2$	[Cd(L2)$_2$]$_2$
Empirical Formula	$C_{48}H_{72}Cd_2O_4P_4S_8$	$C_{44}H_{64}Cd_2O_4P_4S_8$
Colour/shape	green/block	green/block
Formula weight	1318.24	1262.11
Temperature (K)	100(2)	100(2)
Radiation, graphite monochr.	Mo K$_\alpha$ (λ = 0.71073)	Cu K$_\alpha$ (λ = 1.54178)
Crystal system	triclinic	triclinic
Space group	P -1	P -1
a, b, c (Å),	11.3887(4),12.2986(4),12.5052(4)	9.8249(1),11.6464(1),13.6449(1)
α, β, γ (°)	91.902(1), 107.177(1), 116.112(1)	68.440(1), 83.434(1), 69.380(1)
Volume (Å^3)	1475.19(8)	1358.85(2)
Z	1	1
Abs. coefficients (mm^{-1})	1.151	10.560
D$_{calc}$ (mg m^{-3})	1.484	1.542
Max. crystal dim. (mm)	0.04X0.06X0.08	0.04X0.06X0.08
Θ(max) (°)	29.19	71.08
Reflections measured	7876	5076
Range of h, k, l	-15< h< 14, -16< k< 16, -17< l<17	-12< h< 12, -14< k< 14, -15< l< 16
Diffractometer/scan	Bruker Kappa APEX II / phi and w	
No. of reflections with I>2 σ(I)	7298	4902
Corrections applied	Lorentz polarization	
Computer programs	SHELXS-97[18], SHELXL-97[18], ORTEP-3[19]	
Source of scatter. Factors	International Table for X-Ray Crystallography[20]	
Structure solution	Direct methods	
Treatment of hydrogen atoms	Geometric calculation	
No. of parameters varied	298	284
GOF	1.024	1.045
$R = IIF_{o}I - IF_{c}II / IF_{o}I$	0.0194	0.0222
R$_w$	0.0489	0.0589
$(\Delta\rho)_{max}$ (e Å^{-3})	0.499	0.709
$(\Delta\rho)_{min}$ (e Å^{-3})	−0.318	−0.396

to purify, they are converted to their ammonium salts (scheme 1).

The $[Cd(L)_2]_2$ complexes were prepared by the reaction of NH_4L with cadmium(II) cation (scheme 2).

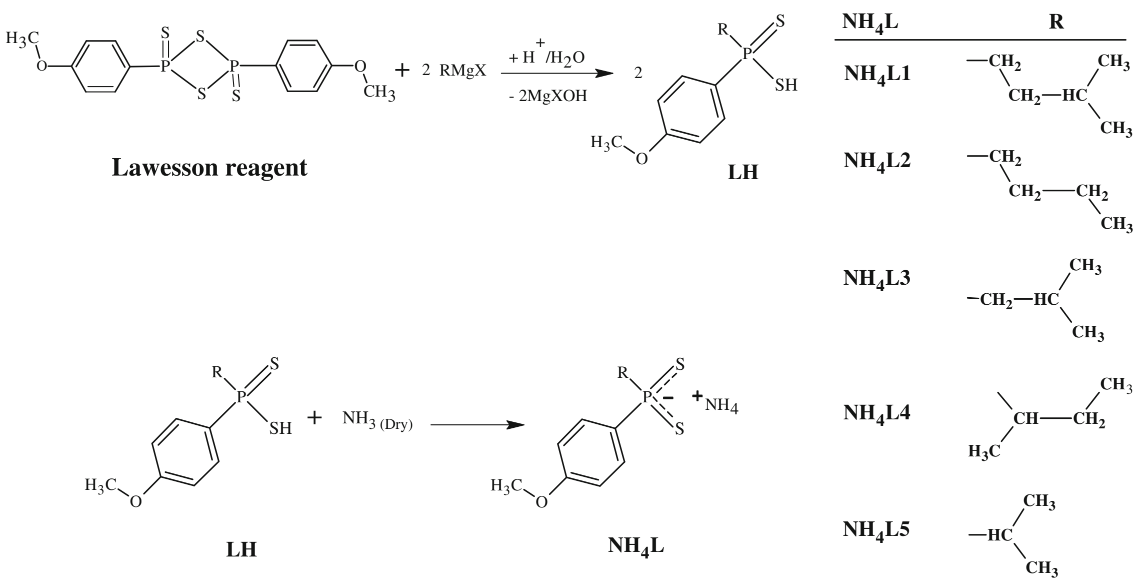
3.2 *Spectroscopic Studies*

3.2.1 *IR and Raman Spectra:* In the IR spectra, the asymmetric and symmetric (PS) stretching signals (ν_{asym} and ν_{sym}) of the compounds appear in the regions of 650–616 cm^{-1} and 552–524 cm^{-1}, respectively. In the Raman spectra, similar signals appear in the regions of 654–632 cm^{-1} and 555–523 cm^{-1}, respectively. The metal-sulphur stretching give rise to the signals between 200 cm^{-1} and 400 cm^{-1} (272–312 cm^{-1} for IR; 273–310 cm^{-1} for Raman).

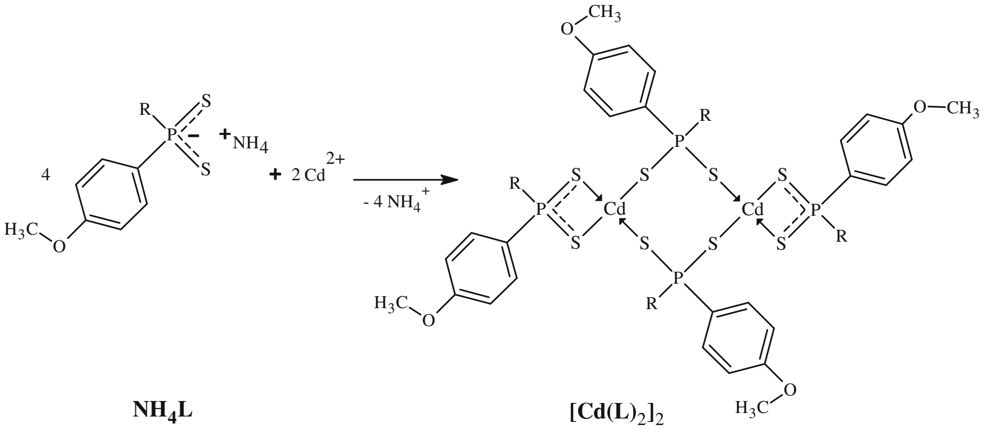
In the IR spectra of NH_4L2, the characteristic ν_{N-H} band is observed at 3183 cm^{-1}; this band is absent in the spectra of the $[Cd(L2)_2]_2$ complex, confirming the exclusion of the NH_4^+ ion.

The frequencies of the corresponding signals in the IR and the Raman spectra of the complexes are quite comparable as expected. All these values are in agreement with the literature.[14c,21] The prominent peaks are given in table 2.

3.2.2 *Mass Spectra:* The mass spectra of the complexes $[Cd(L2)_2]_2$, $[Cd(L4)_2]_2$ and $[Cd(L5)_2]_2$ display molecular ion peaks corresponding to the proposed dinuclear structures. The Mass spectra of all the complexes except $[Cd(L3)_2]_2$, display peaks indicating removal of a ligand leaving back a species of the formula



Scheme 1. Synthesis reaction of NH_4L.



Scheme 2. Synthesis of complexes.

Table 2. Selected FTIR and Raman (R) data (cm^{-1}) assignment of significant bands.

Compound	$\nu_{(M-S)}$		$\nu_{(sym)}$ (PS)		$\nu_{(asym)}$ (PS)		$\nu_{(N-H)}$	
	IR	R	IR	R	IR	R	IR	R
[Cd(L1)$_2$]$_2$	290	289	527	535; 524	638	631; 632	-	-
[Cd(L2)$_2$]$_2$	312	310	529; 519	542; 523	647; 635	647; 633	-	-
[Cd(L3)$_2$]$_2$	280	282	526	542; 525	643	652; 632	-	-
[Cd(L4)$_2$]$_2$	272	273	552; 532	555; 537	650; 639	653; 633	-	-
[Cd(L5)$_2$]$_2$	274	273	548; 524	549;528	649;640	654;635	-	-
NH$_4$L2	-	-	545; 534	549;528	646;616	637;636	3180	-

[Cd$_2$(L)$_3$]. The complexes [Cd(L2)$_2$]$_2$ and [Cd(L5)$_2$]$_2$ display Mass-peaks corresponding to the mono-nuclear [Cd(L2)$_2$] and [Cd(L5)$_2$] moieties. The natural abundance of metal- as well as phosphorus and sulphur isotopes are observable in the structures of the molecular ion signals. Reminiscent signal structures are

Table 3. Selected bond lengths (Å) and angles (°) for [Cd(L1)$_2$]$_2$ and [Cd(L2)$_2$]$_2$.

[Cd(L1)$_2$]$_2$		[Cd(L2)$_2$]$_2$	
Cd1-S1	2.5325(3)	Cd1-S1	2.5460(5)
Cd1-S2	2.6671(3)	Cd1-S2	2.6542(4)
Cd1-S3	2.5354(3)	Cd1-S3^{ii}	2.5442(5)
Cd1-S4	2.5703(3)	Cd1-S4	2.5726(4)
P1-S1	2.0252(5)	P1-S1	2.0253(6)
P1-S2	2.0107(5)	P1-S2	2.0128(6)
P1-C1	1.8014(13)	P1-C1	1.8043(19)
P1-C8	1.8161(14)	P1-C8	1.820(2)
P2-S3	2.0364(4)	P2-S3	2.0349(6)
P2-S4^{i}	2.0093(5)	P2-S4	2.0099(6)
P2-C13	1.7929(13)	P2-C12	1.7955(19)
P2-C20	1.8181(14)	P2-C19	1.8166(19)
S1-Cd1-S2	79.709(11)	S1-Cd1-S2	79.897(14)
S1-Cd1-S3	136.923(11)	S1-Cd1-S3^{ii}	134.434(15)
S1-Cd1-S4	117.464(12)	S1-Cd1-S4	122.969(16)
S2-Cd1-S3	108.310(11)	S2-Cd1-S3^{ii}	107.797(14)
S2-Cd1-S4	103.918(11)	S2-Cd1-S4	99.957(14)
S3-Cd1-S4	101.913(11)	S3-Cd1-S4^{ii}	100.388(15)
P1-S1-Cd1	85.347(15)	P1-S1-Cd1	84.86(2)
P1-S2-Cd1	82.104(15)	P1-S2-Cd1	82.274(19)
P2-S3-Cd1	105.342(16)	P2-S3-Cd1^{ii}	103.67(2)
P2-S4-Cd1^{i}	93.481(15)	P2-S4-Cd1	92.97(2)
S2-P1-S1	111.38(2)	S1-P1-S2	111.62(3)
C1-P1-S1	110.23(5)	S1-P1-C1	111.49(6)
C1-P1-S2	112.15(5)	S1-P1-C8	109.54(7)
C1-P1-C8	103.87(6)	S2-P1-C1	110.68(7)
C8-P1-S1	109.12(5)	S2-P1-C8	109.52(7)
C8-P1-S2	109.80(5)	C1-P1-C8	103.69(9)
S4-P2-S3^{i}	113.81(2)	S3-P2-S4	113.12(3)
C13-P2-S3	110.62(5)	S3-P2-C12	110.44(6)
C13-P2-S4^{i}	111.17(5)	S3-P2-C19	106.92(7)
C13-P2-C20	104.48(6)	S4-P2-C12	111.35(6)
C20-P2-S3	105.87(5)	S4-P2-C19	109.20(7)
C20-P2-S4^{i}	110.35(5)	C12-P2-C19	105.41(9)

Symmetry codes: (i) – x, – y, – z, (ii) 1 – x, – y, 2 – z.

reported for similar compounds.[22] The patterns of disintegration are compatible with those reported for similar structures.[23]

3.2.3 *NMR Studies*

3.2.3a ^{1}*H–NMR Spectra:* ^{1}H-NMR spectral data of NH_4L2 are given in the Experimental section. The aromatic protons, together with the phosphorus atom constitute an AA'MM'X spin system. The AA'MM' parts (proton signals) display essentially an AMX pattern; because $J_{AM'}$ and $J_{A'M}$ are close to zero. So the chemical shift assignments of the aromatic protons can be made on the basis of the magnitudes of the coupling constants to phosphorus. Namely, in the compounds, $[Cd(L1)_2]_2$, $[Cd(L2)_2]_2$, $[Cd(L3)_2]_2$, $[Cd(L4)_2]_2$, $[Cd(L5)_2]_2$ and L2, the protons in *ortho-* position to phosphorus display a ${}^{3}J_{PH}$ of ∼13 Hz and those *meta-* to phosphorus a ${}^{4}J_{PH}$ of ∼2.4 Hz.

The diastreotropic -CH_2- protons at the C8 position of $[Cd(L4)_2]_2$ are partly superimposed but still distinguishable. Similarly the azo-methin proton at the C6 position of the same compound is partly shielded by the intense -CH_3 signal at the C7 position. Similar phenomena are reported for related structures.[16] The splitting patterns of the signals due to the apical -CH_3 groups of the alkyls are all as expected. Similar findings are reported for analogous compounds.[24]

3.2.3b ^{13}*C-NMR Data* ^{13}C-NMR data of NH_4L2 are as given in the Experimental section. Single bond J_{P-C} couplings lie in the range of 77.3–80.3 Hz for the aromatic carbons and 50.3-52.5 Hz for the aliphatic carbons. Similar trends were reported for structurally related compounds.[25] The two-bond ^{31}P-^{13}C coupling for the aromatic carbon atoms *ortho-* to the phosphorus are observed to be in the narrow range of 12.2–13.1 Hz in the anisol groups. Interestingly, the three-bond ^{31}P-^{13}C coupling constants of the aromatic carbons are comparatively higher (in the range of 13.7-14.1 Hz). ${}^{2}J_{P-C}$ values for the aliphatic carbons appear to change in a wide range. A similar trend is valid for the phosphorus-coupling constants of the aliphatic carbons. For example, in the compound $[Cd(L2)_2]_2$, ${}^{2}J_{P-C} = 18.2$ Hz whereas in the compound $[Cd(L4)_2]_2$ ${}^{2}J_{P-C} = 0.0$ Hz. ${}^{3}J_{P-C}$ values aliphatic carbons are in the range 1.2-4.3 Hz.

3.2.3c ^{31}*P–NMR Spectra* The proton-decoupled ^{31}P–NMR spectra of $[Cd(L1)_2]_2$, $[Cd(L2)_2]_2$, $[Cd(L3)_2]_2$, $[Cd(L4)_2]_2$ and $[Cd(L5)_2]_2$ show singlets at 71.9, 71.5, 70.1, 82.5 and 83,6 ppm, respectively. All these signals appear at 5-8 ppm lower fields compared to those related to the corresponding ligands.[12a, 16]

3.2.4 *Descriptions of the crystal structures:*

The X-ray structural determinations of $[Cd(L1)_2]_2$ and $[Cd(L2)_2]_2$ confirm the assignments of their structures from spectroscopic data. Selected bond lengths and angles are given in table 3. The molecular structures along with the atom-numbering schemes are depicted in figures 2 and 3, while the packing diagrams are given in figures 3 and 4, respectively.

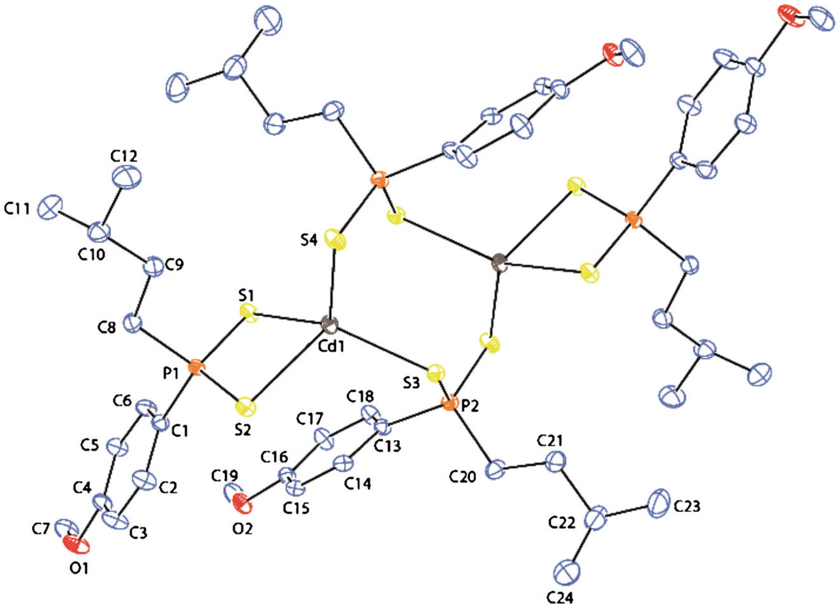


Figure 2. An ORTEP-3[19] view of $[Cd(L1)_2]_2$. The thermal ellipsoids are drawn at the 50% probability level.

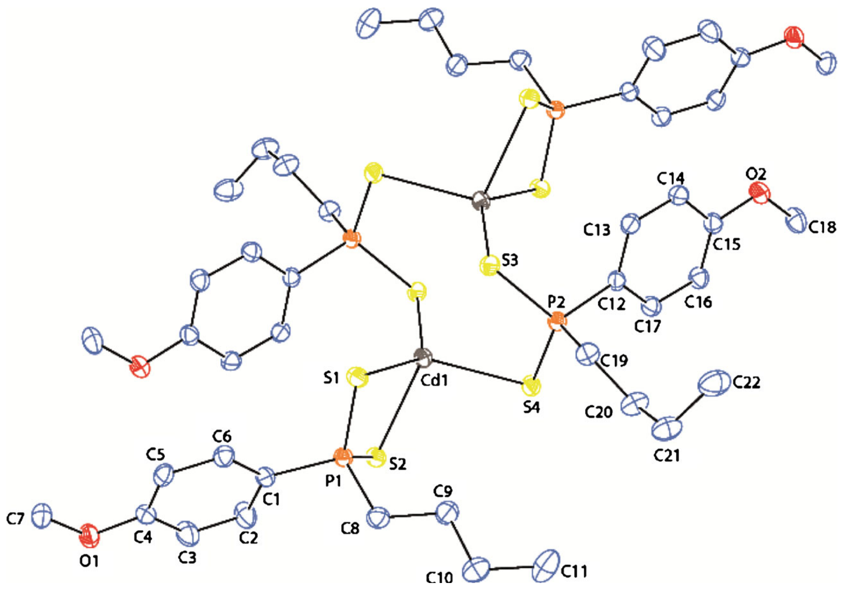


Figure 3. An ORTEP-3[19] view of $[Cd(L2)_2]_2$. The thermal ellipsoids are drawn at the 50% probability level.

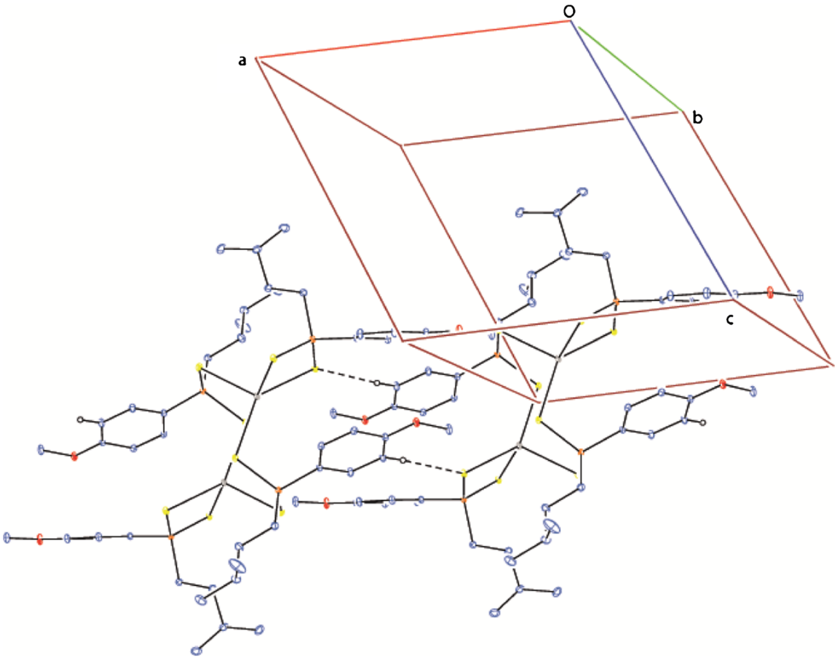


Figure 4. A partial packing diagram of $[Cd(L1)_2]_2$. Hydrogen bonds are shown as dashed lines. Hydrogen atoms not involved in hydrogen bonding have been omitted for clarity.

In the centrosymmetric molecules of $[Cd(L1)_2]_2$ and $[Cd(L2)_2]_2$, the Cd atoms are coordinated by four S atoms, while the P atoms are coordinated by two S atoms and two C atoms (figures 2 and 3). The average Cd-S, P-S and P-C bond lengths and S-P-S and C-P-C bond angles are 2.5763(3) Å, 2.0204(5) Å, 1.8071(14) Å and 112.59(2)° and 104.17(6)° (for $[Cd(L1)_2]_2$) and 2.5792(5) Å, 2.0207(6) Å, 1.8091(19) Å and 112.37(3)° and 104.55(9)° (for $[Cd(L2)_2]_2$), while S-Cd-S and S-P-C bond angles are in the ranges of 79.709(11)°-136.923(11)°, 105.87(5)°-112.15(5)° (for $[Cd(L1)_2]_2$) and 79.897(14)°-134.434(15)°, 106.92(7)°- 111.49(6)° (for $[Cd(L2)_2]_2$), respectively (table 3). The atoms on the PS_2 group of the ligand and the central Cd constitute

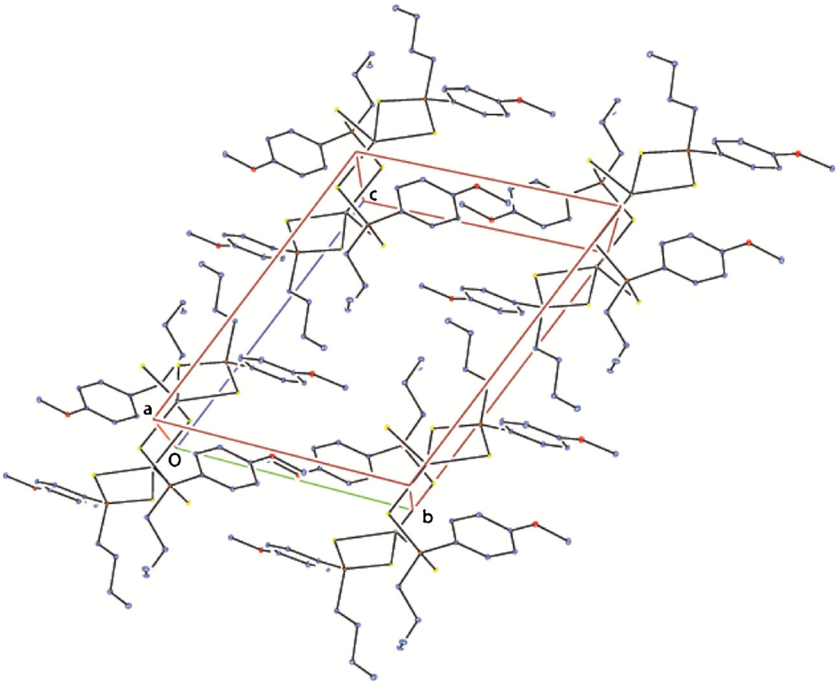


Figure 5. A partial packing diagram of $[Cd(L2)_2]_2$. Hydrogen atoms have been omitted for clarity.

a nearly planar geometry. As an indication, the torsion angle S1-Cd1-S2-P1 is -7.886(14)° in $[Cd(L1)_2]_2$ and -7.585(19)° in $[Cd(L2)_2]_2$. In the both compounds, the Cd atoms have a highly distorted tetrahedral coordination spheres (figures 2 and 3, table 3). This is reflected on S-Cd-S angles. The angle S1-Cd1-S2 is 79.709(11)° in $[Cd(L1)_2]_2$ and 79.897(12)° in $[Cd(L2)_2]_2$; whereas the angle S3-Cd1-S4 is 101.913(11)° and 100.388(15)° respectively.

The ligand cavities may play important roles in the complexations and metal-ion selectivities. The intramolecular Cd1...Cd1^{i} [4.1444(2) Å], S3...S3^{i} [3.8105(5) Å], S4 ...S4^{i} [6.3172(6) Å], P2...P2^{i} [5.6551(5) Å] [symmetry code (i) : – x, – y, – z] (for $[Cd(L1)_2]_2$) and Cd1...Cd1^{i} [3.8875(2) Å], S3...S3^{i} [4.0290(7) Å], S4...S4^{i} [6.1198(7) Å], P2...P2^{i} [5.7787(7) Å] [symmetry code (i) : 1 – x, – y, 2 – z] (for $[Cd(L2)_2]_2$) distances may indicate the hole sizes of the rings. In the four-membered rings *A* (Cd1/S1/S2/P1), the angles between the (Cd1/S1/S2) and (S1/S2/P1) planes are 166.10(2)° (for $[Cd(L1)_2]_2$) and 166.59(2)° (for $[Cd(L2)_2]_2$). Thus, *A* rings may be called to have twisted-chair conformations. The phenyl rings *B* (C1-C6), *C* (C13-C18) (for $[Cd(L1)_2]_2$) and *B* (C1-C6), *C* (C12-C17) (for $[Cd(L2)_2]_2$) are oriented at dihedral angles of 31.73(5)° and 24.95(6)°, respectively. In the crystal structures, intermolecular C17-H17...S1^{ii} interactions (C17-H17 = 0.93 Å, H17...S1^{ii} = 2.87 Å, C17...S1^{ii} = 3.80Å and C17-H17...S1^{ii} = 177°; symmetry code: (ii) 1– x, – y, – z) link the molecules into centrosymmetric dimers through $R_2^2(16)$ ring motifs[26] (for $[Cd(L1)_2]_2$) (figure 4), while the molecules are elongated along the c-axis and stacked along the a-axis (for $[Cd(L2)_2]_2$) (figure 5).

4. Conclusions

The five new dithiophosphinato cadmium(II) complexes and one ligand were prepared. The six novel compounds characterized by, MS, FTIR and RAMAN spectral and elemental analyses. The molecular and crystal structures of the two complexes namely, $[Cd(L1)_2]_2$ and $[Cd(L2)_2]_2$ were also elucidated by X-ray crystallography. The structure of the compounds were analysed by NMR (^{1}H, ^{13}C, ^{31}P). For aromatic carbons, the $^{3}J_{P-C}$ coupling constants are a few Hz higher than the $^{2}J_{P-C}$ values. ^{31}P chemical shifts the complexes were found to be 5-8 Hz downfield compared to those of the related dithiophosphonato ligands. X-ray analyses show that the P-S bonds in the complexes are indeed of the same order; in other words, electron delocalization prevails. In the centrosymmetric molecules of $[Cd(L1)_2]_2$ and $[Cd(L2)_2]_2$, the Cd atoms are coordinated by four S atoms, while the P atoms are coordinated by two S atoms and two C atoms. The ligand cavities may play important roles in the complexations and metal-ion selectivities. In the crystal structure of $[Cd(L1)_2]_2$, intermolecular C-H...S interactions link the molecules into centrosymmetric dimers through $R_2^2(16)$ ring motifs.

Supplementary Information

All additional information relating to the characterization of the complexes, namely, ESI-MS (figure S1), IR spectra (figure S2), Raman spectra (figure S3), NMR (^{1}H, ^{13}C and ^{31}P) spectra (figures S4, S5 and S6) are available at www.ias.ac.in/chemsci. Crystallographic data (excluding structure factors) have been deposited with the Cambridge Crystallographic Data Centre as the supplementary publication no. 1060403 (for $[Cd(L1)_2]_2$, and CCDC 1060404 (for $[Cd(L2)_2]_2$). Copies of the data can be obtained, free of charge, on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: +44-1223-336033; E-mail: deposit@ccdc.cam.ac.uk).

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